



## Review

# Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere

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**Abstract**

Secondary organic aerosol (SOA), particulate matter composed of compounds formed from the atmospheric transformation of organic species, accounts for a substantial fraction of tropospheric aerosol. The formation of low-volatility (semivolatile and possibly nonvolatile) compounds that make up SOA is governed by a complex series of reactions of a large number of organic species, so the experimental characterization and theoretical description of SOA formation presents a substantial challenge. In this review we outline what is known about the chemistry of formation and continuing transformation of low-volatility species in the atmosphere. The primary focus is chemical processes that can change the volatility of organic compounds: (1) oxidation reactions in the gas phase, (2) reactions in the particle phase, and (3) continuing chemistry (in either phase) over several generations. Gas-phase oxidation reactions can reduce volatility by the addition of polar functional groups or increase it by the cleavage of carbon–carbon bonds; key branch points that control volatility are the initial attack of the oxidant, reactions of alkylperoxy (RO<sub>2</sub>) radicals, and reactions of alkoxy (RO) radicals. Reactions in the particle phase include oxidation reactions as well as accretion reactions, non-oxidative processes leading to the formation of high-molecular-weight species. Organic carbon in the atmosphere is continually subject to reactions in the gas and particle phases throughout its atmospheric lifetime (until lost by physical deposition or oxidized to CO or CO<sub>2</sub>), implying continual changes in volatility over the timescales of several days. The volatility changes arising from these chemical reactions must be parameterized and included in models in order to gain a quantitative and predictive understanding of SOA formation.

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*Keywords:* Secondary organic aerosol; Semivolatile organic compounds; Biogenic hydrocarbons; Particle-phase reactions

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## 1. Introduction

Organic compounds make up a substantial fraction of atmospheric fine particulate matter, accounting for 20–90% of aerosol mass in the lower troposphere (Kanakidou et al., 2005). A full understanding of the health, climate, and visibility effects of atmospheric particulate matter thus requires the detailed characterization of the sources and fates of organic aerosols, so that their loading in the atmosphere can be accurately modeled. Given the large number and variability of chemical constituents, sources, and possible chemical transformations of organic aerosol, such characterization presents a major challenge for both experiments and models. The controlling factors and effects of organic particulate matter thus remain highly uncertain, and are the subject of a number of recent review articles (Jacobson et al., 2000; Turpin et al., 2000; Seinfeld and Pankow, 2003; Kanakidou et al., 2005; Pöschl, 2005; Fuzzi et al., 2007; Goldstein and Galbally, 2007; Rudich et al., 2007).

Probably most uncertain is the formation and evolution of secondary organic aerosol (SOA), particulate matter formed by the chemical transformation of atmospheric organic compounds. The most commonly studied (and probably most atmospherically important) mechanism of SOA formation is the oxidation of volatile organic compounds (VOCs), forming products of lower volatility that subsequently partition into the condensed phase. However, reactions of less-volatile organics may lead to the formation of particulate matter as well, so SOA may also be formed from chemical

reactions of organic compounds emitted originally in the condensed phase (Robinson et al., 2007).

SOA accounts for a large, and often dominant, fraction of total organic particulate mass, based on several complementary measurements of ambient aerosol, such as the ratios of organic mass (OM) to organic carbon (OC) (e.g., Turpin and Huntzicker, 1995; Lim and Turpin, 2002), loadings of water-soluble OC (Sullivan et al., 2006), and level of oxidation from online aerosol mass spectrometry (AMS) (e.g., Zhang et al., 2005b; Lanz et al., 2007). As a result, a major focus of laboratory studies of organic aerosol has been the quantification of SOA formation from individual precursors for integration into atmospheric chemical transport models. The standard view is that SOA formation is dominated by a few classes of VOCs (mostly monoterpenes and aromatic compounds) that form aerosol with yields readily measured in laboratory chamber studies. However, models informed by such chamber measurements do not always capture the variability of observed SOA loadings (Heald et al., 2006), and often predict far less SOA than is observed (de Gouw et al., 2005; Heald et al., 2005; Volkamer et al., 2006). This underestimation of SOA strongly suggests the importance of additional pathways of SOA formation not typically studied in experiments or included in models.

The identification of the most important SOA-forming reactions, and hence the accurate prediction of atmospheric SOA, requires an understanding of which pathways form low-volatility organics, compounds of sufficiently low vapor pressures to be present in the condensed phase. This includes

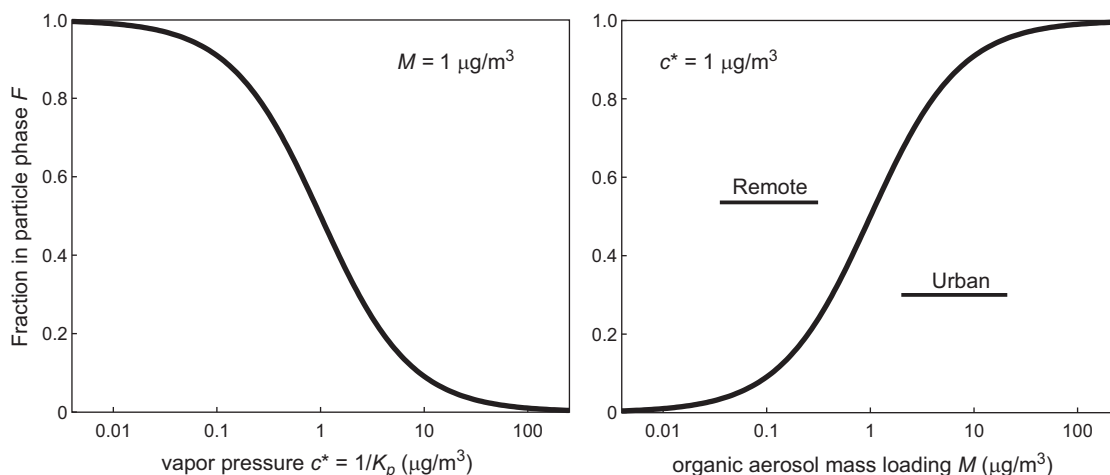


Fig. 1. Left panel: fraction  $F$  of a semivolatile compound in the particle phase as a function of its saturation mass concentration  $c^*$  ( $= 1/K_p$ ), at an absorbing aerosol mass concentration  $M = 1 \mu\text{g m}^{-3}$ . Right panel: particle fraction  $F$  as a function of  $M$  at  $c^* = 1 \mu\text{g m}^{-3}$ . Approximate ranges of  $M$  values under remote and urban conditions are indicated.

compounds present entirely in the condensed phase (nonvolatile organics) as well as those that may be present in appreciable amounts in both the gas and particle phases (semivolatile organics). This definition of semivolatile organics is quite broad, involving saturation vapor pressures spanning at least seven orders of magnitude (Donahue et al., 2006), and so includes a significant fraction of atmospheric organics.

The key concept underlying modern treatments of SOA is that it is composed predominantly of semivolatile organics (Pankow, 1994a, 1994b; Odum et al., 1996), allowing for the description of SOA formation in terms of gas–particle partitioning. The absorptive partitioning of semivolatiles is described by the theory of Pankow et al. (1994a, 1994b), defining an equilibrium partitioning coefficient  $K_p$ :

$$K_p = \frac{P}{GM} \quad (1)$$

in which  $G$  is the mass concentration (mass per volume air, e.g.  $\mu\text{g m}^{-3}$ ) of the semivolatile species in the gas phase,  $P$  is the mass concentration ( $\mu\text{g m}^{-3}$ ) of the semivolatile species in the particle phase, and  $M$  is the mass concentration ( $\mu\text{g m}^{-3}$ ) of the total absorbing particle phase. The partitioning coefficient  $K_p$  ( $\text{m}^3 \mu\text{g}^{-1}$ ) is thus inversely proportional to the saturation vapor pressure ( $c^*$ ) of the pure semivolatile compound.  $M$  refers only to the particulate matter participating in absorptive partitioning (organic aerosol into which semivolatiles can partition, and possibly aqueous aerosol in the

case of highly water-soluble organics). By Eq. (1), as long as any absorbing mass is present, some fraction of a given semivolatile compound can partition into the particle phase, even if its gas-phase concentration is below its saturation vapor pressure. The fraction  $F$  of a semivolatile compound in the particle phase is given by

$$F = \frac{P}{P+G} = \frac{MK_p}{1+MK_p} = \frac{1}{1+c^*/M} \quad (2)$$

Hence as the amount of absorbing material ( $M$ ) increases, compounds of higher volatility (higher  $c^*$ , lower  $K_p$ ) will increasingly partition into the condensed phase.

The dependence of  $F$  on absorbing mass  $M$  and vapor pressure of the semivolatile species  $c^*$  is illustrated in Fig. 1. When  $c^*$  is equal to  $M$ , half of the semivolatile mass resides in the particle phase. If  $c^* \ll M$ , essentially all of the semivolatile species are in the particle phase; conversely, if  $c^* \gg M$ , its fraction in the particle phase approaches zero. Fig. 1 shows the nature of  $F$  both as a function of  $c^*$  at a fixed aerosol loading  $M$  (left panel) and as a function of  $M$  for a single semivolatile compound of vapor pressure  $c^*$  (right panel).

Odum et al. (1996) showed that SOA yield  $Y$  (defined as  $\Delta M/\Delta\text{HC}$ , the mass of aerosol formed per mass of hydrocarbon reacted) can be expressed in terms of the formation of a collection of semivolatile compounds:

$$Y = \frac{\Delta M}{\Delta\text{HC}} = M \sum_i \frac{\alpha_i K_{p,i}}{1 + MK_{p,i}} \quad (3)$$

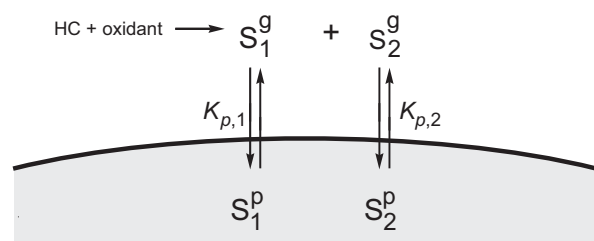


Fig. 2. Schematic of the “two-product model” of SOA formation (Odum et al., 1996). Hydrocarbon oxidation forms two model semivolatiles  $S_1$  and  $S_2$ , of different volatilities, each of which partition between the gas phase and particle phase according to Eq. (1). The “volatility basis set” approach (Donahue et al., 2006) is similar, though with a larger number of lumped semivolatiles which span a wider range of prescribed vapor pressures.

in which  $K_{p,i}$  and  $\alpha_i$  are the partitioning coefficient and mass yield, respectively, of compound  $i$ . SOA yield from a given precursor is therefore not a stoichiometric quantity, but rather increases with increasing total organic particulate loading, consistent with a wide range of experimental results (e.g., Odum et al., 1996; Seinfeld and Pankow, 2003). The SOA-forming potential of a given reaction is determined by the semivolatile product yields ( $\alpha$ 's) and volatilities ( $K_p$ 's), which together make up a “volatility distribution” of the reaction products.

In principle, aerosol formation can be calculated by carrying out the summation in Eq. (3) over all semivolatile compounds formed in a given reaction, but this degree of detail is generally infeasible owing to the large number of products formed and the difficulty in measuring all individual semivolatile compounds. Instead, two surrogate products ( $i = 2$ ) have traditionally been used to express the volatility distribution from SOA-forming reactions. This “two-product model” of SOA formation, shown in Fig. 2, generally represents laboratory SOA growth data well (e.g., Seinfeld and Pankow, 2003; Keywood et al., 2004b), and can be incorporated into atmospheric chemistry models in a straightforward manner (e.g., Chung and Seinfeld, 2002; Koo et al., 2003; Tsigaridis and Kanakidou, 2003; Heald et al., 2005; Henze and Seinfeld, 2006).

Recently, Donahue and coworkers (Donahue et al., 2006; Presto and Donahue, 2006; Pathak et al., 2007) demonstrated that partitioning over a broad range of organic aerosol loadings (including typical ambient levels,  $0.1\text{--}20\ \mu\text{g m}^{-3}$ ) is more accurately represented by a larger number of products (typically  $i = 10$ ) spanning a wide range of volatilities. In this approach the volatility distribution is represented by binning all organics by volatility,

with the bins defined by a set of prescribed vapor pressures (the “volatility basis set”) (Donahue et al., 2006). Fig. 3 shows how the fractional distribution in Fig. 1 is represented in terms of both the “two-product model” and the “volatility basis set”, and how partitioning in each model is affected by a change in absorbing aerosol loading  $M$ .

