

## Chapter 7

### Photochemistry of Secondary Organic Aerosol Formed from Oxidation of Monoterpenes

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Secondary organic aerosol (SOA) formed from atmospheric oxidation of monoterpenes has a complex and highly dynamic chemical composition. This chapter focuses on photochemical processes occurring inside biogenic SOA particles produced by oxidation of monoterpenes. The SOA material is found to significantly absorb solar radiation in the tropospheric actinic window ( $\lambda > 300$  nm). The ensuing photolysis of SOA constituents modifies the SOA chemical composition and leads to emission of small volatile molecules back into the gas-phase. A large number of observed products can be explained by photolysis of organic peroxides and carbonyls. These photochemical processes are likely to occur on atmospherically relevant time scales, and affect chemical properties and toxicity of monoterpene SOA particles.

## SOA from Atmospheric Oxidation of Monoterpenes

Biogenic volatile organic compound (BVOC) emissions are an order of magnitude greater than anthropogenic VOC emissions on a global scale (1, 2). Monoterpenes ( $C_{10}H_{16}$ ) comprise a significant portion of BVOC emissions (2, 3), and it is important to understand the atmospheric fates of monoterpenes and their oxidation products. The most commonly occurring monoterpenes (4) are shown in Figure 1. The emission patterns of the various monoterpenes strongly depend on the type of vegetation and on the environmental conditions, however D-limonene makes up the majority of monoterpene emissions over orange groves, while  $\alpha$ -pinene and  $\beta$ -pinene dominate over most other kinds of forests, especially those composed of oaks and conifers (3, 5). The involvement of monoterpenes in the formation of tropospheric aerosol was recognized in 1960 by Went (6), who observed that a blue haze formed over pine needles in the presence of ozone. Since then, a great deal has been learned about the reactions between naturally emitted monoterpenes and atmospheric oxidants. It is now well established that oxidation of isoprene and monoterpenes is a significant source of SOA, contributing some 60 Tg C/year to the global SOA budget (7-9).

Figure 2 is a highly simplified diagram of the processes involved in the atmospheric processing of monoterpenes. Gas-phase monoterpenes readily react with the major atmospheric oxidants such as ozone ( $O_3$ ), hydroxyl radical (OH), and nitrate radical ( $NO_3$ ). During the day, their concentrations are controlled by OH and  $O_3$ , and at night they are controlled by  $NO_3$ , with monoterpene lifetimes on the order of a few hours in both cases. Regardless of the initial oxidant, gas-phase oxidation of monoterpenes results in a wide variety of polyfunctional carboxylic acids, ketones, aldehydes, peroxides, and alcohols (10-19). Many of these species have sufficiently low vapor pressure to partition into pre-existing particulate matter. In addition, monoterpenes can partition into aqueous particles or cloud droplets by wet deposition and undergo oxidation via aqueous chemistry (20-23), with droplets subsequently drying out into organic particles.

The chemical composition of monoterpene SOA is generally quite complex, with a number of products still remaining uncharacterized. Pinonaldehyde, pinonic acid, nor-pinonic acid, and pinic acid have been identified as major condensed phase products of the laboratory ozonolysis of  $\alpha$ -pinene (24-26). Nopinone was identified as the major particle-phase product of  $\beta$ -pinene ozonolysis (11, 24); norpinic and pinic acids were also produced (11). Limononaldehyde, keto-limonene, keto-limononaldehyde, limononic acid, and keto-limononic acid accounted for ~60% of the observed aerosol mass in ozonolysis of D-limonene (27). The latter three products have also been identified as major constituents of SOA resulting from the photooxidation of D-limonene in the presence of  $NO_x$  (28). In the OH-initiated oxidation of D-limonene, both keto-limonene and limononaldehyde were identified as major low volatility products (17). Oxidation of  $\alpha$ -pinene and D-limonene by  $NO_3$  yielded pinonaldehyde and limononic acid, respectively, and unidentified nitrates (29).

