Aerosol formation and heterogeneous chemistry in the atmosphere

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Abstract. A general presentation of the Earth’s atmosphere is provided, with the associated photochemical processes and oxidizing capacity. The article focuses on the atmospheric reactivity of Volatile Organic Compounds (VOCs) and the associated reaction products in the gas phase (ozone, oxygenated organic compounds, organic nitrates . . .) and in the particle phase, namely, the Secondary Organic Aerosols (SOA). The understanding of the processes leading to SOA formation is currently a “hot topic” because of: i) their high concentrations in the measured total organic matter, and ii) their potential important impacts on health and climate change. The initial theory of SOA formation was based on thermodynamic phase transfers of oxidized reaction products of VOCs, but it failed to explain the presence of high molecular weight (high-MW) compounds observed in SOA as well as a 1 to 2 orders of magnitude discrepancy between models and observations on the quantity of SOA. Therefore, different research investigations have been proposed such as heterogeneous and aqueous phase reactivity of organic compounds.

1. INTRODUCTION: THE EARTH’S ATMOSPHERE, GENERAL PRESENTATION

The Earth’s atmosphere is subdivided into several layers, due to the different temperature gradients occurring in each layer (Figure 1).

The main gases in the atmosphere are nitrogen and oxygen. Water vapor, argon, neon and helium are also present, as well as dozens of other gases of natural and human origin. Air also contains tiny solid and liquid particles (aerosol) such as dust, sea salt, volcanic ash, meteorite dust from space, material from bushfires . . .

The different temperature gradients observed in Figure 1 are mainly due to light absorption (UV) of solar radiation by N₂ and O₂ above 50 km, and by O₃ in the stratosphere (Figure 2).

Ozone is formed in the atmosphere by photochemical initiated reactions. It is highly concentrated in the stratosphere (Figure 3) where it prevents life from being injured by UV-C and UV-B wavelengths, whereas in the troposphere (in much lower amounts), ozone is toxic and phytotoxic.

The formation of ozone in the troposphere is correlated with the photochemical SMOG.

2. THE PHOTOCHEMICAL SMOG: PHOTOCHEMISTRY OF THE TROPOSPHERE

2.1 Introduction

The term SMOG is a condensate between SMOKE and FOG. It was attributed to yellowish fogs observed in Los Angeles in the 70’s, and in all cities in the world since then. It occurs essentially during summer, under warm and sunny conditions. SMOG contains photooxidants and tiny suspended particles, it is toxic, it can drastically reduce visibility (Figure 4), and the suspended particles can play
Figure 1. Diagram of the vertical structure of the atmosphere showing layers and temperature variations with height (The size of the Earth is not on scale!).

Figure 2. Atmospheric absorption of solar radiation (from Finlaysson-Pitts and Pitts, 2000; Seinfeld and Pandis 1998).

an important role in both the direct and the indirect aerosol forcing, thus inducing climate impacts (Kanakidou et al., 2005).

SMOG is a mixture resulting from atmospheric oxidations proceeding via chains of free radical reactions initiated by sunlight. It can be summarized as reaction R1.

\[ \text{VOCs} + \text{NOx} + h\nu \rightarrow O_3 + \text{other photooxidants} + \text{SOA} \] (R1)
Tropospheric ozone, which background concentrations continuously increase (Figure 5), is considered as a tracer for photochemical SMOG, and due to its important impacts on human health, vegetation and on climate (it is a greenhouse gas), its formation pathways have been studied in details (see next paragraph).

Among the high diversity of suspended particles found in the atmosphere, SOA represents a substantial amount. In general, atmospheric aerosols play a major role in environmental issues related to global and regional climate, atmospheric chemistry and human health (Laj et al., 2009). Atmospheric aerosol can scatter or absorb solar radiations, modifying the radiative balance of the atmosphere. Hydrophilic aerosols can also act as cloud condensation nuclei (CCN), and thus have an indirect climatic effect through modification of cloud properties (cloud cover, ability to precipitate…). A number of studies have indicated that organic aerosol (OA) plays an important role in both the direct and the
indirect aerosol forcing (Kanakidou et al., 2005). However, climate impacts of the OA are amongst the largest uncertainties in current climate research (IPCC, 2007). Organic material significantly contributes to the total fine aerosol mass: it represents 20–50% in European continental area and up to 90% in Alpine valleys and boreal forests. Organic aerosols are directly emitted from biomass burning, combustion of fossil fuels, volcanic eruptions and wind-driven suspension of soil, sea salt and biological materials. The latter sources are called primary aerosols. However, the majority of the organic fraction of aerosols is suspected to be of secondary origin: SOA are formed \textit{in situ} by atmospheric physico-chemical processes. SOA can represent up to 50–80% of the atmospheric organic carbon (Claeys et al., 2004a; Kalberer et al., 2004), however, its sources, chemical composition and formation mechanisms remain one of the least understood processes relevant to the atmosphere (Hallquist et al., 2009).

