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Aerosol Chemistry

Suppressed Particle Formation by Kinetically Controlled Ozone Removal: Revealing the Role of Transient-Species Chemistry during Alkene Ozonolysis**

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Atmospheric aerosols show significant impact on human health, the chemistry of trace species in the atmosphere, and global climate through both direct and indirect radiative effects.[1,2] It is generally accepted that semivolatile organic compounds produced in the atmospheric oxidation of anthropogenic and biogenic compounds contribute to the growth and mass of atmospheric aerosols.[2] Although their aerosol formation potential and their influence on the radiation balance of the earth has been known since the early studies of Tyndall, Haagen-Smit, and Went,[3] the magnitude of biogenic contributions to the atmospheric particulate burden is still not well characterized, with estimates ranging from 11.2 to 270 Tg per year.[4–6] Rapid nucleation events have been observed over a broad range of ambient conditions,[7] and various nucleation mechanisms have been proposed in explanation, including ion-induced nucleation, homogenous nucleation of various particle precursors (biogenic compounds, iodide compounds), and nucleation in binary mixtures involving sulfuric acid.[8] However, it remains unclear which of these mechanisms occur, especially in the lower atmosphere. With respect to unsaturated hydrocarbons, besides OH-[9] and NO_3-initiated[10] oxidation, ozonolysis in particular is well known to lead to particle formation.

Over the years, many efforts have sought to unravel nucleation mechanisms during alkene ozonolysis in laboratory or smog-chamber studies.[2,10–17] For liquid- and gas-phase ozonolysis, the first reaction steps proceed along the Criegee mechanism,[14] while secondary oxidation processes are very complex and only partly understood.[15] This situation complicates the direct identification of self-nucleating species and necessitates indirect approaches. For α-pinene (endocyclic double bond) and β-pinene (exocyclic double bond), two of the most abundant terpenes, the effects of alkene structure,[10,11,13,16,17] oxidation initiated or influenced by OH radicals,[10,13] humidity,[10,12] and seed aerosol[16] on secondary organic aerosol (SOA) formation have been studied. It has been shown that simplified oxidation and nucleation models can predict some of these effects.[13,18] In most of the cited studies, the secondary organic aerosol formation mechanism is assumed to follow the traditional picture, in which multifunctional low-volatility products are formed during ozonolysis under supersaturated vapor conditions, which are sufficient to initiate homogenous self-nucleation.[8] However, the vapor pressures of such species can only be roughly estimated,[16,19–21] and hence several candidates have been suggested, such as dicarboxylic acids,[16] secondary ozonides,[11] thermally stabilized Criegee intermediates,[12] or hydroxyhydroperoxides.[22] However, there is uncertainty about the feasibility of homogenous nucleation from these compounds.

In the past decade, the role of heterogeneous chemistry in aerosol formation has emerged. Jang et al. could demonstrate the potential of acid-catalyzed heterogeneous reactions to increase SOA formation.[23] Zhang et al. showed that stable complexes of sulfuric acid and organic acids can lower the nucleation barrier.[24] The presence of oligomers in the aerosol phase was also shown,[17,25,26] contradicting the assumption in the traditional SOA formation picture that oxidation products do not react further in the particle phase. Recently, Bonn et al. proposed a mechanism for organic nucleation involving secondary ozonides as nuclei activated by heterogeneous reactions with peroxy radicals (RO_2).[27] Heaton et al.[28] showed that oligomers are formed in very early stages of organic SOA formation, thus suggesting that a mechanism of only a few steps governs gas-to-particle phase transfer.

The elucidation of phase-transfer mechanisms in reactive systems is complicated by the limited detection sensitivity for the nucleating species. This difficulty holds for SOA but also for soot formation during combustion. It proved useful to study such systems under novel conditions, as in the combined study of the interaction of organic and inorganic aerosol components, which revealed the large influence of heterogeneous chemistry.[23]

In a recent study we evaluated kinetic models describing the formation of soot precursor species and hydrocarbon flame speeds under rather extreme reaction conditions.[29] in this study, submechanisms could be isolated, and reactions sensitive to both soot precursor formation and hydrocarbon flame speeds were revealed. In subsequent studies, the results could be applied to different fuel molecules.[30] These studies have inspired us to examine the particle formation potential of alkenes under unusual ozonolysis conditions. The idea is to remove ozone in a kinetically controlled way from the reaction system. If the ozone is rapidly consumed by the initial reaction with the alkene, transient species coupled to