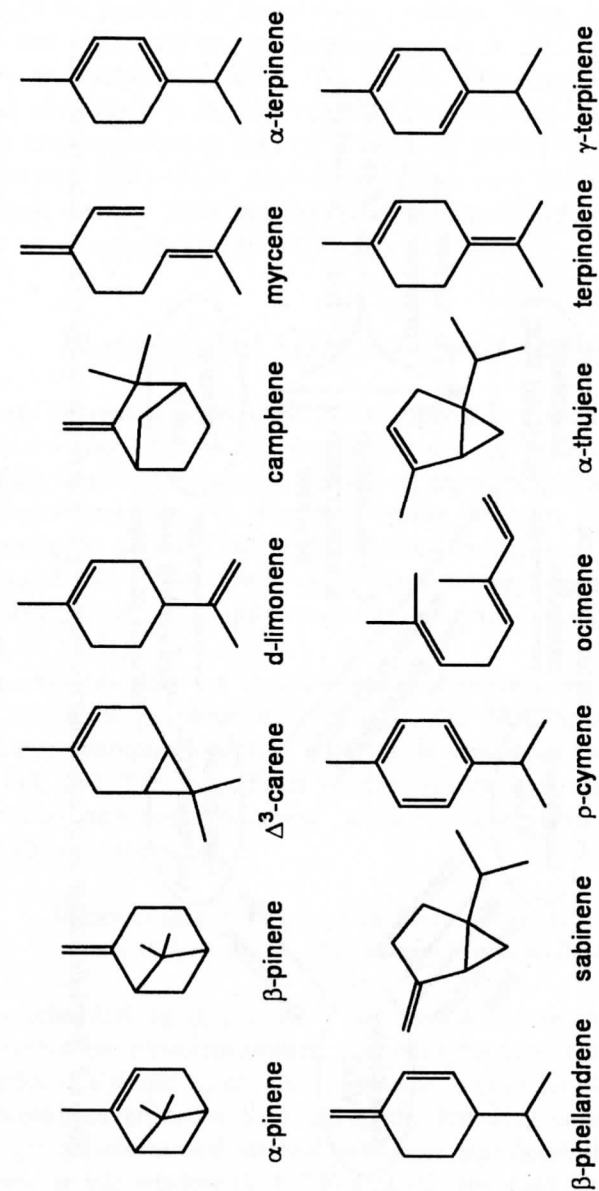


Figure 1. Structures of the most commonly occurring monoterpenes.

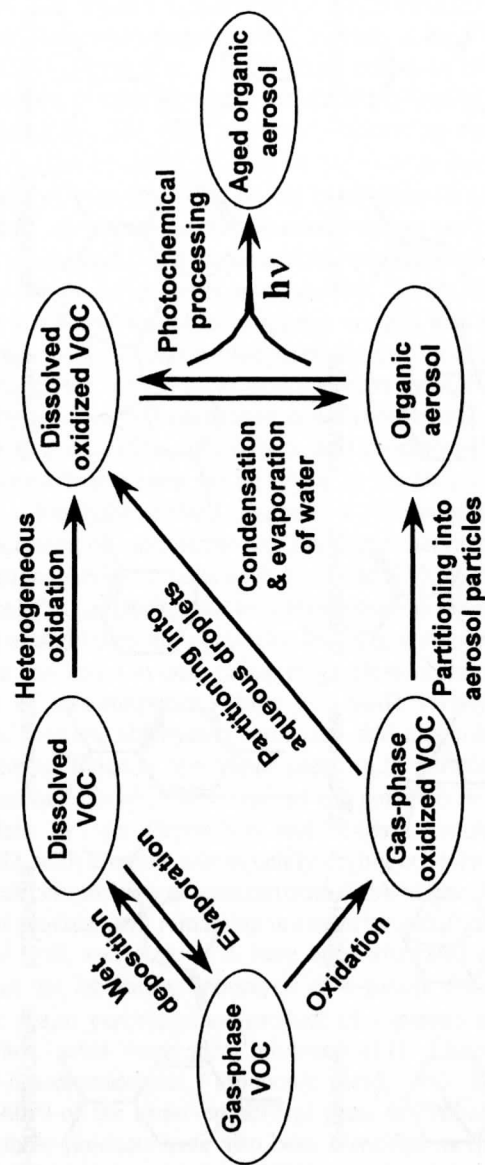


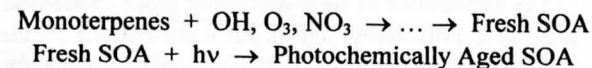
Figure 2. Simplified diagram of atmospheric processing of monoterpenes and their oxidation products.