The description of SOA formation in terms of semivolatile partitioning (Eqs. (1)–(3)) is the primary focus of an earlier review (Seinfeld and Pankow, 2003). The subject of the present review is the detailed chemistry of the formation and evolution of semivolatile organics, which controls their amount and volatility, and remains poorly understood. In particular, we focus on the three primary factors that determine the volatility, and hence the SOA-forming potential, of organic compounds in the atmosphere:

- (1) oxidation reactions of gas-phase organic species, which lower volatility by addition of functional groups but can also increase volatility by cleavage of carbon–carbon bonds;
- (2) reactions in the particle (condensed) phase, which can change volatility either by oxidation or formation of high-molecular-weight species; and
- (3) the extent to which these reactions occur, as the volatility distribution of oxidation products will continually evolve as a result of ongoing chemistry.

These correspond to three major developments arising from recent studies of SOA formation: the description of SOA production in terms of known VOC oxidation mechanisms, the characterization of complex chemistry occurring within particles, and an improved understanding of SOA formation kinetics. In the following three sections of this review, each of these factors will be discussed individually. Together they suggest possible explanations for discrepancies between modeled and measured ambient aerosol, and suggest areas of future research, discussed in the final section.

Because of the focus on the chemistry of the formation and evolution of low-volatility organics, this review is not intended to be a comprehensive literature review of all studies of SOA formation. Many important aspects of the field, such as laboratory techniques, ambient measurements, model simulations, aerosol properties, and new particle formation are not discussed in detail.

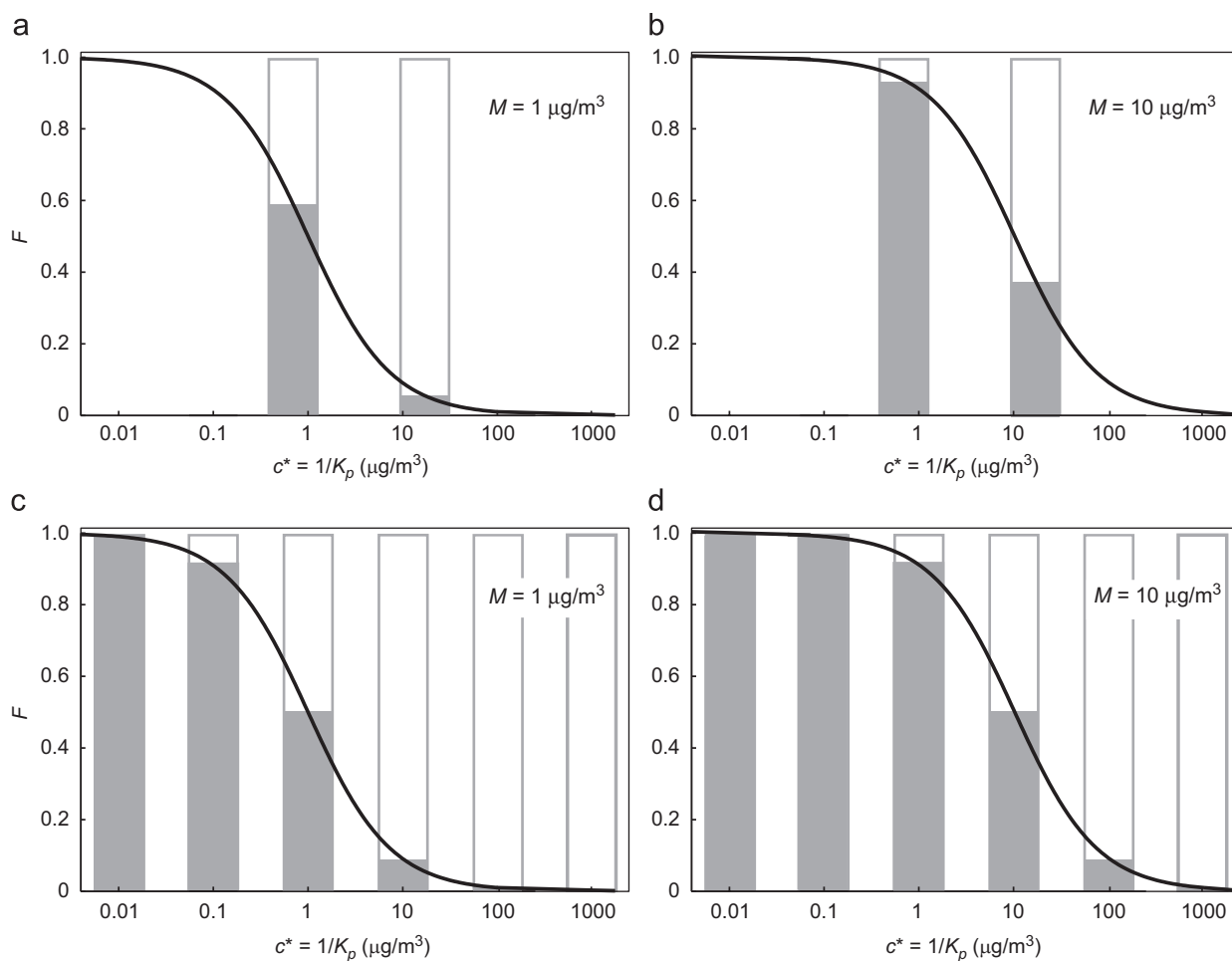


Fig. 3. Representation of gas–particle partitioning for a complex mixture of semivolatiles using (a–b) the “two-product model”, in which the semivolatiles are represented by two model compounds with experimentally determined vapor pressures, and (c–d) the “volatility basis set”, which employs a larger number of lumped compounds with prescribed vapor pressures. Partitioning at two mass loadings of organic aerosol (1 and  $10 \mu\text{g m}^{-3}$ ) is shown for each. Note that these plots show only the fraction  $F$  of each semivolatile compound in the particle phase; particle-phase concentrations are obtained by multiplying  $F$  by total mass concentration of each semivolatile.

Laboratory studies of SOA formation under carefully controlled conditions represent the foundation from which our understanding of the chemistry of SOA formation is derived. This review relies heavily on what has been learned from such studies.

## 2. Gas-phase oxidation

Gas-phase oxidation, initiated by reaction with species such as the hydroxyl radical (OH), nitrate radical ( $\text{NO}_3$ ), and ozone ( $\text{O}_3$ ), is the primary process by which the volatilities of organic species in the atmosphere evolve. Oxidation of a VOC can produce species of sufficiently low vapor pressure to be condensable, leading to the formation of SOA; products of higher volatility than the parent VOC

(such as  $\text{CO}_2$ ,  $\text{CH}_2\text{O}$ , etc.) may be formed as well. As a result of the chemical complexity of these oxidation processes, the exact chemical mechanisms leading to changes in volatility of atmospheric organics (and in particular the formation of SOA) remain poorly constrained. However, in recent years the measurement of SOA yields and composition over a range of oxidative conditions, and the detailed modeling of chemical and physical processes underlying SOA formation, have afforded substantial insight into the identity of the gas-phase processes that most strongly affect product volatility.

The vapor pressure of a molecule is determined largely by its polarity and size. As a result, a key determinant of the volatility of an oxidation

Table 1

Changes to vapor pressure of an organic compound upon addition of common functional groups, based upon group-contribution method predictions of Pankow and Asher (2007)

Functional group	Structure	Change in vapor pressure (298 K) <sup>a</sup>
Ketone	–C(O)–	0.10
Aldehyde	–C(O)H	0.085
Hydroxyl	–OH	$5.7 \times 10^{-3}$
Hydroperoxyl	–OOH	$2.5 \times 10^{-3}$
Nitrate	–ONO <sub>2</sub>	$6.8 \times 10^{-3}$
Carboxylic acid	–C(O)OH	$3.1 \times 10^{-4}$
Peroxyacid	–C(O)OOH	$3.2 \times 10^{-3}$
Acyl peroxyxynitrate	–C(O)OONO <sub>2</sub>	$2.7 \times 10^{-3}$
Extra carbon <sup>b</sup>	–CH <sub>2</sub> –, etc.	0.35 <sup>b</sup>

<sup>a</sup>Multiplicative factor.

<sup>b</sup>For comparison between changes in polarity (by addition of a functional group) and changes to size of the carbon skeleton. Vapor pressure also depends on carbon skeleton structure; see Pankow and Asher (2007).

product is the importance of reactions that add polar functional groups relative to those that break the carbon skeleton. (The exception to this is cyclic compounds, which due to “tethering” do not fragment upon bond cleavage.) Owing to variations in polarity, the identity of the added functional group also plays a major role in volatility. Shown in Table 1 are the approximate effects of common functional groups on the vapor pressure of organics, as predicted by the group-contribution model proposed by Pankow and Asher (2007). The addition of any oxygen-containing functional group has a greater effect on vapor pressure than an increase in the size of the carbon skeleton by one carbon atom. However, this change is moderate for aldehydes and ketones, which are relatively non-polar. Much larger decreases in volatility result from the addition of hydroxyl, hydroperoxyl, nitrate, and acid groups, each of which may lower vapor pressure by over two orders of magnitude. Thus the reaction pathways that lead to the addition of these polar functional groups to the carbon skeleton, with little to no fragmentation by the breaking of C–C bonds, are those most likely to lead to the formation of low-volatility organics and hence SOA.

Atmospheric oxidation mechanisms for a wide range of VOCs have been reviewed in detail by Atkinson and Arey (2003); a generic (and highly simplified) reaction mechanism is shown in Fig. 4. Within the context of this simple mechanism, three key branch points govern the volatility distribution

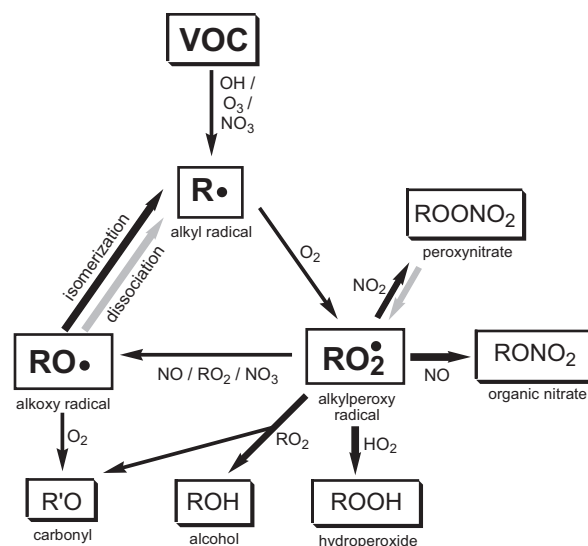


Fig. 4. Simplified mechanism for the atmospheric oxidation of a generic VOC. Thick black arrows denote reactions that can lead to a substantial decrease in volatility; gray arrows denote reactions that can lead to a substantial volatility increase. Details of alkene ozonolysis are omitted for clarity and are shown in Fig. 5.

of the oxidation products: (1) the initial attack of the oxidant; (2) the reactions of the organic peroxy (RO<sub>2</sub>) radical; and (3) the reactions of the alkoxy (RO) radical. These are discussed below, along with their role in SOA formation as determined from recent experimental and modeling studies.

### 2.1. Initiating oxidant

The oxidant (OH, O<sub>3</sub>, NO<sub>3</sub>, etc.) that initiates the degradation of a VOC plays a major role in determining the product distribution, and thus is expected to be a controlling factor in the product volatility. This effect is not well-constrained experimentally, as there are only a few studies that explicitly compare SOA yields from different oxidants (Griffin et al., 1999; Bonn and Moortgat, 2002). Further, such studies have generally not been carried out under comparable conditions (similar NO<sub>x</sub> level, etc.); and there is a relative lack of yield measurements from reactions initiated solely by OH (most photooxidation studies include a mixture of oxidants) or NO<sub>3</sub>. Nonetheless, general trends in product volatility can be ascertained.