In order to understand the chemical pathways leading to SMOG formation, it is necessary to examine first the gas phase photooxidation of VOCs.

\subsection*{2.2 Atmospheric gas phase photooxidation of VOCs}

\subsubsection*{2.2.1 Formation of tropospheric ozone}

Ozone is formed in the atmosphere by the reaction of an atom of oxygen with a molecule of oxygen:

\begin{equation}
O + O_2 \rightarrow O_3 \quad (R2)
\end{equation}

While in the stratosphere, the atom of oxygen comes from the photolysis of O\textsubscript{2} molecules (at $\lambda < 242$ nm), in the troposphere, sunlight irradiation is not energetic enough to photodissociate O\textsubscript{2} (the sunlight spectrum starts at 290 nm: see figure 2) and the atom of oxygen comes from the photolysis of NO\textsubscript{2} (at $\lambda < 420$ nm):

\begin{equation}
NO_2 + hv \rightarrow O + NO \quad (R3)
\end{equation}
Figure 6. Scheme of the Leighton cycle.

Figure 7. The Leighton cycle is broken by the oxidation of VOCs. NO is transformed into NO$_2$ via VOC oxidation steps, resulting in a lack of ozone sink, and thus in ozone accumulation.

NO is highly reactive towards ozone, leading back to NO$_2$:

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2
\]

The sequence of these 3 reactions is called the Leighton cycle (Figure 6) which budget is null.

However, the Leighton cycle does not correctly represent real atmospheric reactions because it does not take into account the reactivity of VOCs, which are ubiquitous in the atmosphere. Several steps in the atmospheric oxidation of VOCs transform NO into NO$_2$ faster than ozone (R4): see Figure 7.

Before investigating in details the atmospheric photooxidation of VOCs, it is important to examine the different radicals available in the troposphere, and thus to explore the initiation reactions.

2.2.2 Initiation reactions

It can be seen in Figure 8 that several compounds present in the troposphere can photodissociate in the UV part of the solar spectrum available at ground level (i.e. between 290 and 400 nm). This is the case for NO$_2$, O$_3$, HONO, HCHO and H$_2$O$_2$.

- Nitrogen dioxide: NO$_2$

\[
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}^3\text{P}\quad \text{at} \quad \lambda < 420\text{nm}
\]  

Followed by: $\text{O}^3\text{P} + \text{O}_2 (+\text{M}) \rightarrow \text{O}_3 (+\text{M})$  

\[ (R2) \]

\[ (R3) \]
Figure 8. Absorption coefficients of species relevant to the troposphere and solar spectrum at ground level (from Penkett et al. 1994).

- **Ozone**: $O_3$
  
  In the troposphere, 2 processes are in competition:
  
  The 1\textsuperscript{st} needs less energy:
  
  $$O_3 + h\nu \rightarrow O_2 + O(^3P) \quad \text{at } \lambda < 340 \text{ nm}$$  \hspace{1cm} (R5)
  
  Followed by: $O(^3P) + O_2(+M) \rightarrow O_3(+M)$  \hspace{1cm} (R2)

  The 2\textsuperscript{nd} needs more energy:

  $$O_3 + h\nu \rightarrow O_2 + O(^1D) \quad \text{at } \lambda < 320 \text{ nm}$$  \hspace{1cm} (R6)
  
  Followed by: $O(^1D) + H_2O_{\text{vap}} \rightarrow 2OH$  \hspace{1cm} (R7)

  OH radicals are among the most oxidative species in the atmosphere, they oxidize most of the VOCs.