In addition to the "usual suspects" listed above, several research groups have identified organic peroxides (30-32) and polyfunctional species (12, 14, 15, 33) amongst the products of monoterpene oxidation. There is also increasing evidence that oligomeric species play a key role in the monoterpene SOA formation and subsequent aging (14, 34-43). For example, hundreds of individual compounds in the  $m/z$  range of 200-700 were observed by high-resolution mass spectrometry amongst products of ozonolysis of  $\alpha$ -pinene (40) and D-limonene (38). Such oligomeric species were attributed to various condensation reactions involving aldehydes, hydroperoxides, carbonyl oxides, and other reactive groups (20, 30, 31, 41, 44).

### Photochemical Aging of Organic Aerosol

Aerosol can remain suspended in the atmosphere for several days, especially under dry conditions (9, 45, 46). During this time, particles can significantly change their chemical composition because of exposure to gas-phase oxidants (47) and solar radiation (48, 49). Additionally, reactions between different species inside the particles can modify the composition long after the initial particle growth (36, 37, 50). These "aging" processes may play an important role in determining hygroscopic and toxicological properties of organic particulate matter (8, 47, 51-53).

Most previous work on chemical aging of organic aerosol focused on reactive uptake of gas-phase oxidants (OH, O<sub>3</sub>, NO<sub>3</sub>, halogen atoms) by representative atmospheric organic materials as summarized in two excellent reviews (47, 54). The main focus of this chapter is on aging caused by photochemical processes occurring *inside* organic particles, which is schematically represented by



Such photochemical aging processes may include direct photodissociation, photoisomerization, photosensitization, and other chemical reactions triggered by absorption of a photon by an SOA constituent. In order for photochemistry to have a significant effect on SOA aging, the following conditions must be satisfied: (1) organic aerosol material must have significant absorption in the tropospheric actinic window ( $\lambda > 300$  nm); (2) the yield for photochemical reactions, such as photodissociation, must be large compared to that for fluorescence, vibrational relaxation, geminate recombination, and other non-

reactive processes. Our recent experiments (48) suggest that monoterpene SOA satisfy both requirements. Furthermore, direct effect of UV radiation on the yield of monoterpene SOA was observed in several recent studies. During the ozonolysis of  $\alpha$ -pinene, exposure to UV radiation decreased the aerosol yield by as much as 20-40% (13, 55), most likely due to a shift in the product volatility distribution to higher volatility species. Presto et al. (13) observed this yield reduction only during particle nucleation, implying that photolysis of non-volatile SOA precursors in the gas phase, prior to nucleation, was responsible. Similar observations were made for D-limonene SOA (56). SOA formed by photochemical oxidation of isoprene was found to be even more susceptible to photodegradation. The fraction of condensable peroxides (36) and the effective yield (57) of SOA particles prepared by photooxidation of isoprene decreased with irradiation time, implying that photochemical aging was occurring after the initial particle formation. The particles lost a significant fraction of their volume as a result of this photochemical aging (57).

Aerosol photochemistry is certainly not limited to direct photolysis of organic species. A review by Vione et al. (58) discussed the importance of secondary photochemical processes in fog and cloud water. Dissolved nitrate, nitrite, iron (III) compounds, and hydrogen peroxide can all undergo photochemical transformations in cloud droplets leading to OH radical and other reactive species, which can then go on to oxidize organics present in the droplet. In this way, even organic molecules that are relatively impervious to direct photolysis can still be chemically modified via photochemistry. For example, photodegradation of several dissolved organic nitrogen species was observed in irradiated fog waters and aerosol aqueous extracts (59, 60). Similar processes may be occurring in monoterpene SOA particles internally mixed with inorganic chromophores, e.g., with nitrates or hydrogen peroxide.

Even if SOA constituents have low initial absorption cross-sections in the tropospheric actinic window, efficient organic absorbers can be generated *in situ* as aerosol ages. For example, uptake of small carbonyls by acidic solutions was shown to lead to the appearance of light-absorbing aldol condensation products (44, 61, 62), and make potentially significant contributions to the absorption index of particles containing sulfuric acid. Our own measurements (49, 63) showed that films of unsaturated organics become photochemically active after exposure to ozone. In summary, there is sufficient evidence to suggest that monoterpene SOA constituents can be photodegraded on atmospherically relevant timescales.