A radical (OH, NO<sub>3</sub>, or halogen atom) initiates oxidation either by abstraction of a hydrogen atom or addition to a C–C double bond. In the case of abstraction, the organic products and their volati-

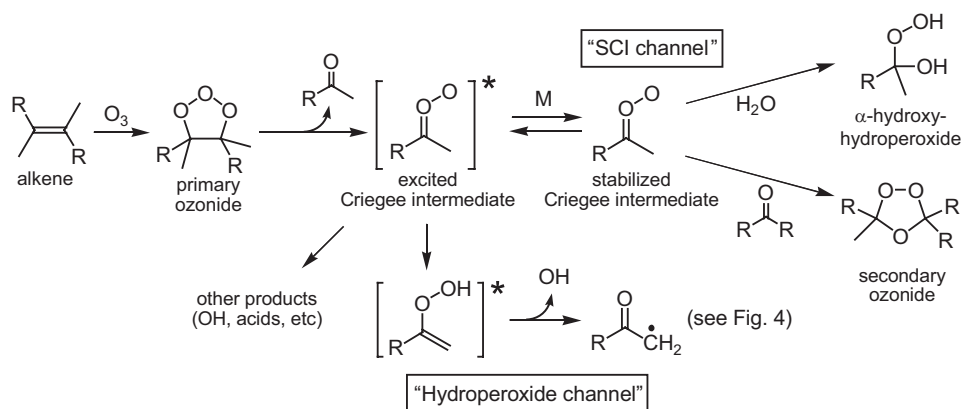


Fig. 5. Simplified mechanism of alkene ozonolysis. Different Criegee intermediates (syn and anti) are lumped for clarity. Low-volatility products can be formed by either the “hydroperoxide channel” or the “SCI channel”. Only two possible reactions in the SCI channel are shown; in some cases the  $\alpha$ -hydroxyhydroperoxide is unstable and will decompose (see text).

lities are unaffected by the identity of the radical. In the case of addition reactions, the vapor pressures of the organics are lowered according to the specific functional group added. Thus the volatilities of products from  $\text{NO}_3$  addition to an alkene are expected to be about the same as those from OH addition to the same alkene, as nitrate and hydroxyl groups have roughly the same influence on vapor pressure (Table 1). At a given aerosol mass loading, SOA yields from most  $\text{NO}_3$ -initiated reactions appear to be higher (by a factor of  $\sim 2$ ) than those from OH-initiated reactions (Griffin et al., 1999; Hallquist et al., 1999); this may be in part a result of differences in molecular mass rather than in volatility. An important difference between OH and  $\text{NO}_3$  reaction mechanisms is that nitrate groups may degrade later in the reaction sequence, forming  $\text{NO}_2$  (Barnes et al., 1990). Such a step involves a substantial increase in volatility, and may explain the anomalously low yields of SOA formed from  $\text{NO}_3 + \alpha$ -pinene, as well as the gas-phase products observed (Hallquist et al., 1999; Spittler et al., 2006). This degradation pathway is not well-constrained and warrants future study.

SOA formation from the addition of a halogen atom to an alkene has been studied only once (Cai and Griffin, 2006). Yields from Cl+monoterpenes are generally equal to or lower than those from monoterpene photooxidation, indicating that the addition of chlorine has a smaller effect on vapor pressure than the addition of a hydroxyl group.

Oxidation of alkenes by ozone proceeds by a fundamentally different mechanism than radical-initiated oxidation. The ozonolysis mechanism is described in detail elsewhere (Atkinson and Arey,

2003; Chuong et al., 2004; Docherty et al., 2005); key reactions are shown in Fig. 5. The alkene is cleaved by ozone to form a carbonyl and an energetically excited carbonyl oxide (“Criegee intermediate”). This intermediate can decompose (via the “hydroperoxide channel”) to form OH and an alkyl radical, which then reacts according to the mechanism in Fig. 4. Otherwise, it is quenched to form a stabilized Criegee intermediate (SCI), which can react with water or oxygenated organics (the “SCI channel”). Products from each channel have been identified in the aerosol phase (e.g., Yu et al., 1999b; Tobias and Ziemann, 2000; Jaoui and Kamens, 2003; Heaton et al., 2007); the relative importance of the two in SOA formation appears to be highly dependent on molecular structure of the parent alkene. For example, under atmospheric conditions the SCI channel is often dominated by reaction with water vapor (Tobias and Ziemann, 2001), forming a low-volatility  $\alpha$ -hydroxyhydroperoxide. When formed from linear alkenes this species is an important component of SOA (Tobias et al., 2000), whereas  $\alpha$ -hydroxyhydroperoxides from cyclic alkenes are unstable, decomposing to more volatile products and contributing little to SOA formation (Ziemann, 2002).

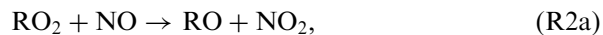
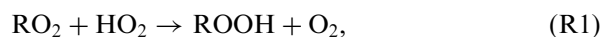
A key general feature of the ozonolysis reaction mechanism is the initial cleavage of the C–C double bond. For acyclic (and cyclic *exo*) alkenes, this leads to a decrease in the size of the carbon skeleton, which may offset decreases in volatility from the addition of functional groups. By contrast, the ozonolysis of a cyclic *endo* alkene may add several functional groups with no loss in carbon number; further, the tethering of the carbonyl and the

carbonyl oxide fragments allows for the formation of secondary ozonides (Bonn et al., 2002; Chuong et al., 2004), which may be an important component of SOA (Kamens et al., 1999; Tobias et al., 2000). As a result, for  $\beta$ -pinene (an *exo* cycloalkene), ozonolysis forms less SOA than does reaction with OH, whereas for  $\alpha$ -pinene (an *endo* cycloalkene), the reverse is true (Griffin et al., 1999; Bonn and Moortgat, 2002).

In addition to reaction with radicals or ozone, oxidation of a gas-phase organic species may also be initiated by photolysis (not shown in Fig. 4). In the actinic region this reactive pathway is available only to oxygenated organics (carbonyls, peroxides, and nitrates). Most photolytic processes involve bond cleavage, and so will generally lead to an increase in volatility; however, more complex photochemical transformations are also possible (Paulson et al., 2006). Presto et al. (2005b) have shown that gas-phase photolytic processes are likely responsible for the observed reduction in SOA yield from  $O_3 + \alpha$ -pinene in the presence of UV light.

## 2.2. Reactions of the organic peroxy ( $RO_2$ ) radical

The alkyl radicals formed after the initial oxidation reaction rapidly form  $RO_2$  radicals, which play a central role in the production of lower-volatility products. This was first suggested by Hatakeyama et al. (1991), who explained the observed dependence of SOA yield on  $NO_x$  level in terms of competitive  $RO_2$  chemistry:



Reaction with  $HO_2$  (R1) forms a hydroxperoxide, which can be quite low in volatility (Table 1) and is predicted to be a major component of SOA (Bonn et al., 2004; Johnson et al., 2004, 2005; Camredon et al., 2007). Further, peroxides may react further in the particle phase to form even lower-volatility peroxyhemiacetals (Tobias and Ziemann, 2000) (see Section 3). Composition measurements find that peroxides are indeed major components of SOA formed from alkene ozonolysis (Docherty et al., 2005) and low- $NO_x$  isoprene photooxidation (Surratt et al., 2006), as well as of oxidized organic surfaces (Gomez et al., 2006). The reaction of  $HO_2$  with acylperoxy ( $RC(O)O_2$ ) radicals instead forms

acids or peracids, which can also be very low in volatility. Thus reaction (R1) represents a channel by which SOA may be efficiently formed, consistent with the measurement of substantial SOA formation at low- $NO_x$  conditions (discussed at the end of this section).

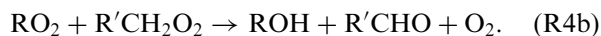
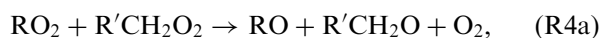
Under conditions in which  $NO_x$  is present,  $RO_2$  will instead react with NO, forming an alkoxy radical (R2a) or organic nitrate (R2b). Organic nitrates can be low in volatility and have been observed in laboratory-generated SOA (Palen et al., 1993; Holes et al., 1997; Dekermenjian et al., 1999; Hallquist et al., 1999; Gong et al., 2005; Lim and Ziemann, 2005; Presto et al., 2005a; Sax et al., 2005; Surratt et al., 2006) and in ambient aerosol (Mylonas et al., 1991; Nielsen et al., 1998; Garnes and Allen, 2002; Laurent and Allen, 2004; Reemtsma et al., 2006). However this is not the dominant product of the  $RO_2 + NO$  reaction, accounting for <25% of reaction (R2) (Arey et al., 2001; Espada et al., 2005). The major channel is alkoxy radical formation (R2a); hence SOA formation in the presence of  $NO_x$  is determined by further reactions of RO, which are discussed in the following subsection. Two other reactive pathways of  $RO_2$  radicals are first briefly outlined.

In the presence of  $NO_x$ ,  $RO_2$  radicals may also react with  $NO_2$ :



Peroxy nitrates are only temporary reservoirs for  $RO_2$  and  $NO_x$ : lifetimes at 298 K are <1 s for alkyl peroxy nitrates and 10's of minutes to hours for peroxyacyl nitrates (PANs). Nonetheless they may still be of sufficiently low volatility to partition into the aerosol phase: models suggest PANs may constitute a significant fraction of SOA (Bonn et al., 2004; Johnson et al., 2004; Camredon et al., 2007), and there is mass spectrometric evidence of  $RO_2NO_2$  in laboratory SOA studies (Gong et al., 2005). In the particle phase these species likely thermally dissociate, allowing for further  $RO_2$  reactions.

Under  $NO_x$ -free conditions,  $RO_2$  radicals can also undergo self- and cross-reactions:



Reaction (R4a), like reaction (R2a), forms alkoxy radicals (discussed below), whereas (R4b) is chain-terminating. The hydroxyl group added by this



channel represents a significant decrease in volatility relative to the parent VOC; however, a carbonyl is formed as well, so that reaction (R4b) generally leads to products that, on average, are more volatile than those formed from  $\text{RO}_2 + \text{HO}_2$  (R1). The averaged volatilities of the products formed from  $\text{RO}_2 + \text{RO}_2$  reactions are determined by the branching between (R4a) and (R4b) (Docherty and Ziemann, 2003; Jenkin, 2004; Keywood et al., 2004a), as well as the fate of the alkoxy radical (discussed below). In addition, self-reactions of large  $\text{RO}_2$  radicals may instead form organic peroxides (ROOR), which will likely be very low in volatility (Ziemann, 2002), though the importance of this channel is poorly understood at present. It should be noted that the importance of the  $\text{RO}_2 + \text{RO}_2$  reaction tends to be larger in laboratory studies than in the atmosphere, owing to relatively high hydrocarbon (and hence  $\text{RO}_2$ ) concentrations. For example, in studies of monoterpene ozonolysis, the  $[\text{RO}_2]/[\text{HO}_2]$  ratio may be as high as 1200 (Jenkin, 2004), over 100 times higher than what has been measured at ambient (low- $\text{NO}_x$ ) conditions (Stevens et al., 1997; Hanke et al., 2002; Mihelcic et al., 2003).

### 2.3. Reactions of the alkoxy (RO) radical

There are three primary reactions available to alkoxy radicals, recently reviewed by Atkinson (2007) and shown in Fig. 6: (R5a) dissociation, the cleavage of a carbon–carbon bond adjacent to the alkoxy carbon, forming a carbonyl and an alkyl radical, (R5b) isomerization, a 1,5-hydrogen shift in

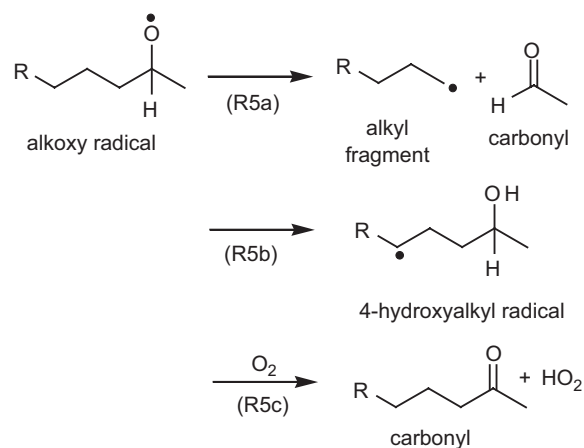


Fig. 6. Reactions of alkoxy radicals. (R5a) Dissociation; (R5b) isomerization; (R5c) reaction with O<sub>2</sub>.

Table 2  
Rates of alkoxy radical reactions, based upon recommendations by Atkinson (2007)

Reaction type	Rate constant at 298 K (s <sup>-1</sup> )
<i>Dissociation<sup>a</sup></i>	
Leaving radical	
•CH <sub>3</sub>	1.5 × 10 <sup>2</sup>
•CH <sub>2</sub> R	4.7 × 10 <sup>4</sup>
•CHR <sub>2</sub>	4.2 × 10 <sup>5</sup>
•CR <sub>3</sub>	2.7 × 10 <sup>6</sup>
•CH <sub>2</sub> OH	4.5 × 10 <sup>6</sup>
•CHROH	6.7 × 10 <sup>7</sup>
•CR <sub>2</sub> OH	1.3 × 10 <sup>8</sup>
•C(O)H	2.0 × 10 <sup>4</sup>
•C(O)R	9.5 × 10 <sup>7</sup>
<i>Isomerization<sup>b</sup></i>	
Carbon from which H atom is abstracted	
–CH <sub>3</sub>	2.5 × 10 <sup>5</sup>
–CH <sub>2</sub> R	2.5 × 10 <sup>6</sup>
–CHR <sub>2</sub>	8.5 × 10 <sup>6</sup>
–CH <sub>2</sub> OH <sup>c</sup>	1.0 × 10 <sup>7</sup>
–CHROH <sup>c</sup>	3.4 × 10 <sup>7</sup>
<i>Reaction with O<sub>2</sub><sup>d</sup></i>	4.7 × 10 <sup>4</sup>

<sup>a</sup>To obtain these values,  $\Delta H_{\text{dissoc}}$  is assumed to be 7 kcal mol<sup>-1</sup>. Substantially higher accuracy can be obtained by using actual  $\Delta H_{\text{dissoc}}$  values from individual reactions (Atkinson, 2007).