- **Nitrous acid**: HONO

  $$\text{HONO} + h\nu \rightarrow \text{NO} + \text{OH} \quad \text{at } 290 < \lambda < 320 \text{ nm}$$  \hspace{1cm} (R8)

- **Formaldehyde**: HCHO

  $$\text{HCHO} + h\nu \rightarrow \text{HCO} + \text{H} \quad \text{at } 290 < \lambda < 350 \text{ nm}$$  \hspace{1cm} (R9)

  $$\text{HCHO} + h\nu \rightarrow \text{H}_2 + \text{CO} \quad \text{at } 290 < \lambda < 350 \text{ nm}$$  \hspace{1cm} (R10)

  The above 2 processes are simultaneous on the same wavelength range, but the quantum yields are different depending on the wavelengths.
Reaction R9 is important in the atmosphere because it is immediately followed by reactions R11 and R12, leading to the formation of HO2 radicals:

\[ H + O_2(+M) \rightarrow HO_2(+M) \]  \hspace{1cm} (R11)

\[ HCO + O_2 \rightarrow HO_2 + CO \]  \hspace{1cm} (R12)

M is a molecule in high concentration, such as N2 or O2. Peroxy radicals HO2 are rapidly converted into OH radicals through reaction R13:

\[ HO_2 + NO \rightarrow NO_2 + OH \]  \hspace{1cm} (R13)

**-Hydrogen peroxide: H2O2**

\[ H_2O_2 + hv \rightarrow 2OH \text{ at } \lambda < 300 \text{ nm} \]  \hspace{1cm} (R14)

OH, HO2 and O3 are the main atmospheric oxidants during the day. During the night, NO3 radical is responsible for a large amount of VOC oxidation. This radical is mainly formed through reaction R15:

\[ NO_2 + O_3 \rightarrow NO_3 + O_2 \]  \hspace{1cm} (R15)

Due to its fast photodissociation at \( \lambda < 630 \text{ nm} \), NO3 radical is of negligible amount during day time.

\[ NO_3 + hv \rightarrow NO_2 + O(^3P) \text{ at } \lambda < 630 \text{ nm} \]  \hspace{1cm} (R16)

### 2.2.3 Photooxidation of VOCs

All VOCs react towards OH, NO3, O3 or by direct photodissociation, mainly in the troposphere. For small VOCs such as CO and methane, these reactions result in the direct formation of volatile oxygenated species such as CO2 or HCHO (Figure 9), and in the indirect accumulation of ozone due to the fast conversion of NO into NO2 by HO2 or CH3O2 radicals, thus avoiding the O3 + NO reaction (Figures 7 and 9). Figure 9 also shows the photooxidation scheme represented for methane (it can be generalized for all VOCs): OH radicals are recycled, HCHO is formed as a side reaction product, and the oxidation of one VOC molecule (CH4 or higher) induces the accumulation of two molecules of ozone.

In the real atmosphere, the kinetics of these chain reactions depend on the environment, and in particular to the VOC / NOx ratio. Schematically, in “clean” atmosphere (far from VOC and NOx sources such as in marine atmosphere), CO and CH4 are the predominant VOCs, and NOx concentrations are lower than 1 ppbV, not sufficient to participate into the chain reactions. In that case, HO2 and RO2 radicals undergo termination reactions (with formation of hydroperoxydes), and the ozone is consumed by photodissociation. In moderately polluted areas (such as in rural and peri-urban places), where NOx concentrations are comprised between 1 and 10 ppbV, the chain reactions described in Figure 9 are very efficient, and ozone accumulates. Finally, in heavily polluted atmospheres (such as in the centre of mega-cities), where NOx concentrations are higher than 10 ppbV, NO2 concentrations can be high enough to react with OH radicals, leading to the formation of HNO3, and intercepting most of OH radicals, thus preventing the chain reactions of VOCs. This results in ozone consumption by reaction R4, and the formation of suspended particles containing HNO3.

However, ozone is not the only side reaction product of these chain reactions. For VOCs containing more than one carbon atom, Figure 10 shows a general scheme of photooxidation in the troposphere, with a focus on all the potential side organic reaction products.

The atmospheric photooxidation of VOCs leads to the formation of polyfunctional species (oxygenated and/or nitrated organic compounds), most of them are water soluble, and their saturation vapour pressures are lower than that of their precursors. Some of these reaction products are thus able to transfer into the condensed phase of the atmosphere. However, these phenomena depend on
Photooxydation of methane:

- \( \text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O} \)
- \( \text{CH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2 \)
- \( \text{CH}_2\text{O}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{CH}_3\text{O} \)
- \( \text{CH}_3\text{O} \rightarrow \text{HO}_2 + \text{HCHO} \)
- \( \text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \)

Photooxydation of carbone monoxide:

- \( \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \)
- \( \text{H} + \text{O}_2 \rightarrow \text{HO}_2 \)
- \( \text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \)

Figure 9. Atmospheric photooxidation of methane and CO.