### Absorption Spectra of Monoterpene SOA

In principle, one could envision modeling the absorption spectra of SOA as an appropriately weighed linear combination of the spectra of all individual

SOA constituents. This approach is impractical because of the very large number of compounds found in SOA. Alternatively, the absorption spectra of monoterpene SOA can be deduced from spectroscopy of actual particle samples. Measurements of absorption spectra of aerosol are non-trivial because one has to separate the scattering and absorption contributions to the overall extinction (64). Our laboratory uses a simple technique that allows measurements to be made on thin films of SOA material, thus avoiding possible complications from solvents and scattering. The SOA samples are prepared by reaction between monoterpene vapor and ozone in a Teflon chamber filled with dry air. The resulting particles are collected onto a calcium fluoride ( $\text{CaF}_2$ ) window using a single-jet impactor, with the amount of collected material determined gravimetrically. A relatively uniform film is prepared by pressing the collected SOA material between two  $\text{CaF}_2$  windows; the films are then analyzed in a UV spectrometer. Spectra are measured relative to clean  $\text{CaF}_2$  windows, and corrected for the expected reflection losses.

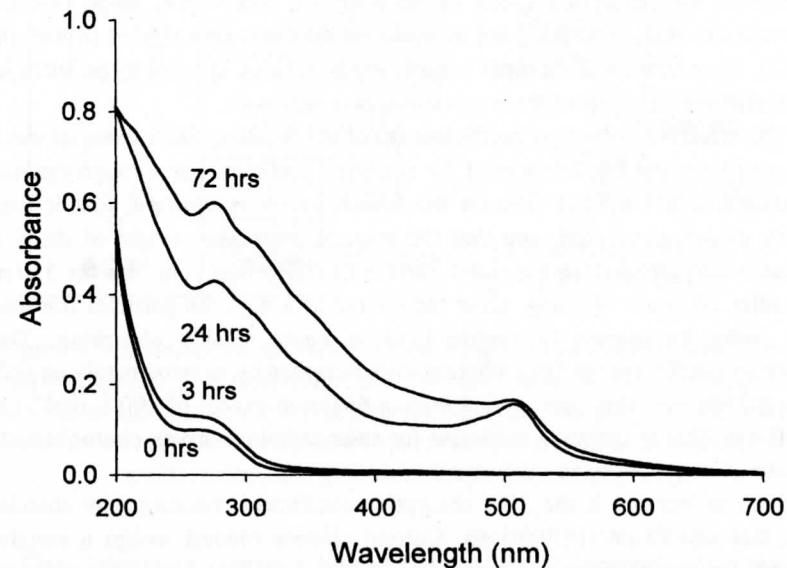


Figure 3. Representative absorption spectrum of organic material formed in ozonolysis of D-limonene as a function of storage time in ambient air in darkness. The changes in the absorption profile are accompanied by a visible transition of the particles from colorless (bottom spectrum) to red-brown.

Figure 3 shows a sample absorption spectrum of a D-limonene SOA sample. Initially the collected SOA material is transparent to visible light, but

there is a significant absorption tail extending into the tropospheric actinic range. The shape of the absorption spectrum obtained immediately after collection suggests a mixture of peroxides (sharp decrease in absorption with increasing wavelength) and carbonyl functional groups (weak absorption around 300 nm) in agreement with the standard mechanism of ozonolysis of alkenes. An interesting observation is that the SOA material acquires a reddish color when stored in open air in darkness for several hours. In addition to an unstructured absorption extending over a broad range of wavelengths, two distinct peaks appear at 280 nm and 510 nm. We attribute the short wavelength band to overlapping  $n \rightarrow \pi^*$  transitions of all carbonyls in SOA. The long wavelength band has not been assigned. However, the observed time-dependence of the absorption spectrum of SOA strongly suggests that aging processes increase the degree of conjugation in the SOA species. A possible scenario involves cross-aldol condensation reactions of carbonyl compounds (44, 61, 62). Indeed, the aldol condensation of aliphatic aldehydes in concentrated sulfuric acid was shown to produce a large increase in the absorption index in the near UV and visible range (44, 62). Although the SOA material is not as acidic as solutions investigated in Ref. (44, 61, 62), the presence of multiple organic acids in SOA appears to be sufficient for an efficient catalysis of these condensation reactions.