<sup>b</sup>Multiply rate constants by 1.3 for each adjacent non-methyl carbon, or 3.5 if the adjacent carbon has a hydroxyl group.

<sup>c</sup>Hydrogen abstraction from the carbon only.

<sup>d</sup>At 760 Torr air.

which the alkoxy radical center abstracts a hydrogen located four carbons away, and (R5c) reaction with oxygen, forming a carbonyl and HO<sub>2</sub>. The rates of these three reactions are a strong function of the molecular structure of the individual alkoxy radical, so the dominant pathway can vary from radical to radical. Recommended rate constants (Atkinson, 2007) for a number of common classes of alkoxy radicals are given in Table 2.

The rate of the dissociation pathway (R5a) is a function of the level of substitution of the alkyl radical formed, with the formation of substituted radicals being highly favored. As a result, branched organics are much more likely to undergo bond cleavage than unbranched (linear) ones. Dissociation is also highly favored when the adjacent carbon has a ketone or alcohol moiety, so this pathway is expected to be increasingly favored as the level of oxidation of the parent organic increases.

The isomerization reaction (R5b) is a 1,5-hydrogen atom shift, so will occur only when there is

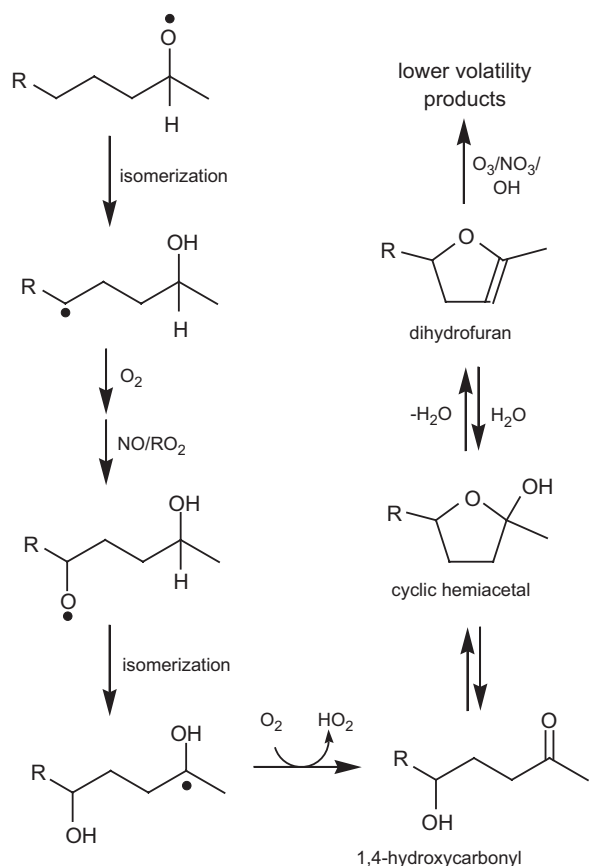


Fig. 7. Further reactions following alkoxy radical isomerization. If possible, the new alkoxy radical will isomerize again to form a 1,4-hydroxycarbonyl. This species can then isomerize to form a dihydrofuran, which is subject to rapid oxidation by  $O_3$ ,  $NO_3$ , or  $OH$  (Gong et al., 2005; Lim and Ziemann, 2005).

a hydrogen atom located four carbons away from the radical center. The rate of isomerization increases with the level of substitution of the carbon from which the H is abstracted; it is also greatly enhanced when that carbon has an  $-OH$  group, or is adjacent to a carbon with one. As a result, a subsequent isomerization reaction will generally involve a hydrogen attached to the carbon of the original alkoxy radical (assuming there is one), forming a 1,4-hydroxycarbonyl (Fig. 7). This may itself rapidly isomerize and dehydrate to form a dihydrofuran, which is low in volatility and subject to rapid oxidation, probably lowering volatility further (Gong et al., 2005; Lim and Ziemann, 2005).

The reaction of large alkoxy radicals with oxygen (R5c) is typically too slow at room temperature to compete with the other two channels. It is compe-

titive when isomerization is not possible and dissociation forms primary alkyl radicals only, as well as at very low temperatures, where the dissociation and isomerization reactions are exceedingly slow (Atkinson, 2007). Otherwise, this channel can generally be neglected for large organics.

The importance of alkoxy radical isomerization relative to the other two channels (Table 2) is a major determinant of the volatility of reaction products. The isomerization product is an alkyl radical of the same carbon number as the alkoxy radical, only with an additional functional (hydroxyl) group. Subsequent isomerization steps will lead to the formation of multifunctional species (polyols, hydroxycarbonyls, or dihydrofurans), representing substantial decreases in volatility. By contrast, the dissociation pathway involves a cleavage of the carbon skeleton of the molecule, forming organic fragments that can be substantially more volatile than the parent organic. Alkoxy radicals therefore serve as an important connection between molecular structure and the change in volatility of a compound upon oxidation. Compounds with structural features that favor the isomerization pathway—relatively little branching, with 1,5-hydrogen shifts possible—are likely to substantially decrease in volatility upon oxidation, as will those in which dissociation will not lead to a significant reduction in carbon number (i.e., cyclic compounds). Decreases in volatility are not expected to be as dramatic for organics whose structures favor alkoxy radical fragmentation—i.e., small, acyclic, highly branched, and/or oxidized species.

The role of the isomerization channel in SOA formation has been established by the recent work of Ziemann and coworkers. In studies of  $NO_3$  + terminal alkenes (Gong et al., 2005) and  $OH$  +  $n$ -alkanes (Lim and Ziemann, 2005), online mass spectrometry was used to detect an array of particulate products (1,4-bifunctional compounds and substituted tetrahydrofurans) consistent with isomerization reactions. Additionally, it was shown that when alkoxy radical isomerization cannot occur (with no 1,5-hydrogen shift possible), SOA formation is strongly suppressed (Gong et al., 2005).

#### 2.4. $NO_x$ dependence of SOA formation

The relationship between product volatility and individual reaction steps in VOC oxidation allows for an understanding of how specific reaction

conditions govern the formation of SOA. Perhaps most important is the dependence of SOA yields and composition on the concentration of nitrogen oxides ( $\text{NO}_x$ ), the focus of a number of studies in the last several years. In the oxidation of small hydrocarbons (10 carbons or fewer), including isoprene (Kroll et al., 2006), monoterpenes (Hatakeyama et al., 1991; Pandis et al., 1991; Zhang et al., 1992; Presto et al., 2005a; Ng et al., 2007a), and simple aromatics (Hurley et al., 2001; Johnson et al., 2004; Song et al., 2005; Ng et al., 2007b), SOA yields are generally found to decrease substantially as  $\text{NO}_x$  increases. (Exceptions include the photooxidation of benzene (Martín-Reviejo and Wirtz, 2005) and the ozonolysis of limonene (Zhang et al., 2006), which exhibit little or no  $\text{NO}_x$  dependence.) Studies of larger hydrocarbons reveal a reverse  $\text{NO}_x$  dependence: for two sesquiterpenes studied (longifolene and aromadendrene), SOA yields are largest at high  $\text{NO}_x$  levels (Ng et al., 2007a), and high yields have been measured from the oxidation of large ( $>C_{12}$ ) alkanes in the presence of ppm levels of NO (Lim and Ziemann, 2005).

These results can largely be explained in terms of the three major branch points in VOC oxidation discussed above (choice of initiating oxidant, fate of  $\text{RO}_2$  radicals, and fate of RO radicals).  $\text{NO}_x$  level influences the initial oxidation step, by controlling the relative proportions of the hydroxyl radical, nitrate radical, and ozone, thereby changing the amount of SOA produced (Hurley et al., 2001; Nøjgaard et al., 2006). However, there are not always clear correlations between relative oxidant levels and SOA yields in photooxidation experiments (Martín-Reviejo and Wirtz, 2005; Song et al., 2005), and  $\text{NO}_x$ -dependent SOA yields have been observed even when only one oxidant is dominant (Presto et al., 2005a; Kroll et al., 2006), suggesting the importance of further radical ( $\text{RO}_2$  and RO) chemistry.  $\text{NO}_x$  level determines the fate of  $\text{RO}_2$  radicals, by controlling the branching between reaction (R2) ( $\text{RO}_2 + \text{NO}$ ) and reactions (R1) and (R4) ( $\text{RO}_2 + \text{peroxy radicals}$ ). For relatively small hydrocarbons,  $\text{RO}_2 + \text{NO}$  forms organic nitrates in low yields, and any alkoxy radicals formed will largely fragment or react with  $\text{O}_2$  (reactions (R5a) and (R5c)). Thus the production of low-volatility organics will be highest at low levels of  $\text{NO}_x$ , as hydroperoxides and acids are formed from the  $\text{RO}_2 + \text{HO}_2$  reaction (Hatakeyama et al., 1991; Johnson et al., 2004; Presto et al., 2005a; Kroll et al., 2006; Ng et al., 2007b). When  $\text{NO}_x$  is present,

SOA formation from these hydrocarbons generally begins only when NO drops to sub-ppb levels, and  $\text{RO}_2 + \text{HO}_2$  reactions can occur (e.g., Hoffmann et al., 1997; Hurley et al., 2001; Johnson et al., 2004, 2005; Song et al., 2005; Kroll et al., 2006).

By contrast,  $\text{RO}_2$  radicals formed from the oxidation of larger hydrocarbons react with NO to form organic nitrates in higher yields, and alkoxy radicals formed will predominantly react via the isomerization channel (reaction (R5b)). The predominance of these low-volatility channels at high  $\text{NO}_x$  likely explains the positive  $\text{NO}_x$  dependence of SOA yields observed for sesquiterpenes (Ng et al., 2007a) and the product distribution of SOA formed in the oxidation of large hydrocarbons (Lim and Ziemann, 2005).

It should be noted that the  $\text{NO}_x$  dependence of SOA formation likely extends beyond the role of the above reactions in controlling product volatility distributions. For example, the production of  $\text{HNO}_3$  may affect SOA formation, possibly via acid catalysis (Kalberer et al., 2004) (see Section 3). Additionally, while SOA yields from small hydrocarbons generally increase as  $\text{NO}_x$  decreases, some studies have found at low NO levels this dependence reverses (Pandis et al., 1991; Zhang et al., 1992; Kroll et al., 2006). Camredon et al. (2007) show this may be a result of the lower levels of OH, which in turn leads to a slower formation of semivolatiles. Similarly, when OH levels are very high, some SOA formation from aromatic precursors is observed even in the presence of NO (Stroud et al., 2004; Ng et al., 2007b), likely due to the rapid buildup of semivolatiles formed from the  $\text{RO}_2 + \text{NO}$  reaction. These effects result not from the volatility of reaction products but from reaction kinetics, and are discussed in greater detail in Section 4.

## 2.5. Overview and uncertainties

The simple VOC oxidation scheme shown in Fig. 4, in combination with the effects of common functional groups on vapor pressures (Table 1), provides a framework for estimating changes in volatility of organic compounds upon gas-phase oxidation, and helps explain observed dependences of reaction conditions (such as  $\text{NO}_x$  level) on SOA yields and composition. At the same time, it should be emphasized that such a simple scheme might not allow for the detailed prediction of product

volatility (or SOA yields) from individual hydrocarbons, as these may be governed by specific structural details. Quantitative prediction likely requires detailed mechanisms (e.g., Kamens et al., 1999; Colville and Griffin, 2004; Jenkin, 2004; Camredon et al., 2007), and continued experimental studies of SOA yields and composition from a wide range of precursors.

Qualitatively, the products predicted by the general VOC oxidation scheme in Fig. 4 to be lowest in volatility are the same as the (low-MW) organics found in SOA, including peroxides, nitrates, and hydroxylated compounds. An important exception is organic acids, which are expected to be formed only under  $\text{NO}_x$ -free conditions (by  $\text{HO}_2$  + acylperoxy radicals), but are found to be a major component of SOA formed in the presence of  $\text{NO}_x$  as well (Forstner et al., 1997a, 1997b; Fisseha et al., 2004; Sax et al., 2005; Surratt et al., 2006; Sorooshian et al., 2007b). Criegee intermediates from alkene ozonolysis form acids in low yields (<10%), likely too low to account for this (Orzechowska et al., 2005; Orzechowska and Paulson, 2005). Acids might be formed from isomerization reactions of acyloxy radicals (Jenkin et al., 2000) or peracids (Winterhalter et al., 2000), the oxidation of 1,2-hydroxycarbonyls (Butkovskaya et al., 2006), or reactions occurring in the particle phase. This uncertainty in the formation mechanism of a major SOA component underscores the need for continued study of gas-phase reaction mechanisms, particularly for the oxidation of large, oxygenated (and multifunctional) organics.