Figure 10. General scheme of atmospheric photooxidation a generic VOC (from Kroll and Seinfeld 2008). 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.

the physico-chemical properties of each reaction product, which in turn depends on the chemical structure of the precursor VOC. For example, it has been observed for a long time that the atmospheric photooxidation of the most complex VOCs such as aromatic compounds and terpenes (C7 – C10) leads not only to the formation of ozone, but also to that of significant amounts of SOA (Kroll and Seinfeld 2008; Hallquist et al. 2009). The phase transfer of reaction products also depends on the atmospheric
conditions such as temperature, relative humidity, initial VOCs and oxidants concentrations, ambient NOx concentrations... All these factors can drastically influence the formation of SOA.

3. PHASE TRANSFER / GAS-PARTICLE PARTITIONING THEORY

Phase transfer from the gas-phase into the condensed phase are generally described by three distinct processes: nucleation, condensation and coagulation (Figure 11).

Nucleation is the first step leading to SOA formation. Clusters of a few nm are formed from gas-phase semi-volatile compounds. Homomolecular nucleation is the nucleation of several molecules of the same species, while heteromolecular nucleation is the nucleation of different compounds. It is thought that nucleation phenomena mainly depend on the affinity between the nucleating species and their saturation vapour pressure. The size of the formed aerosols is extremely small (a few nm), and their lifetime is of a few minutes. Depending on their dimensions and their surface tension, they can either evaporate back, or grow up through condensation and coagulation phenomena.

Condensation is the phase transfer of gas-phase molecules to the pre-existing particles. Condensation depends on the particles’ dimensions, the diffusion coefficients of the gas phase species, and their saturation vapour pressure at the particle’s surface. Condensation phenomena induce particle size increase with a stable number of particles.

Coagulation is the collision between aerosols followed by their combination. It induces particle size increase, a decrease of the total number of particles with a stable total mass. Coagulation depends on the particles concentrations, and on the particle agitation type: thermal, dynamic or cinematics agitation. Coagulation is fast, especially in urban atmospheres where high aerosol concentrations are encountered.

3.1 Limitations of this theory

The gas-particle partitioning theory implies that condensation should be more important than nucleation in places where pre-existing aerosols are present, and nucleation should occur only in places were the concentrations of pre-existing particles are low compared to condensable gases. In clean atmospheres such as in the canopy of the boreal forest and in marine atmospheres, the formation of new particles has been observed (Figure 12a and b). However, the formation of new particles has also been observed in urban atmospheres (Figure 12c, d and e). These episodes are less frequent than in clean areas, but they show that condensation on pre-existing particles does not inhibit nucleation. Furthermore, even if all nucleation events are observed at the maximum sunlight of the day (Figure 12) in good correlation with SMOG episodes, some observations tend to show that these nucleation events can be due to atmospheric transport from the upper troposphere (Delmas et al., 2005).
Figure 12. Diurnal variations of aerosol size distribution and total number concentration in “clean” atmospheres (a: marine atmosphere in Antarctica, and b: boreal forest in Finland) and in urban areas influenced by photochemistry (c: Marseille (France), d: Athen (Greece), and e: New Delhi (India)) (from Kulmala et al., 2004). (dN/dlogDp = normalized number of particles).
The gas-particle partitioning theory does not take into account the chemical reactivity of species in each phase, although fast reactions can occur simultaneously in both phases, and possibly modify the gas-particle equilibria.

Due to the complexity of these phenomena, great uncertainties remain on the chemical nature of the species implicated in nucleation/condensation processes, their saturation vapour pressure, and the associated meteorological conditions.

3.2 Discrepancies between models and observations

Although large uncertainties remain as discussed above, there is a consensus among recent modelling studies on the fact that there are indeed problems in predicting SOA in the atmosphere with current models (Kroll and Seinfeld 2008; Hallquist et al. 2009; Carlton et al. 2009). Several studies have shown that predicted SOA concentrations are 10 to 100 times lower than the measured ones (Figure 13).

This underestimation of the SOA concentrations has been strengthened by the observations of high molecular weight (high-MW) compounds such as polyfunctional compounds, oligomers and Humic Like Substances (HULIS) in SOA sampled in the atmosphere and in simulation chamber experiments. The traditional gas-particle partitioning theory cannot explain the presence of such compounds in SOA.