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the ozone concentration will have a much smaller contribution to secondary reactions, because many of them take place on significantly longer time scales.[31] Experiments aiming at controlled ozone removal require comparatively high alkene and ozone concentrations, causing a loss of sensitivity to the properties of the species with the lowest volatility. Therefore, the present study explicitly aims to reveal kinetic effects and global mechanistic features. Such kinetic effects have received less attention, although they have been noted in some studies, for example, by Bonn et al. for the influence of humidity on aerosol yields.[11]

For ozonolysis experiments with high reactant concentrations, the use of a small reactor is appropriate, because with larger reactors or smog chambers most of the ozone would be uncontrollably consumed during initial mixing, owing to large local concentration gradients. Therefore we employed a 5 L reactor, which was previously used to study hydrocarbon oxidation reactions.[32] It is equipped with a sensitive IR detector to monitor concentrations of reactants and products. Before each experiment the cell was purged four times with synthetic air or nitrogen, and IR spectroscopy was used to check that no remainders of the previous mixture were present. For the present study, the setup was augmented with a Scanning Mobility Particle Sizer (TSI 3936) and connected to an ozone generator/reservoir. Owing to high initial reactant concentrations, a favorable ratio of reactive collisions to wall collisions is maintained, despite of the small volume. We used methylcyclohexene (MCHe) and methylenecyclohexane (MCHa) as alkene model compounds. Both alkenes are known to produce particles under suitable conditions via their oxidation products,[16,17] and they are prototypes for endocyclic and exocyclic terpenes such as α- and β-pinene. They show significantly higher vapor pressures than the pinenes, allowing for much higher excess concentrations. MCHe and MCHa have the same molecular mass and show comparable secondary ozonolysis chemistry, but their reaction rates with ozone differ by roughly a factor of 15,[16] making them ideal reactants for kinetic probing.

In Figure 1 the conditions used in our experiments are compared to several recent studies. For both alkenes and ozone we used concentrations that are often one order of magnitude above those applied by other groups, while our experiments with the lowest concentrations are comparable to several experiments by Bonn et al.[11] and Uherek.[33] We performed several series of experiments involving mixtures of the alkene and ozone with an ozone concentration of 5 ppm and alkene concentrations of 5–60 ppm for MCHe and 5–250 ppm for MCHa. The experiments were performed at 1 bar using synthetic air.

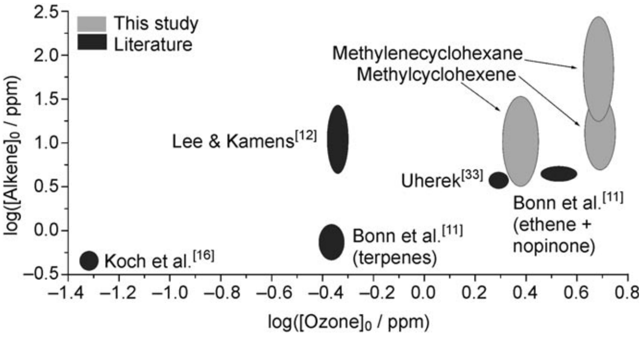

Figure 1. Overview of alkene/ozone concentrations applied in previous studies of particle formation from alkene ozonolysis[11,12,16,33] compared to the present study.

Our experiments reveal an unexpected feature of alkene gas-phase ozonolysis that has not been reported to date. For both alkenes, a drastic drop in total particle number density is seen for increased relative alkene concentrations. Measured particle mobility–size distributions for selected excess alkene concentrations are shown for both substances in Figure 2. We see that the median particle diameter decreases slightly for MCHa from 140 to 110 nm and is constant around 115 nm for MCHe. The most prominent difference is the much lower alkene excess needed to achieve suppression when MCHe is used compared to MCHa. This feature is better illustrated in Figure 3, in which the particle number concentration is plotted as a function of the alkene/ozone concentration ratio.

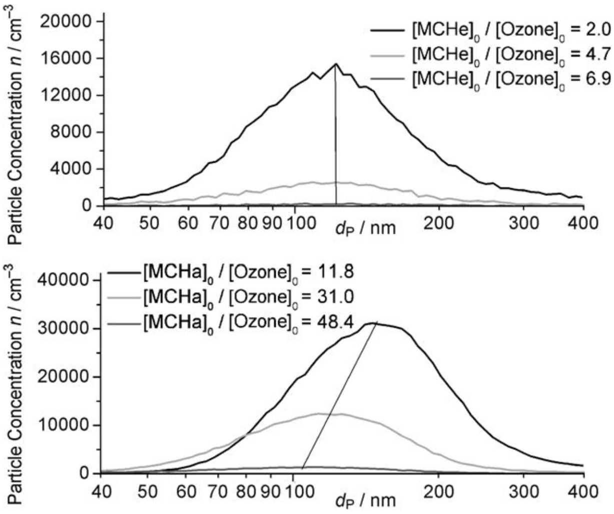

Figure 2. Influence of alkene excess on the particle-size distributions from the ozonolysis of MCHe (top) and MCHa (bottom).