### 3. Particle-phase reactions

Organic compounds may also undergo chemical reactions in the condensed phase, affecting their chemical properties and volatility. As first suggested by Haagen-Smit (1952), and inferred by the ambient measurements of Ellis et al. (1984), these reactions may form products of low volatility. Particle-phase reactions, which include both heterogeneous and multiphase reactions (Ravishankara, 1997), are expected to be significant if they occur on timescales shorter than the lifetimes of tropospheric particles (4–7 days). In the last several years there has been substantial progress in understanding the chemistry of these reactions, which can be either non-oxidative (in which the oxidation state of the total carbon is unchanged) or oxidative (in which the carbon is oxidized).

#### 3.1. Non-oxidative processes

Considerable attention has been paid to the atmospheric formation of oligomeric (and other high-MW) species, via non-oxidative association reactions, also termed “accretion reactions” (Barsanti and Pankow, 2004). Since the vapor pressure of an organic species will decrease by about an order of magnitude for every two carbons added (Table 1), even a single dimerization reaction of a moderately sized ( $\text{C}_6$ – $\text{C}_{10}$ ) organic can lead to a large reduction in volatility. As a result, such reactions can play an important role in the formation of SOA, leading to more aerosol mass than would be inferred on the basis of the vapor pressure of the gas-phase species alone (e.g., Jang et al., 2002; Czochke et al., 2003; Jenkin, 2004; Johnson et al., 2004, 2005). Association products can include noncovalent adducts (Hoffmann et al., 1998), but much of the focus has been on longer-lived, covalently bound species.

The clearest experimental evidence for the occurrence of accretion reactions is the measurement of high-MW species in SOA (Kalberer et al., 2004; Tolocka et al., 2004; Iinuma et al., 2004; Gao et al., 2004a, 2004b). The formation of compounds with higher carbon numbers than the parent VOC are unlikely in the gas phase (exceptions include bimolecular reactions of Criegee intermediates, and possibly some  $\text{RO}_2 + \text{RO}_2$  reactions (Ziemann, 2002)), strongly suggesting a particle-phase process. These components often exhibit repetitive mass spectral signatures, characteristic of oligomeric species. High-MW species in laboratory-generated aerosols have been detected using a range of mass spectrometric techniques, including (matrix-assisted) laser desorption ionization (Kalberer et al., 2004, 2006; Dommen et al., 2006; Holmes and Petrucci, 2006; Surratt et al., 2006; Reinhardt et al., 2007), electrospray ionization (Tolocka et al., 2004; Iinuma et al., 2004, 2007a, 2007b; Gao et al., 2004a, 2004b; Hamilton et al., 2006; Sadezky et al., 2006; Surratt et al., 2006, 2007a; Reinhardt et al., 2007; Sato et al., 2007), online mass spectrometry (Bahreini et al., 2005; Zahardis et al., 2005; Alfaraa et al., 2006; Gross et al., 2006; Kroll et al., 2006; Liggió et al., 2005, 2007; Liggió and Li, 2006a; Heaton et al., 2007), gel permeation chromatography (Angove et al., 2006), and derivatization/GC-MS (Surratt et al., 2006; Szmigielski et al., 2007). Aside from these studies,

the importance of accretion reactions under tropospheric conditions can be inferred from several other lines of evidence:

- Particle-phase aldehyde concentrations much higher than expected based on their vapor pressures (Forstner et al., 1997a, 1997b; Kalberer et al., 2000; Jang and Kamens, 2001a; Matsunaga

et al., 2003, 2004, 2005; Lee et al., 2004, 2005), likely due to the reversion of high-MW species to their higher-volatility monomers during analysis (Tobias et al., 2000);

- Increased SOA yields in the presence of acidic seed particles (Jang and Kamens, 2001b; Jang et al., 2002; Czoschke et al., 2003; Gao et al., 2004a, 2004b; Inuma et al., 2004; Edney et al., 2005;

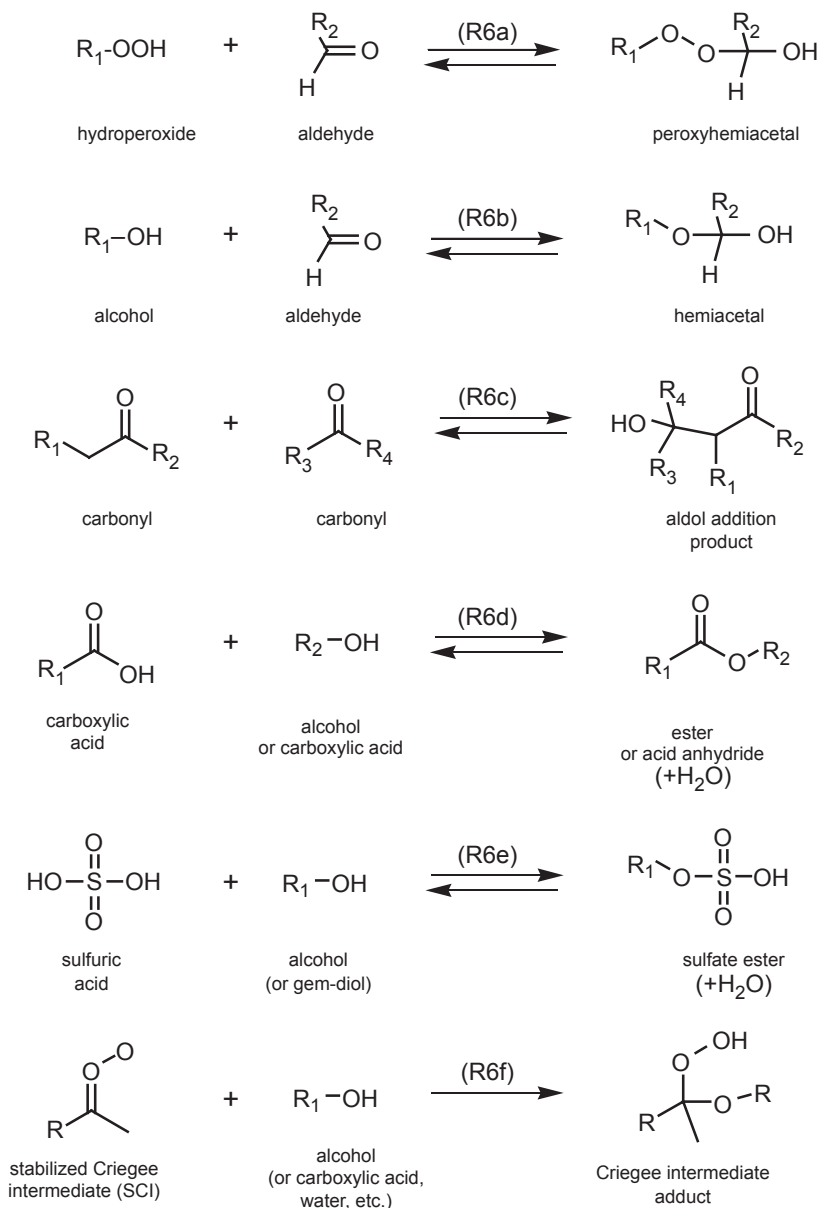


Fig. 8. Particle-phase accretion reactions that may affect the volatility of atmospheric organics. (R6a) Peroxyhemiacetal formation; (R6b) hemiacetal formation; (R6c) aldol condensation; (R6d) ester (acid anhydride) formation; (R6e) organosulfate formation; (6f) Criegee reactions with alcohol/water/acids (reactions with carbonyls or other intermediates are also possible). Not shown: accretion reactions of alkenes, the products of which are poorly constrained.

Czoschke and Jang, 2006b; Kleindienst et al., 2006; Surratt et al., 2006, 2007b);

- The observed uptake of gas-phase glyoxal (a volatile C<sub>2</sub> dialdehyde) into aqueous ammonium sulfate particles (Jang and Kamens, 2001b; Hastings et al., 2005; Kroll et al., 2005b; Liggio et al., 2005), as well as other VOCs into acidic aerosol; and
- Formation of low-volatility components of SOA even after the completion of gas-phase chemistry (Tobias and Ziemann, 2000; Kalberer et al., 2004; Dommen et al., 2006; Paulsen et al., 2006).

Shown in Fig. 8 are several classes of condensed-phase accretion reactions which have been investigated experimentally for their role in SOA formation. The first to be identified was (R6a) the reaction of hydroperoxides with aldehydes to form peroxyhemiacetals (Tobias et al., 2000; Tobias and Ziemann, 2000). Others include (R6b) hemiacetal formation (Jang and Kamens, 2001b; Jang et al., 2002; Garland et al., 2006; Surratt et al., 2006; Zhao et al., 2006); (R6c) aldol condensation (Nozière and Riemer, 2003; Esteve and Nozière, 2005; Zhao et al., 2005; Czoschke and Jang, 2006a; Garland et al., 2006; Casale et al., 2007); (R6d–e) formation of acid anhydrides (Gao et al., 2004a, 2004b) esters (Surratt et al., 2006; Hamilton et al., 2006; Szmigielski et al., 2007), and organosulfates (Levitt et al., 2006; Liggio and Li, 2006b; Surratt et al., 2007a, 2007b; Iinuma et al., 2007a, 2007b); and (R6f) reactions of Criegee intermediates (e.g., Sadezky et al., 2006; Heaton et al., 2007; Zahardis and Petrucci, 2007). In the presence of strong acid, condensed-phase reactions of alkenes (not shown) have been observed (Limbeck et al., 2003; Liggio et al., 2007), though to date there exist no speciated molecular data to constrain the products or mechanism. Laboratory studies have also found evidence for particle-phase reactions which do not form high-MW products but rather increase volatility, such as carbocation rearrangements (Czoschke and Jang, 2006a) and retroaldol reactions (Nozière and Riemer, 2003).

A particle-phase reaction will have a significant influence on organic volatility and SOA formation only if it is both thermodynamically and kinetically favorable. The thermodynamics of many of the above reactions were modeled by Barsanti and Pankow (2004, 2005, 2006) and Tong et al. (2006). Accretion reactions of simple volatile monocarbonyls were generally found to be unfavorable, in contrast to the observed uptake of several aldehydes

(Jang and Kamens, 2001b; Jang et al., 2003a, 2003b). However, uptake reactions of glyoxal, observed in several studies (Jang and Kamens, 2001b; Hastings et al., 2005; Kroll et al., 2005b; Liggio et al., 2005), were predicted to be thermodynamically favored (Barsanti and Pankow, 2005; Tong et al., 2006). The formation of esters and amides from the reaction of carboxylic acids with alcohols or amines (R6d) was also found to be favorable (Barsanti and Pankow, 2006), consistent with the measurement of esters in SOA (Surratt et al., 2006; Hamilton et al., 2006; Szmigielski et al., 2007).

The kinetics of particle-phase accretion reactions are less well understood, owing in part to uncertainties in relating laboratory conditions to the atmosphere. If a particle-phase reaction is observed to occur in the laboratory, but occurs negligibly slowly (with a timescale of over 1 week) under ambient conditions, it is probably atmospherically unimportant.

A major uncertainty is the role of particle-phase acidity. The rates of most reactions shown in Fig. 8 are greatly enhanced in acidic environments, likely explaining the increase in SOA yields in the presence of acidic seed particles (Jang et al., 2002). This effect is largest for SOA formation from the most volatile species, as a reduction in volatility cannot substantially affect the partitioning of organics that are already predominantly in the particle phase. Hence the “acid effect” for isoprene is substantially larger than that for  $\alpha$ -pinene (Kleindienst et al., 2006), which in turn is higher than that for limonene (Iinuma et al., 2007b).

Oligomer formation does not necessarily require strong acidity to occur rapidly, as oligomeric species have been measured in SOA when no inorganic seed is present (Kalberer et al., 2004, 2006; Gao et al., 2004a, 2004b; Heaton et al., 2007) and even under conditions in which no acids of any sort are present (Surratt et al., 2006). On the other hand, several of the reactions shown in Fig. 8, including aldol condensation and the reactive uptake of alkenes, require exceedingly high acidities to occur on reasonable timescales. Because of neutralization by ammonia, tropospheric particles are generally substantially less acidic than the H<sub>2</sub>SO<sub>4</sub> solutions often employed in laboratory studies (50–100% neutralization is typical in most environments) (e.g., Lewandowski et al., 2007; Peltier et al., 2007; e.g., Zhang et al., 2007). Specific types of particles may be more acidic due to low ammonia availability,

such as those that are freshly nucleated, recently produced from coal or diesel combustion, or formed in remote (marine, arctic, or upper tropospheric) regions. Even under these conditions aldol reactions (R6c) of simple carbonyls are too slow to occur to an appreciable extent (Esteve and Nozière, 2005; Casale et al., 2007); continued study of the detailed kinetics of a wide range of accretion reactions is necessary to understand the potential role of particle acidity on SOA formation.