The effective extinction coefficient ( $\epsilon$ ) of the resulting SOA material can be estimated from the known mass of the collected particles. For a rough estimate, we assume that the SOA film on the  $\text{CaF}_2$  window is uniform, that it has a density of  $1.5 \text{ g/cm}^3$  (65), and that the average molecular weight of the SOA species is 200 g/mol. This translates into  $\epsilon \sim 10\text{-}100 \text{ L mol}^{-1} \text{ cm}^{-1}$  for the 510 nm peak after 24 hours of aging. Over the course of a day, the particles transition from being transparent to visible light to being weakly absorbing. Their extinction coefficient for UV radiation also increases by approximately an order of magnitude over this time, giving them a final  $\epsilon$  in excess of  $100 \text{ L mol}^{-1} \text{ cm}^{-1}$  at 300 nm. This is certainly sufficient for solar radiation-driven photochemistry to occur on atmospherically relevant time scales.

Such an increase in the SOA absorption coefficient resulting from chemical aging has significant implications. Current climate models assign a negative radiative forcing to organic particles because of their light scattering and cloud condensation roles (66, 67). If organic particles can be converted from scatterers to absorbers of visible radiation after spending a few days in the air, their contribution to the radiative forcing could potentially shift from negative to positive. In fact, there is evidence for brown aerosol amplifying warming over Asia (68) but the question of whether biogenic SOA contribute to this effect is still open.

## Photodissociation Spectra of Monoterpene SOA

The fact that SOA particles absorb radiation in the near-UV and visible ranges of the solar spectrum does not immediately imply that SOA material is susceptible to solar photodegradation. The absorbed photon energy can be re-emitted as fluorescence or lost to vibrational relaxation. Even if the absorber succeeds in breaking one of its bonds, chances are it will be re-formed because of the likely caging effects in the surrounding SOA matrix. To fully understand the impact of photochemistry on SOA aging, knowledge of photodissociation spectra and photodissociation quantum yields for representative SOA species is required.

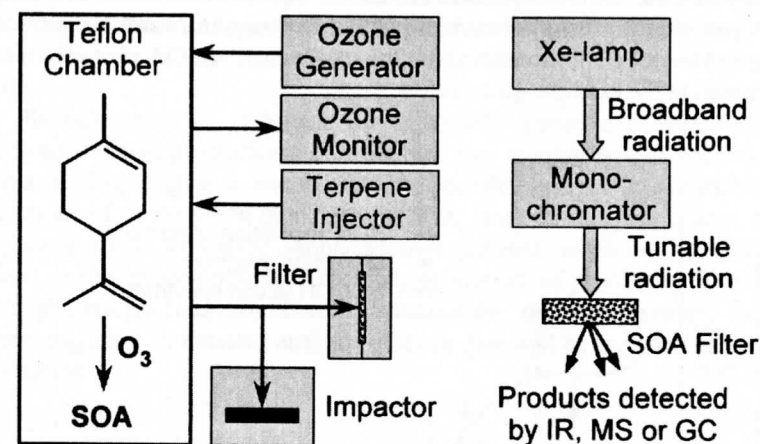


Figure 4. Experimental approach for studying SOA photochemistry. The left section depicts SOA generation, and the right shows the basic principle of photodissociation action spectroscopy for SOA filter samples. IR, MS, and GC refer to infrared cavity ring down spectroscopy, chemical ionization mass spectrometry, and gas chromatography, respectively.

Our laboratory recently developed a new approach for studying photochemistry of organic aerosol materials based on photodissociation action spectroscopy (48, 49, 63). Figure 4 illustrates the basic idea of this approach. SOA particles are synthesized by a dark reaction between a monoterpene and ozone, collected on a quartz filter, and purged with clean nitrogen to remove the most volatile fraction. The filter is then placed in a custom-built photochemical cell where it is exposed to wavelength-tunable UV radiation. The resulting gas-phase photolysis products are sensitively detected in real time either by cavity ring-down infrared spectroscopy (49) or chemical ionization mass-spectrometry.

Alternatively, the products are trapped and analyzed off-line by GC/MS. The relative yield of a specific photolysis product as a function of the excitation wavelength is a *photodissociation action spectrum*. The SOA material can also be extracted from the filter before and after the irradiation and analyzed by electrospray ionization mass-spectrometry in order to assess the degree of chemical change due to photolysis.