3.3 Observations of unexpected organic high molecular weight compounds

The chemical composition of SOA has been investigated by numerous studies using very different techniques such as FTIR and NMR spectroscopy, mass spectrometry coupled with gas phase or liquid phase chromatography… Polyfunctional compounds comprising at least two alcohol, carbonyl or acid functions are ubiquitous in SOA such as oxo-dicarboxylic acids, hydroxyacids, mono- or polysubstituted phenols, polyfunctional terpenoids, furans, furanones, organosulfates, and nitro organosulfates. Combinations of these different chemical functions induce a high diversity of compounds, and thus complicated identification problems.

Oligomers are small polymers comprising 2 to 10 monomeric units, which usually hold a large number of chemical functions. They have been observed on SOA sampled in the ambient air, and in simulation chamber experiments (Nguyen et al. 2010; Kalberer et al. 2006; Denkenberger et al. 2007; Claeys et al. 2004a). Oligomers with molecular masses up to 1000 daltons have been observed to form
during experimental simulations of atmospheric photooxidation of anthropogenic precursors such as trimethylbenzene (Kalberer et al., 2004), and biogenic precursors such as isoprene (Claeys et al. 2004a; Surratt et al. 2006), monoterpenes and sesquiterpenes (Ng et al., 2007).

Humic Like Substances (HULIS) have also been observed on ambient SOA. These macromolecules hold a larger number of chemical functions than polyfunctional compounds. Their molecular masses are comprised between 250 and more than 1000 g/mol (Reinhardt et al., 2007). Some of their physical and chemical properties resemble those of fulvic and humic acids found in soils and surface waters. HULIS can constitute an important fraction of SOA found in marine and terrestrial aerosols, and wood combustion aerosols (Graber et al. 2006; Lukacs et al. 2007; Feczko et al. 2007; Baduel et al. 2009; Baduel et al. 2010; Stone et al. 2009; Salma et al. 2008; Reinhardt et al. 2007), but their origins, and formation processes are still unknown.

These three classes of « new » compounds have molecular masses ranging from 100 to more than 1000 g/mol, which is higher than their gaseous precursors by 1 to 3 orders of magnitude. This observation rejects the traditional gas-particle partitioning theory to explain the formation of these types of SOA. It is likely that other precursors and other mechanisms can contribute to the SOA formation in the atmosphere.

4. DIFFERENT RESEARCH INVESTIGATIONS PROPOSED TO CLOSE THE GAP BETWEEN MODEL AND OBSERVATIONS OF SOA

Numerous studies have recently proposed new processes to explain the atmospheric formation of SOA containing polyfunctional and high molecular weight compounds. These new processes consist in heterogeneous physico-chemical interactions and also aqueous phase processes (Kroll and Seinfeld 2008; Hallquist et al. 2009).

4.1 heterogeneous physico-chemical interactions

Heterogeneous reactions can play an important role in the formation of SOA and atmospheric ageing of SOA. Up to date, two types of heterogeneous reactions have been investigated: heterogeneous oxidation of primary aerosols, and heterogeneous accretion reactions.

4.1.1 Heterogeneous oxidation of primary aerosols

Heterogeneous oxidation of primary aerosols by atmospheric gas phase oxidants (OH, NO₃ radicals, O₃ or direct photolysis) induce a change in the chemical composition of the aerosol surface. This process can also occur on the surface of SOA, and in this case, it is called atmospheric ageing of SOA. This process thus leads to more oxidized and less volatile compounds in SOA.

In general, the chemical mechanisms of heterogeneous oxidation reactions are the same as those in the homogeneous gas phase. However, the branching ratios among the various pathways may be quite different, which can have profound effects on the vapour 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 allyoxy (RO) radical decomposition: see Figure 10) and addition of polar functional groups (Kroll and Seinfeld, 2008).

Heterogeneous ozonolysis of alkenes have been extensively studied. It is broadly consistent with gas-phase ozonolysis, but the branching ratios leading to the formation of high-MW species are more important in particles than in the gas phase.