The observed formation of oligomers in laboratory studies may be enhanced by the high concentrations of reactive species in the particle phase. Atmospheric particles are generally substantially less concentrated in reactive organics, which could lead to a reduction in the rate of oligomer formation (Kalberer et al., 2004). Assuming the kinetics of oligomer formation are of second order (or higher), these differences could be sufficiently large to affect SOA formation dramatically (Chan et al., 2007).

The reversibility of accretion reactions is also highly uncertain. If high-MW products do not revert to monomeric reactants over atmospherically relevant timescales, then their formation is effectively irreversible, leading to a substantial low-volatility fraction of SOA, and high SOA yields (Chan et al., 2007). On the other hand, if high-MW species are formed reversibly (with fast reversion to reactants), then they are only temporary reservoirs for semivolatile organics, and their formation can be approximated as a possibly small increase in the gas–particle partitioning coefficient  $K_p$  (Kroll and Seinfeld, 2005). This distinction has major implications for atmospheric aerosol, as predicted aerosol loadings are far higher when SOA is formed irreversibly than when it is formed by reversible processes (Tsigaridis and Kanakidou, 2003).

The available experimental evidence regarding the reversibility of accretion reactions is somewhat contradictory. On one hand, as discussed in the Introduction, most laboratory studies of SOA growth are consistent with the partitioning of semivolatile species, which is inherently reversible. Themodenuder (An et al., 2007) and dilution (Grieshop et al., 2007) studies of SOA from  $\alpha$ -pinene ozonolysis also indicate reversible SOA formation. On the other hand, some of the high-MW compounds identified in SOA, such as peroxyhemiacetals, esters, and organosulfates, are thermally stable, suggesting irreversible formation. How such compounds are formed within the context of semivolatile partitioning is not obvious.

One possibility is that semivolatiles either react in the particle phase to form nonvolatile species, or are lost in the gas phase by channels other than SOA formation; the competition between the two pathways may lead to aerosol growth consistent with semivolatile partitioning (Kroll et al., 2007).

### 3.2. Oxidative processes

Oxidation of particle-phase organics by atmospheric oxidants (OH, NO<sub>3</sub>, O<sub>3</sub>, etc.), sometimes called “aerosol aging”, is another mechanism by which organic aerosols may evolve chemically. This class of reaction has recently been reviewed by Rudich et al. (2007), so is discussed here only in the context of changes to organic volatility. In general, the chemical mechanisms of oxidation reactions in the particle phase are the same as those in the gas phase (Section 2). However, the branching ratios among the various pathways may be quite different, which can have profound effects on the vapor pressures of the products. As with gas-phase oxidation, the key determinant of changes to organic volatility is the competition between carbon–carbon bond cleavage (e.g., by alkoxy radical decomposition) and addition of polar functional groups.

Particle-phase alkenes are subject to reaction with ozone (de Gouw and Lovejoy, 1998). The particle-phase ozonolysis reaction that has received by far the most study is O<sub>3</sub> + oleic acid (an alkenoic acid, C<sub>18</sub>H<sub>34</sub>O<sub>2</sub>) (Morris et al., 2002), the subject of a recent comprehensive review (Zahardis and Petrucci, 2007). The reaction mechanism is found to be broadly consistent with gas-phase ozonolysis (Fig. 5), forming both volatile products (such as nonanal and nonanoic acid) from the initial cleavage of the C–C double bond and low-volatility, high-MW species consistent with further reactions of SCIs (e.g., Ziemann, 2005; Reynolds et al., 2006; Zahardis and Petrucci, 2007). Such reactions (via the “SCI channel”) are more likely to be important in particles than in the gas phase, owing to greater thermalization of the Criegee intermediate and higher concentrations of condensed-phase organics; there exists little evidence for the “hydroperoxide channel” occurring in particles.

All particle-phase organics are subject to oxidation by radicals (OH, NO<sub>3</sub>, Cl), which has received considerably less study. The general mechanisms are believed to be the same as those in the gas phase (Fig. 4), but the branching ratios of the individual

reactions may vary. In particular, the reactions of alkoxy radicals (Fig. 6) may be substantially different. Hearn et al. (2007) report evidence that alkoxy + O<sub>2</sub> (reaction (R5c)) is an important channel; to date, there is no evidence of particle-phase alkoxy isomerization reactions (R5b). The volatility of the reaction products is thus strongly influenced by the alkoxy radical dissociation channel (R5a), which is the subject of some debate. Some studies of the oxidation of model condensed-phase organics report rapid volatilization or formation of volatile products (Eliason et al., 2004; Molina et al., 2004), whereas others find volatilization to be negligible or minor (Moise and Rudich, 2001; Docherty and Ziemann, 2006; Knopf et al., 2006; George et al., 2007; Hearn et al., 2007; Lambe et al., 2007). It has been suggested that these differences may be a result of different experimental conditions (Hearn et al., 2007) or phase of the model organic (Docherty and Ziemann, 2006); constraining such dependences is crucial for understanding how atmospheric aging affects the properties of particle-phase organics. Such studies have so far been carried out only on relatively reduced organic compounds, acting as surrogates for primary organic aerosol. Similar studies have not been carried out for highly oxidized organic aerosol such as SOA, though there is some indication that volatilization may be increasingly important in that case (George et al., 2007; Hearn et al., 2007).

The oxidation state and volatility of organics in the particle phase may also be affected by photolytic processes. Irradiation of SOA and other oxidized condensed-phase organics by light in the actinic region efficiently forms formaldehyde and formic acid, likely from the photolysis of particulate peroxides (Gomez et al., 2006; Park et al., 2006; Walser et al., 2007). Similarly, irradiation of SOA from the low-NO<sub>x</sub> oxidation of isoprene leads to substantial volatilization (Kroll et al., 2006) and reduction in peroxide content (Surratt et al., 2006), also consistent with peroxide photolysis (though roles of OH reactions and/or gas-phase processes could not be ruled out).

While most studies of aerosol aging involve purely organic phases, aqueous-phase organics may also undergo oxidation. Such reactions have been studied for their role in cloud processing (Blando and Turpin, 2000; Gelencsér and Varga, 2005), and may be important in aqueous aerosol particles as well. The OH-initiated oxidation of aqueous 3,5-dihydroxybenzoic acid forms high-MW

products that strongly absorb light in the visible and UV ranges (Gelencsér et al., 2003; Hoffer et al., 2006). The oxidation of pyruvic acid and glyoxal also leads to oligomeric products (Altieri et al., 2006; Carlton et al., 2006, 2007), though these degrade to form smaller species. Final products include oxalic acid, indicating that aqueous-phase oxidation may be an important channel for the conversion of aldehydes and ketones to lower-volatility carboxylic acids. Isoprene, methacrolein, and related species have been shown to form polyols in the presence of H<sub>2</sub>O<sub>2</sub>/acid solutions, also suggesting oxidation in the aqueous phase (Claeys et al., 2004; Böge et al., 2006).

### 3.3. Evidence for particle-phase reactions in the atmosphere

Several lines of evidence suggest that particle-phase reactions occur in the atmosphere, influencing the volatility of atmospheric organics. A number of products from non-oxidative (accretion) reactions that have been generated in the laboratory have been measured in ambient aerosol, including dimeric hemiacetals and esters from isoprene oxidation (Surratt et al., 2006) and organosulfates from isoprene and monoterpene oxidation (Gao et al., 2006; Surratt et al., 2006; Inuma et al., 2007a). Organosulfates have also been detected in ambient aerosol using FTIR (Blando et al., 1998; Maria et al., 2003; Gilardoni et al., 2007) and ESI-MS (Romero and Oehme, 2005; Reemtsma et al., 2006). High-MW species with repetitive mass spectral signatures characteristic of oligomers have also been observed (Kalberer et al., 2006; Denkenberger et al., 2007), though not in all environments (Gao et al., 2006). Additionally, high concentrations of volatile oxygenates have been measured in ambient aerosol (Matsunaga et al., 2003, 2004, 2005), suggesting the importance of accretion reactions of these species. The role of aerosol acidity in promoting such reactions and affecting organic aerosol loading is unclear. Some studies report enhancements in aerosol volume (Brock et al., 2003), OC (Chu, 2004), and SOA tracer species (Lewandowski et al., 2007) in the presence of acidic aerosol, whereas others report little to no enhancement of organic aerosol under acidic conditions (Zhang et al., 2005b, 2007; Takahama et al., 2006; Peltier et al., 2007).

An important role of oxidative chemistry in the evolution of tropospheric aerosol is also apparent.



Measurements of oxalic acid (and other small diacids) suggest a formation mechanism via cloud processing (Warneck, 2003; Crahan et al., 2004; Yu et al., 2005; Sorooshian et al., 2006, 2007a). Photochemical aging of particulate organics has been inferred from the changes in relative concentrations of speciated organics, including hopanes, alkenoic acids, and PAHs (Robinson et al., 2006a, 2006b). Size-dependent measurements of the carbonyl content of organic aerosol also suggest photochemical processing of particles (Maria et al., 2004).

An unresolved question is how the high-MW products formed from particle-phase reactions relate to the formation of “humic-like substances” (HULIS) (Graber and Rudich, 2006). These water-soluble, macromolecular, low-volatility compounds are of an origin that appears to be at least partly photochemical in nature (Decesari et al., 2002; Samburova et al., 2005). The species formed from non-oxidative accretion reactions of secondary organics may be sufficiently large to have some relation to HULIS, though their aromatic content and light-absorbing properties have not been reported. The aqueous oxidation of aromatic species, on the other hand, has been shown to form light-absorbing, high-MW products (Gelencsér et al., 2003; Hoffer et al., 2006). It seems likely that HULIS of photochemical origin arises from a complex matrix of precursors, undergoing a large number of oxidative as well as non-oxidative particle-phase reactions.

#### 4. Multigenerational chemistry

All organic compounds in the atmosphere, whether in the gas phase or the particle phase, are susceptible to oxidation. Thus, even after a particular oxidation reaction has gone to completion, and/or SOA is formed, the organic products will continue to evolve chemically. As discussed in the previous two sections, this chemical evolution can occur in the gas or particle phases, involving increases or decreases in organic volatility. As a result, over the course of their atmospheric lifetimes, organic aerosol particles (even if formed from a single precursor hydrocarbon) will continually undergo changes in both loading and physicochemical properties. Such changes will continue until all OC is oxidized to CO and CO<sub>2</sub>, or is removed from the atmosphere by physical processes (wet or dry deposition). As a result, the extent of oxidation of an organic compound has a governing influence on

the volatility distribution of the products and hence on SOA yields.

##### 4.1. Multiple generations of oxidation

This evolution can be described in terms of the number of oxidation steps undergone, or “generation number” of product formed (Donahue et al., 2005). The role of multiple oxidation steps in SOA formation can be inferred from the time dependence of SOA formation in chamber studies (Bowman et al., 1997; Hoffmann et al., 1997; Yu et al., 1999b; Ng et al., 2006, 2007a, 2007b; Zhang et al., 2006). This is clearly illustrated using “growth curves” (Ng et al., 2006), plots of SOA formed vs. precursor hydrocarbon reacted over the course of an experiment (Fig. 9). Shown in Fig. 9a are growth curves from several  $\alpha$ -pinene ozonolysis experiments, carried out over a range of hydrocarbon concentrations. In all cases SOA growth ceases when  $\alpha$ -pinene is completely consumed, and all experiments follow the same general curve, corresponding to the “final growth” from each experiment. This is consistent with the known ozonolysis mechanism, in which O<sub>3</sub> reacts only with the one double bond in  $\alpha$ -pinene. In the absence of OH no additional oxidation can occur, and the SOA formed is a first-generation product.

Fig. 9b shows growth curves from the ozonolysis of terpinolene (a monoterpene with two double bonds). In contrast with the  $\alpha$ -pinene case, there is substantial growth after the complete consumption of the parent hydrocarbon (the “hook” near the end of each curve). This indicates an additional rate-limiting step to SOA formation; measurements of gas-phase intermediates strongly suggest this additional step is the oxidation of the second double bond of the terpene. In this case, more than one generation of oxidation products play a role in the formation of SOA; this kinetic behavior appears to be general for most alkenes with more than one double bond (Ng et al., 2006), though there are some exceptions (Zhang et al., 2006). The kinetics of SOA formation from the oxidation of aromatic compounds also suggests multiple oxidation steps are involved, though the slowest is the initial oxidation step (aromatic+OH), consistent with the known chemistry of the oxidation of aromatics (Ng et al., 2007b). Multigenerational chemistry can instead lead to an increase in organic volatility, as SOA from the low-NO<sub>x</sub> oxidation of isoprene decreases in mass upon further oxidation (Kroll et al., 2006).