For a single isolated molecule, the photodissociation action spectrum represents the product of absorption cross-section with photodissociation quantum yield for a particular product channel. Therefore, comparison between the absorption spectrum and photodissociation spectra recorded for all possible product channels carries rich information about the mechanism of photodissociation. For a complicated mixture of molecules contained in a sample of SOA particles, this comparison is arguably less straightforward. Nevertheless, it can provide useful information about the mechanism of SOA photochemistry, as illustrated in the example given below.

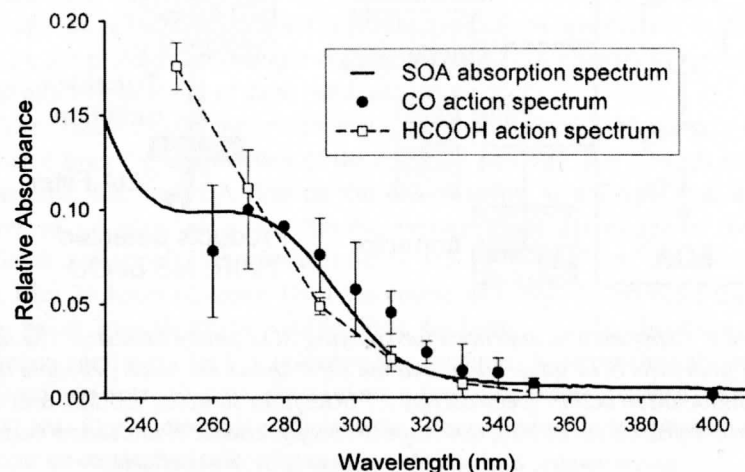


Figure 5. Comparison of the absorption spectrum and two photodissociation action spectra for D-limonene SOA (carbon monoxide and formic acid channels).

Figure 5 shows a comparison between the absorption spectrum of D-limonene SOA, recorded immediately following particle collection to minimize the aging effects, and two photodissociation action spectra. The first action spectrum was recorded by measuring the relative yield of formic acid (HCOOH) as a function of UV irradiation wavelength (48). The second action spectrum tracked the yield of carbon monoxide (CO). Both action spectra were arbitrarily scaled to facilitate the comparison with the absorption spectrum.

The HCOOH and CO action spectra are reproducibly different from each other, reflecting the different photochemical pathways leading to their production (Figure 6). HCOOH is a good marker for photolysis of secondary ozonides formed on ozonolysis of terminal alkenes (48, 49, 63), and therefore the action spectrum recorded for the HCOOH product channel should be similar to the spectra of simple organic peroxides. Peroxides are characterized by a strong  $n \rightarrow \sigma^*$  band in the deep UV that has a broad tail extending into the actinic region. At wavelengths longer than 250 nm, the absorption cross sections of peroxides decay with a dependence that is very nearly exponential. This is consistent with the observed shape of the HCOOH action spectrum. The emission of CO is a signature of carbonyl photolysis (Figure 6). Aliphatic carbonyls are characterized by a weak  $n \rightarrow \pi^*$  band centered in the vicinity of 300 nm. This band is visible in both the absorption spectrum of SOA and the CO action spectrum in agreement with its assignment to the carbonyl functional group.

Photochemistry of carbonyls can potentially generate a large number of additional volatile products via Norrish type I or Norrish type II photochemical cleavage (69); Figure 6 shows just two possible channels. Given the high abundance of carbonyls in monoterpene SOA, one could expect a large number of photoproducts including simple alkanes, alkenes, alcohols, and carbonyls. Indeed, we have been able to detect a large number of products of D-limonene SOA photodegradation by chemical ionization mass-spectrometry and gas-chromatography. A detailed analysis of these data will be reported in a separate publication.

## Summary and Future Directions

The most interesting conclusion emerging for this work is that both primary (49, 63) and secondary (48) organic particles can undergo aging processes driven by direct photolysis of organic peroxides, ketones, and aldehydes inside the particles. This photochemical aging has the potential to significantly influence the physicochemical and toxicological properties of organic particles. For example, selective photodegradation of peroxy groups in SOA particles is likely to affect their toxicological properties as peroxides are implicated in many of the adverse health effects of particulate matter (70, 71). The change in composition of organic particles may also affect their ability to act as cloud condensation nuclei, thus indirectly affecting the climate (52, 53). Finally, photochemical reactions in organic particles can generate a radiation-driven flux of small volatile organics from the aerosol phase back into the gas phase (72).