All particle-phase organics are subject to oxidation by radicals (OH, NO₃, Cl), which has received considerably less study than ozonolysis. Some studies of the oxidation of model condensed-phase organics report rapid volatilization or formation of volatile products, whereas others find volatilization to be negligible or minor. It has been suggested that these differences may be a result of different
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experimental conditions or phase of the model organic. Such studies have so far been carried out only on relatively reduced organic compounds, acting as surrogates for primary organic aerosol (Kroll and Seinfeld, 2008).

4.1.2 Accretion reactions: non-oxidative processes

Accretion reactions consist in the heterogeneous trap of gaseous VOCs on primary aerosols. They induce an increase in the aerosol mass, and thus can explain the formation of oligomers (Barsanti and Pankow, 2004). Since the vapour pressure of an organic species will decrease by about an order of magnitude for every two carbons added, even a single dimerization reaction of a moderately sized (C_6–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. Association products can include noncovalent adducts, but much of the focus has been on longer-lived, covalently bound species.

Figure 14 shows several classes of condensed phase accretion reactions which have been investigated experimentally for their role in SOA formation.

A particle-phase reaction will have a significant influence on organic volatility and SOA formation only if it is both thermodynamically and kinetically favourable:

- **Thermodynamics:** Accretion reactions of simple volatile monocarbonyls were generally found to be thermodynamically unfavorable, whereas uptake reactions of dicarbonyls such as glyoxal and methylglyoxal were predicted to be favored (Barsanti and Pankow, 2005). The formation of esters and amides from the reaction of carboxylic acids with alcohols or amines (R_6d) was also found to be thermodynamically favorable (Barsanti and Pankow, 2006), consistent with the measurement of esters in ambient air SOA (Surratt et al., 2006).

- **Kinetics:** 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 (Kroll et Seinfeld, 2008).

A major uncertainty is the role of particle-phase acidity. The rates of most reactions shown in Figure 14 are greatly enhanced in acidic environments, likely explaining the increase in SOA yields in the presence of acidic seed particles. 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 terpenes (Kroll et Seinfeld, 2008).

Atmospheric field studies have shown that oligomer formation does not necessarily requires strong acidity to occur rapidly: oligomeric species have been measured in SOA when no inorganic seed is present 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 Figure 14, 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_2SO_4 solutions often employed in laboratory studies (50–100% neutralization is typical in most environments).

4.2 Aqueous-phase reactions of organic compounds

While most studies of heterogeneous reactivity 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; Hallquist et al. 2009), and may be important in aqueous aerosol particles as well. Clouds and aqueous aerosol particles occupy a large part of the lower atmosphere (more than 60% of the earth surface on the first 4–6 km in altitude), thus providing a huge surface of interactions
Figure 14. 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; (R6f) reactions of Criegee diradical intermediates with alcohol/water/ acids (reactions with carboxyls or other intermediates are also possible) from Kroll et Seinfeld, 2008.
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for chemical species. Clouds continuously appear and disappear through evapo-condensation cycles (Pruppacher, 1986). While only 10% of clouds precipitate, the remaining 90% dissipate, inducing volatile species’ evaporation, and the condensation of the low volatile compounds. Clouds and aqueous aerosols provide an efficient medium for liquid phase reactions of water soluble species: more than 60% of the total sulfate on a global scale is estimated to be produced from aqueous phase oxidation of SO2 (Kanakidou et al., 2005). Recent studies suggest that, as sulfate, SOA can also be produced through aqueous phase reactions in clouds, fogs and aerosol water (Blando and Turpin 2000; Ervens et al. 2003; Ervens et al. 2004a; Ervens et al. 2004b; Ervens et al. 2008; Gelencsér and Varga 2005; Lim et al. 2005; Altieri et al. 2006; Altieri et al. 2008; Carlton et al. 2006; Carlton et al. 2007; Poulain et al., 2007; Liu et al., 2009; El Haddad et al. 2009; Poulain et al. 2010). Briefly, reactive organics are oxidized in the interstitial spaces of clouds to form highly water-soluble compounds (e.g. aldehydes) that readily partition into the droplets. The dissolved organics may undergo chemical conversions in the aqueous phase (hydrolysis, further oxidation, polymerization…), to form less volatile organics. These products remain, at least in part, in the particle phase upon droplet evaporation, leading to SOA mass production (Kanakidou et al. 2005; Blando and Turpin 2000; Carlton et al. 2009; Hallquist et al. 2009) (Figure 15). The results obtained from several experimental studies support the in-cloud SOA hypothesis.