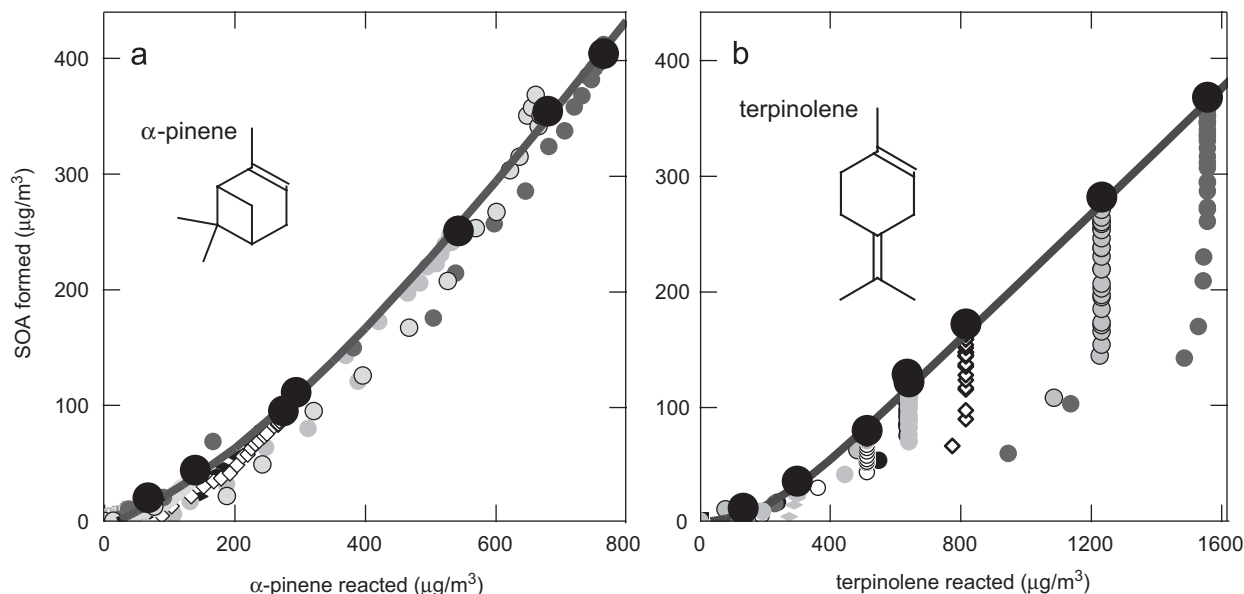


Fig. 9. “Growth curves”, plots of SOA growth ( $\Delta M$ ) vs. hydrocarbon reacted ( $\Delta HC$ ) over the course of an experiment, from the ozonolysis of  $\alpha$ -pinene (a) and terpinolene (b). Different symbols denote individual experiments with differing initial hydrocarbon concentrations. Large black circles indicate “final” SOA growth, from which SOA yields are typically determined; lines are the two-product fits Eq. (3) to those data. The vertical sections (“hooks”) in the terpinolene experiments indicate SOA formation from processes other than the initial  $O_3$ -alkene reaction, likely ozonolysis of the second double bond (multigenerational oxidation). Only one generation of products is possible for  $\alpha$ -pinene ozonolysis, and SOA is formed promptly. Adapted from Ng et al. (2006).

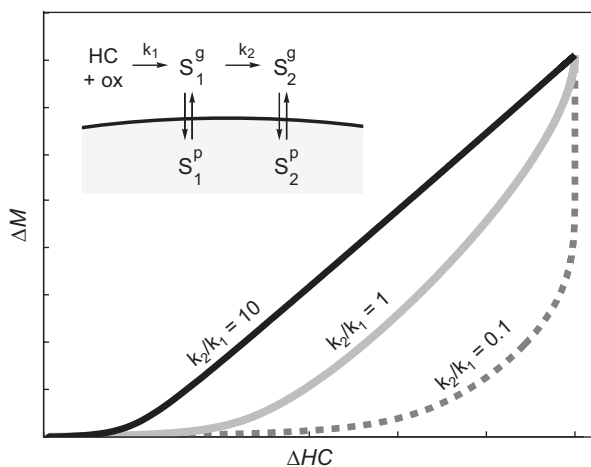


Fig. 10. Aerosol “growth curves” illustrating the effect of two generations of oxidation on SOA formation. It is assumed that the second-generation product  $S_2$  is much less volatile than the first-generation product  $S_1$  ( $K_{p2}/K_{p1} = 10$ ) and that  $1 \mu\text{g m}^{-3}$  of absorbing aerosol is present initially. The relative rates of the two oxidation steps ( $k_2/k_1$ ) determine the dependence of aerosol growth ( $\Delta M$ ) on the amount of hydrocarbon reacted ( $\Delta HC$ ).

The kinetics of SOA formation over multiple generations was recently examined by Chan et al. (2007). Fig. 10 depicts modeled SOA formation

from two generations of oxidation products, in which the second-generation product  $S_2$  is an order of magnitude less volatile than the first-generation product  $S_1$  ( $K_{p2}/K_{p1} = 10$ ). An initial amount of absorbing aerosol,  $M = 1 \mu\text{g m}^{-3}$  is assumed to be present, and no other reactions are considered. Three kinetic cases are considered, in which the rate of the second oxidation reaction ( $k_2$ ) is varied relative to that of the first oxidation reaction ( $k_1$ ) by two orders of magnitude. When the second oxidation is slow relative to the first ( $k_2/k_1 = 0.1$ ), much of the SOA formation takes place after the hydrocarbon has been completely reacted, corresponding to the case shown in Fig. 9b. On the other hand, when the second step is relatively fast ( $k_2/k_1 = 10$ ), SOA formation is governed largely by the rate of the initial oxidation reaction. In this simple example, in all cases the amount of SOA generated eventually is identical, because as  $S_1^g$  is oxidized to  $S_2^g$ ,  $S_1^p$  is drawn back out of the aerosol phase. However, under more realistic conditions, in which aerosol lifetimes are finite and competing reactions can occur, these differences in SOA formation kinetics may affect the total SOA produced; this is discussed in the following subsection.

The role of multiple generations of oxidation products in the formation and evolution of laboratory SOA has been inferred from approaches other than the kinetic (growth curve) arguments above. In the oxidation of long-chain alkanes and alkenes, large differences in volatility and chemical composition can be used to distinguish first- vs. later-generation SOA components (Gong et al., 2005; Lim and Ziemann, 2005); the later-generation products are likely from the rapid oxidation of unsaturated dihydrofurans (see Fig. 7). Additionally, in order to more directly probe the multi-generational chemistry of SOA formation, several studies have investigated aerosol formation from the further oxidation of known hydrocarbon oxidation products. This includes products from the oxidation of aromatics (Grosjean, 1984, 1985), isoprene (Kroll et al., 2005a, 2006; Surratt et al., 2006), and monoterpenes (Nozière et al., 1999; Spittler et al., 2006; Donahue et al., 2007). Such studies allow for the identification of which specific pathways within complex oxidation mechanisms are most important in the formation of lower-volatility products.

In most of these cases, multistep reactions involve the oxidation of double bonds, relatively fast chemistry occurring on timescales of most chamber experiments. Time-dependent, batch laboratory chamber studies are typically carried out for durations of 12 h or less, whereas steady-state, continuous-flow chambers have residence times in the range of several hours. Such experiments are generally too short to include the influence of photochemical “aging”, changes in volatility by oxidation reactions occurring over longer timescales (days to weeks). An important set of aging reactions are H-atom abstractions by OH; because of their slow rates ( $< 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), their influence on SOA formation and evolution is not well constrained. It is, however, clear that such reactions can have a substantial impact on organic volatility: the multistep oxidation of diesel exhaust (a complex mixture of alkanes) leads to significant SOA production (Robinson et al., 2007; Sage et al., 2007; Weitkamp et al., 2007), and further oxidation of OH +  $\alpha$ -pinene reaction products leads to increases in the loading (Ng et al., 2007a) and level of oxidation (Alfarra et al., 2006) of SOA. While the detailed chemistry and identity of reaction products remain uncertain, these studies indicate that oxidation reactions subsequent to the initial fast chemistry typically observed in chamber studies can

indeed influence volatility distributions. This is likely to have an influence on SOA formation in the atmosphere: at the conclusion of most chamber studies, there is typically a substantial amount of organic carbon remaining in the gas phase (e.g., Larsen et al., 2001; Lee et al., 2006a, 2006b), which may serve as a source of potential SOA mass over longer timescales. Several generations of oxidation may be accessible experimentally using flow reactors, which allow for much higher concentrations of oxidants, though the much faster reaction rates and higher concentrations of radicals (such as OH or RO<sub>2</sub>) may introduce chemistry that is unrepresentative of the atmosphere.

#### 4.2. Reactions of semivolatile organics

Multigenerational chemistry can also play a major role in the evolution of existing organic particulate matter: all semivolatile organics have some fraction in the gas phase, where they are continually subject to gas-phase oxidation processes. Such reactions can lead to large changes (increases or decreases) in the volatility of organics, implying continual changes not only in the chemical properties of the aerosol, but also in the total aerosol loading. However, timescales for the gas-phase oxidation of semivolatiles is typically longer than those of volatile organics, as they are governed not just by the oxidative lifetime (as defined by the rate constant and the oxidant level), but also by the fraction of the species present in the vapor phase (as determined by gas–particle partitioning). Thus the effects of such reactions may be even less obvious over the timescales of most laboratory experiments. Nonetheless, there are indications that gas-phase reactions of semivolatile organics may have an effect on measured SOA yields in chamber studies (Chan et al., 2007; Kroll et al., 2007). Over much longer timescales (several days), such effects can be large (Camredon et al., 2007; Robinson et al., 2007), so that reactions of semivolatiles may play a major role in total SOA production.

Reactions of semivolatile organics have important implications for laboratory measurements of SOA formation, and the application of SOA yields to atmospheric conditions. Fig. 11 shows a simplified schematic of reactions available to a given semivolatile compound: after formation in the gas phase (reaction i) the compound partitions between the gas and particle phases, and may undergo reactions (ii and iii) in either phase. The total

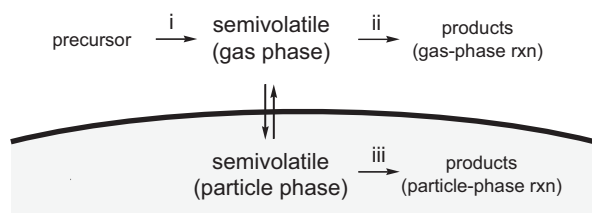


Fig. 11. Chemical and partitioning processes available to a single semivolatile compound formed in the gas phase: (i) formation, (ii) reaction in the gas phase, and (iii) reaction in the particle phase. Adapted from Kroll et al. (2007).

concentration of the semivolatile organic is governed by the balance between these formation and loss processes. Assuming first-order loss rates do not change, then the concentration of the semivolatile compound depends on the rate of formation; as a result, SOA yields may depend critically on the oxidation rate of the parent hydrocarbon (Chan et al., 2007). This “rate effect” may explain discrepancies in measured yields from aromatic compounds (Ng et al., 2007b), as well as the complexities in the observed  $\text{NO}_x$  dependence of some SOA yields (Camredon et al., 2007).

Additionally, the degree to which semivolatile products partition into the aerosol phase depends on the amount of organic aerosol present. If no organic aerosol is present initially (as is the case in most chamber studies), partitioning will not occur immediately, and the gas-phase reaction (ii) may proceed to an extent greater than it would under most atmospheric conditions (Kroll et al., 2007). Conversely, when aerosol loadings are much higher than those in the ambient atmosphere (often the case late in chamber experiments), partitioning into the particle phase will be efficient, effectively “trapping” semivolatiles in the particle phase, promoting particle-phase reactions and preventing further gas-phase reactions that would otherwise occur. In either case, aerosol yield could be different than it would be under atmospheric conditions; the sign and magnitude of this effect depend on how volatility changes upon further reaction (ii and iii).

In summary, the yield and composition of SOA from a given parent hydrocarbon are not fixed quantities, but rather are functions of “generation number”, the extent to which oxidation products undergo further reaction. Because of the relatively short timescale of most chamber experiments (on the order of hours), yields from only the first few

generations of oxidation products are typically measured, whereas atmospheric oxidation can continue for several days; this can lead to substantial differences in volatility distributions and hence aerosol loading.

## 5. Conclusions

Since the volatility of an organic compound in the atmosphere can change by reactions in the gas phase (Section 2) and reactions in the particle phase (Section 3), over the course of several generations of oxidation (Section 4), the reaction scheme underlying SOA formation is probably something like that shown in Fig. 12. Note that this scheme shows only a single product from each reaction; in most cases there is likely to be substantially more branching, with each step forming a number of products, possibly spanning a wide range of vapor pressures.