It is clear that we have merely scratched the surface with respect to understanding the mechanism of photochemical aging of monoterpene SOA. The effects of reagent concentration, type of oxidant, humidity, temperature,

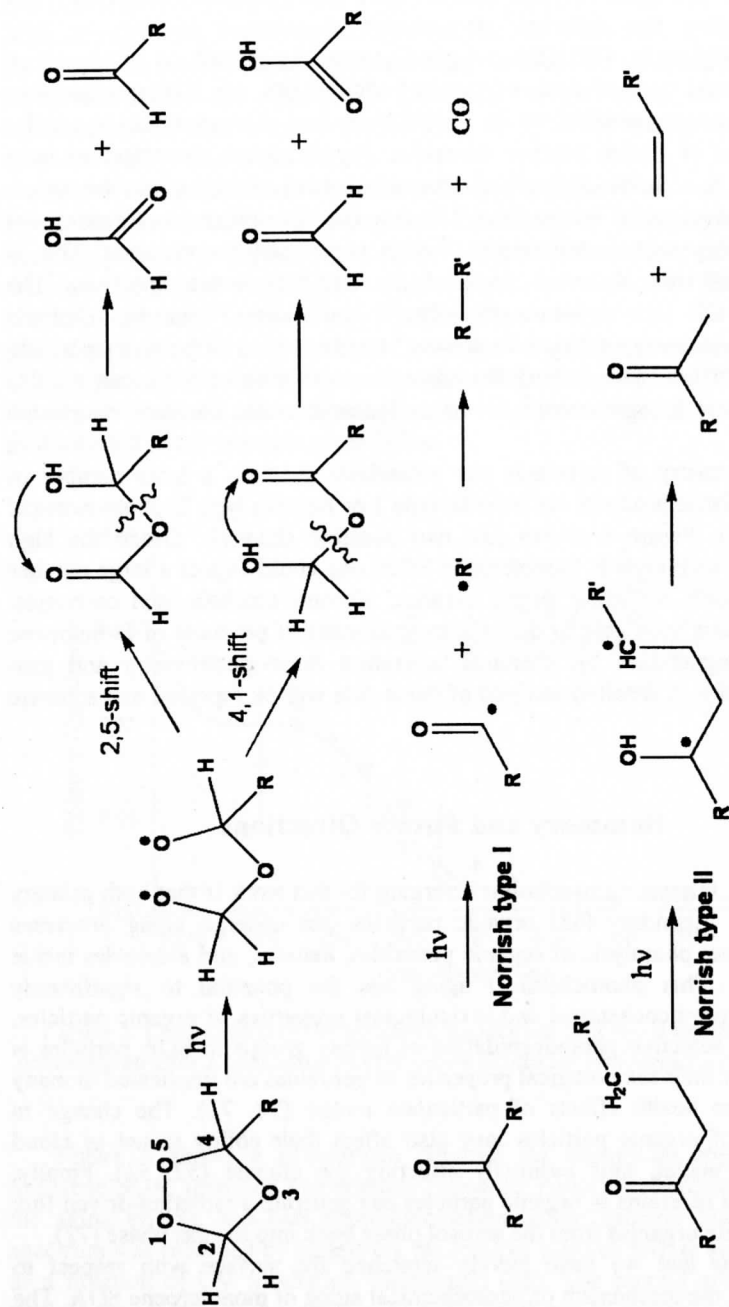


Figure 6. Possible photodissociation pathways for secondary ozonides and carbonyls. For simplicity, only two selected pathways of Norrish type I and II photocleavage are shown. Formic acid and carbon monoxide are markers for photolysis of secondary ozonides and carbonyls, respectively.

and inorganic seed particles used during SOA generation all need to be carefully addressed in future experiments. Similarly, the roles that particle size, chemical heterogeneity, and presence of adsorbed water play in the mechanism of photochemical reactions are currently unknown. We also stress that the role of photochemical processes has been explored only for laboratory generated SOA; the effect of solar radiation on field samples of particulate matter was not studied. On a more fundamental side, the cage effects for photodissociation of simple molecules in characteristic SOA materials, as well as the solvent effects of SOA medium on absorption spectra of simple chromophores will need to be explored in detail. With sufficient quantitative information on photodissociation rates, we anticipate that photochemical aging processes can start to be included in air pollution and regional climate models.

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