In some locations, SOA surrogates are more strongly correlated with liquid water content than with organic matter concentrations in ambient aerosols in contrast to expectations based on the gas-particle partitioning theory (Hennigan et al. 2008; Hennigan et al. 2009). Furthermore, a number of field studies have shown that the high amount of non volatile organic acids (such as oxalic, malonic, malic, succinic, glutaric acids) found in atmospheric waters and aerosols originate from aqueous phase processes (Legrand et al., 2007; Yao et al. 2003; Crahan et al. 2004; Yu et al. 2005; Sorooshian et al. 2007). These observations were in good agreement with the fact that, in the aqueous phase, the atmospheric reactivity is different from the gas phase one, leading to the formation of less volatile products. It has also been suggested that in-cloud biological activity is an important process, but its contribution has not yet been quantified. A larger number of studies have focused on the aqueous phase chemistry (Hallquist et al., 2009).

Laboratory experiments have shown that the kinetics of these reactions are very fast (Monod et al. 2005; Monod and Doussin 2008), and that OH-oxidation of dihydroxy-aromatic acids leads to the formation of HULIS (Gelencsér et al. 2003; Hoffr et al., 2004). Their secondary origin, observed in summer in cities, is suspected to be principally aqueous phase reactions (Baduel et al. 2010). Until recently, isoprene, accounting for about half of all natural VOC emissions, was not considered as a significant contributor to SOA. However, some of its photooxidation products (methacrolein and methacrylic acid) are oxidized in acidic aqueous solutions by H2O2, leading to polyols (Claeys et al. 2004b) which have been detected in aerosols in a continental rural site in Hungary, in Amazonian forest (Claeys et al. 2004b) and in a boreal forest (Kourtechev et al. 2005). Very recently, some laboratory studies have shown that oligomers are produced in the liquid phase after aqueous phase hydration and/or photooxidation of some of the oxidation products of isoprene, i.e. glyoxal (Hasting et al. 2005; Loeffler et al. 2006; Carlton et al. 2007), methylglyoxal (Loeffler et al. 2006; Altieri et al. 2008), pyruvic acid (Guzmán et al. 2006; Altieri et al. 2006; Carlton et al. 2006), methacrolein (Liu et al. 2009; El Haddad et al. 2009), and glycolaldehyde (Perri et al. 2009). The chemical pathways leading to the observed oligomers have been investigated by very few authors. Detailed studies of the oligomeric structures lead some authors to propose molecular addition mechanisms such as acid catalyzed esterification during aqueous phase photooxidation of methylglyoxal (Altieri et al. 2008) or hemiacetal formation in evaporating aqueous glyoxal and methylglyoxal (Loeffler et al. 2006). Alternatively, there is evidence that radical processes may also contribute to the formation of oligomers in the aqueous phase. Kinetic studies of the formation of oligomers lead some authors to propose combination reactions of organic radicals during the aqueous phase direct photolysis of pyruvic acid (Guzmán et al. 2006) (Figure 16) or during OH-initiated oxidation of methacrolein and methylvinylketone (Liu et al. 2009; Liu et al. 2010). For all aqueous phase studies, the formed oligomers have shown molecular masses up
to 1400 Da (see the mass spectrum in Figure 15), and are thus non volatile material, which is likely a source of SOA after cloud’s processing. It has been shown very recently that oligomers, formed in the aqueous phase after photooxidation of methacrolein and methylvinylketone (Liu et al. 2009; Zhang et al. 2010), lead to the formation of significant amounts of organic aerosols after cloud’s evaporation (El Haddad et al. 2009; Liu et al. 2010), and the obtained organic aerosol had specific hygroscopic and volatility properties (Michaud et al. 2009).

However, the scientific knowledge of photochemical processes of organics, especially polyfunctional compounds, in the atmospheric aqueous phases is still quite limited and needs further investigation. In particular, it is necessary to study the influence of different parameters relevant to the atmosphere such as pH, initial concentrations and inorganic content, which are likely to be highly variable in evaporating droplets, and could greatly affect the oligomerization processes (Hallquist et al. 2009).

References


Figure 16. Radical processes explaining the formation of oligomers during the photolysis of pyruvic acid in the aqueous phase under atmospheric conditions (from Guzmán et al. 2006). PA = pyruvic acid; ISC = intersystem crossing; K = ketyl radical; A = 2,3-dimethyltartaric acid; D = multifunctional dicarboxylic acid. The rapid decarboxylation of D may form two products, B1 and B2.


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