Because of this complexity, accurately describing SOA formation by simulation of full underlying chemical mechanisms presents an immense challenge. The majority of low-volatility species involved in SOA formation have not been identified, let alone characterized in terms of volatility and further chemistry. As a result, models that describe

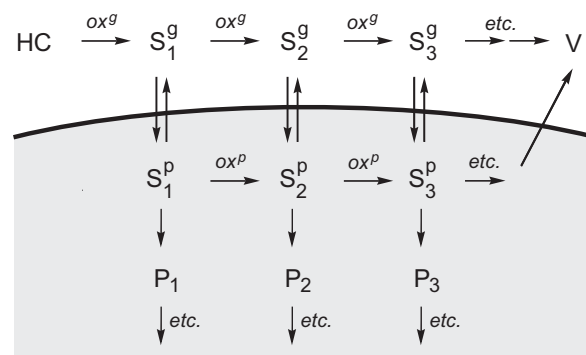


Fig. 12. Mechanism of SOA formation and evolution, showing multiple generations of gas-phase and particle-phase reactions. “S” corresponds to semivolatile compounds; “P” to compounds formed in the particle phase (which can be semivolatile, or, in the case of high-MW species, nonvolatile); and “V” to fully volatile compounds ( $\text{CO}_2$ ,  $\text{CO}$ , and light organics). Each reaction is likely accompanied by a change in volatility, the magnitude and sign of which is a strong function of chemical structure and reaction conditions (see Section 2). Note that only one product from each reaction is shown; in reality most reactions will produce several products spanning a range of vapor pressures. Oxidation in the particle phase ( $\text{ox}^p$ ) is likely much slower than in the gas phase ( $\text{ox}^g$ ), and branching ratios may be very different.

SOA formation in terms of detailed chemical reactions and the calculated vapor pressures of products generally have difficulty reproducing laboratory observations. Such models do not accurately reproduce measured concentrations of individual gas- or particle-phase species (e.g., Kamens and Jaoui, 2001; Leungsakul et al., 2005a, 2005b), and/or predict less aerosol formation than is observed (Colville and Griffin, 2004; Jenkin, 2004; Johnson et al., 2004, 2005; Chen and Griffin, 2005). In the latter case, agreement with observations requires partitioning coefficients to be scaled up (vapor pressures to be reduced) by one or more orders of magnitude, suggesting the formation of compounds of lower volatility than models predict.

Even if SOA could be accurately described in terms of the full set of underlying reactions, such a computationally expensive approach is probably infeasible within global transport models, and simpler treatments of SOA formation are necessary. Parameterizations based upon gas–particle partitioning of semivolatile organics (Eq. (3)) have been shown to represent laboratory SOA yields from a single precursor hydrocarbon under a single set of experimental conditions well. Most common is the “two-product model” (depicted in Fig. 1) (Odum et al., 1996); a more flexible approach is the “volatility basis set” (Donahue et al., 2006), which involves a larger number of lumped semivolatile compounds.

As mentioned in the Introduction, models based on laboratory measurements of volatility distributions (SOA yields) from traditional SOA precursors, such as monoterpenes and aromatics, underpredict ambient aerosol loadings (de Gouw et al., 2005; Heald et al., 2005; Volkamer et al., 2006). Possible reasons for this discrepancy between modeled and measured SOA include:

- (1) SOA yields under atmospheric conditions from known SOA precursors exceed those measured in laboratory experiments;
- (2) uncertainties in current treatments of SOA formation in models lead to biases that generally result in underpredictions of SOA loading; or
- (3) there exist additional classes of SOA precursors that have yet to be studied in the laboratory or included in models.

It seems likely that all three potential errors contribute to the model-measurement discrepancies in SOA. Each possibility is discussed below.

### 5.1. Differences between SOA formation in chambers and in the atmosphere

It is clear that SOA formation is highly dependent on a wide range of experimental conditions, including  $\text{NO}_x$  level, particle acidity, preexisting aerosol mass, and oxidation rate. The full range of atmospheric conditions has not yet been achieved in laboratory studies, so SOA formation in the atmosphere could occur under regimes different from those employed in chambers so far. Indeed, AMS measurements (Bahreini et al., 2005; Alfarra et al., 2006) indicate that most laboratory-generated SOA is substantially less oxidized than ambient oxygenated organic aerosol (OOA) (Zhang et al., 2005a). This may be due in part to the high aerosol loadings typically employed in chamber experiments: particle-phase organics at low organic loadings are substantially more oxidized than those at higher concentrations (Baltensperger et al., 2005; Tolocka et al., 2006), consistent with semivolatile partitioning. This underscores the need for laboratory experiments to be carried out under atmospherically relevant organic aerosol loadings. Such conditions allow for more accurate determination of atmospheric SOA yields than those inferred from higher-concentration experiments (Presto and Donahue, 2006), and ensure that reactions of semivolatile organics occur at rates relevant to the atmosphere (Kroll et al., 2007). Another major difference between atmospheric conditions and most chamber experiments is  $\text{RO}_2$  chemistry (Section 2.2); simulating atmospheric conditions by control of the relative concentrations of  $\text{HO}_2$ ,  $\text{RO}_2$ ,  $\text{NO}$ , and  $\text{NO}_2$  presents a substantial challenge. Other potential differences between chamber and atmospheric conditions include oxidant levels, inorganic seed composition, temperature, relative humidity, and level of irradiation.

Additionally, as discussed in Section 4, chamber studies generally are not carried out for more than  $\sim 12$  h. In the atmosphere, oxidation reactions can proceed as long as the organic material is airborne; thus, chamber studies cannot capture sustained, multiday oxidation and its effects on volatility and associated SOA formation. There is some evidence that “aged” laboratory aerosol, which has gone through several generations of oxidation, exhibit mass spectra and levels of oxidation (as measured by the  $\text{CO}_2^+$  ion,  $m/z$  44) more similar to those of ambient measurements (Alfarra et al., 2006; Robinson et al., 2007; Sage et al., 2007).

## 5.2. Treatments of SOA in models

Most semiempirical models neglect the effects of specific reaction conditions and extent of oxidation on SOA formation, instead of using a single parameterization of SOA yield for each precursor. This is likely to be a major source of model-measurement discrepancy. One difficulty is that many such effects are known to be important from laboratory studies but remain largely unquantified. The  $\text{NO}_x$  dependence of SOA yields has been parameterized only recently (Presto and Donahue, 2006; Ng et al., 2007a) and is not yet widely included in models. The effects of rapid particle-phase reactions (oligomer formation) are inherent in SOA yield measurements, but the effects of specific reaction conditions (RH, acidity, etc.) are largely unknown. Moreover, most models treat the formation of semivolatiles as a single-step chemical process, and exclude the effects of multigenerational chemistry on SOA formation. Recent models have begun including the effects of multiday aging on organic volatility and SOA loading, using either the “volatility basis set” approach (Robinson et al., 2007) or a detailed chemical mechanism (Camredon et al., 2007), though the changes in volatility upon oxidation are not directly informed by experiments. Further, cloud processing has been shown to be a potentially large source of SOA (Ervens et al., 2004; Lim et al., 2005), but is not included in most regional or global models.

## 5.3. Additional SOA precursors

The traditional contributors to SOA are monoterpenes, which are believed to dominate SOA formation globally (e.g., Chung and Seinfeld, 2002; Tsigaridis and Kanakidou, 2003; Henze and Seinfeld, 2006), and aromatics (Henze et al., 2007), which may contribute an appreciable fraction of SOA on the urban scale. In recent years, however, it has been shown that lower- and higher-volatility hydrocarbons may also be important SOA precursors. Higher-volatility precursors include isoprene (e.g., Claeys et al., 2004; Edney et al., 2005; Kroll et al., 2005a), and acetylene (which forms glyoxal in high yields); lower-volatility species include “intermediate volatility” and semivolatile organics, such as those in diesel exhaust (Robinson et al., 2007; Weitkamp et al., 2007). There is also strong evidence for the presence of a pool of hydrocarbons that is largely unaccounted for in models (Lewis

et al., 2000; Di Carlo et al., 2004; Holzinger et al., 2005). Thus atmospheric SOA formation may be influenced by a number of as-yet unidentified SOA precursors, with a wide range of volatilities. These can be difficult to study experimentally, as the formation of SOA from the oxidation of highly volatile species is likely to be very small and/or occur over several generations of oxidation, whereas relatively low-volatility precursors can be difficult to prepare and measure in the gas phase. Low concentrations and vapor pressures also complicate the measurement of ambient concentrations of these lower-volatility compounds, preventing their straightforward inclusion in models. For example, large ( $> \text{C}_{12}$ ) alkanes have been shown to have high ( $> 50\%$ ) SOA yields (Lim and Ziemann, 2005), but are not included in most models of SOA formation, in part due to the lack of *in situ* measurements.

## 5.4. Overview and future directions

Obtaining a quantitative, predictive understanding of SOA formation, and resolving the current discrepancies between modeled and measured SOA presents significant challenges for laboratory measurements, ambient measurements, and atmospheric modeling. There is a need for laboratory studies to be carried out under the full range of atmospherically relevant conditions, with volatility distributions (SOA yields) parameterized as a function of these conditions, and in such a way that simulates multigenerational photochemical processing. Further chemical characterization of low-volatility organic species (in the gas and particle phases) would be extremely useful for both laboratory and *in situ* studies. In particular, ambient measurements of low-volatility SOA precursors that have been identified in the laboratory (such as large alkanes) are crucial for informing models. Modeling challenges include incorporation of additional chemistry known to affect aerosol formation and evolution; this includes a larger range of SOA precursors, multigenerational photochemical processing, and the role of  $\text{NO}_x$  level and other reaction conditions.

A fundamental question with major policy implications that remains unanswered at present is the fraction of SOA that is anthropogenic in origin. Global models, based upon estimated emission ratios and laboratory measurements of yields from common SOA precursors, suggest the vast majority of SOA is biogenic in nature, with anthropogenic hydrocarbons making only a minor contribution to

SOA formation (Chung and Seinfeld, 2002; Tsigaridis and Kanakidou, 2003; Henze and Seinfeld, 2006). Radiocarbon ( $^{14}\text{C}$ ) dating indicates that in most regions a dominant fraction of SOA (OM that is water-soluble, present in the fine particle mode, and independent of biomass burning) is composed of modern rather than fossil carbon, even in urban areas (Klinedinst and Currie, 1999; Lemire et al., 2002; Lewis et al., 2004; Lewis and Stiles, 2006; Szidat et al., 2004, 2006; Bench et al., 2007; Gelencsér et al., 2007). This predominance of modern carbon in SOA suggests that biogenic precursors dominate regional SOA formation. Ambient filter measurements of SOA tracer species (species identified in chamber studies) also suggest the importance of SOA from biogenic hydrocarbons (e.g., Kavouras et al., 1998; Yu et al., 1999a; Edney et al., 2003; Surratt et al., 2006, 2007a; Kleindienst et al., 2007), though few tracers of anthropogenic SOA have been identified for comparison.

On the other hand, ambient measurements of SOA at the regional scale, such as AMS measurements of organic aerosol mass (de Gouw et al., 2005) and particle-into-liquid sampler measurements of water-soluble OC (Sullivan et al., 2006; Weber et al., 2007), find that SOA is coupled strongly with tracers of anthropogenic emissions. The important role of anthropogenic SOA has also been inferred from measurements of oxidized organic aerosol within Mexico City (Volkamer et al., 2006) and downwind of Tokyo (Takegawa et al., 2006), and from modeling of the chemistry downwind of London (Johnson et al., 2006). Laboratory AMS spectra of SOA from anthropogenic precursors are generally more similar to ambient spectra than those of biogenic precursors (Bahreini et al., 2005; Sage et al., 2007), though this may be in part a result of specific experimental conditions, or the rapid multigenerational oxidation of some anthropogenic hydrocarbons (Ng et al., 2007b).

Thus the anthropogenic and biogenic fractions of SOA on the local, regional, and global scales remain poorly constrained, and represent an important question for future laboratory experiments, *in situ* measurements, and modeling studies. Specific research directions include continued comparison of the chemical composition (from both online and filter-based measurements) of SOA measured in the laboratory and the field, as well as the exploration of possible synergistic effects between anthropogenic emissions and SOA from biogenic (modern) precursors. Probably most important is the con-

tinued study of SOA formation from the full range of organic compounds emitted to the atmosphere, including both traditional SOA precursors (monoterpenes and aromatics) and more recently identified sources of SOA (high- and low-volatility compounds). This requires characterization of emissions, measurement and parameterization of evolving volatility distributions (SOA yields) upon oxidation, and inclusion of these processes into atmospheric chemical transport models.

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