For MCHe, which is more rapidly consumed than MCHa, we see a continuous drop in the total particle number with increasing MCHe concentration and finally an almost complete suppression of aerosol formation at 5 ppm ozone and 35 ppm MCHe. For MCHa the total particle number concentration first rises and then starts to drop for concentration ratios above 7:1, and a significantly higher alkene excess of 250 ppm MCHa is needed to achieve near suppression. The rise for low concentrations ratios is expected from the slow reaction rate of MCHa with ozone. In this case, the maximum of the particle number concentration is not captured, because sampling for all experiments started after the same time period (10 min).

Although a small reactor is used, effects of initial mixing still have to be considered with respect to the comparatively short reaction time for large excess alkene concentrations. In our experiments, ozone is added to the cell first. The alkene is

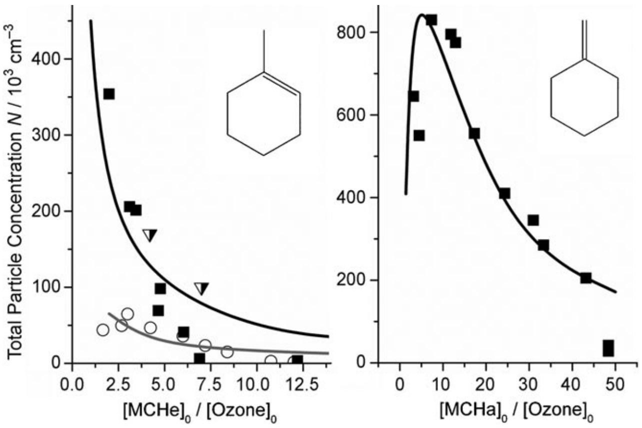

Figure 3. Maximum total particle concentrations from the ozonolysis of MCHe (left) and MCHa (right). Squares/triangles: 5 ppm O_3 in synthetic air. Circles: 2.5 ppm O_3 in synthetic air. Triangles indicate reverse filling order. Experiments were performed at 1 bar and 298 K. Curves show qualitatively predicted particle precursor concentrations after 10 min.

then automatically injected within 5 s, followed by the bath gas during another 5 s. The chemistry that takes place in the mixing zone is under the strong influence of diffusion and involves a broad range of alkene/ozone ratios. Moreover, the concentration of the second compound is locally enhanced compared to the compound injected first. To investigate the influence of these effects, in several experiments we changed the sequence of filling by adding the ozone after the alkene. As a consequence, the excess concentration needed for suppression was higher (by a factor of 2.5, not shown) and for $[\mathrm{MCHe}]_0/[\mathrm{ozone}]_0$ ratios around 7:1, significant particle formation was observed (Figure 3, triangles), in contrast to the standard filling sequence. This result is expected, as the reaction partly takes place under ozone excess in the mixing zone for high reaction rates at large alkene excesses. Additional experiments were conducted to characterize the nucleation suppression. The results of a series of experiments with 2.5 ppm ozone and 3–30 ppm MCHe are included in Figure 3 (left). The suppression of particle formation is also observed, but a much smaller slope is seen.

We note that the alkene concentrations necessary to achieve the suppression of nucleation can hardly be generated using pinenes and other biogenic terpenes owing to their low vapor pressures. In several experiments with MCHe and 5 ppm ozone, we added 230–450 ppm cyclohexane (CH) as an OH scavenger. Fewer but larger particles were formed, but the nucleation suppression was not influenced (see the Supporting Information).

How can these observations be rationalized? The different rate of ozone removal for MCHe and MCHa suggests that we see a kinetic effect. This assumption is also supported by the experiments with 2.5 ppm ozone, for which the rate of ozone consumption is reduced by a factor of four for the same MCHe/ozone concentration ratio, resulting in a significantly smaller slope in Figure 3. These findings suggest that either ozone itself or transient species with concentrations closely coupled to that of ozone are involved in secondary reactions in the nucleation mechanism. Ozone only reacts quickly with radicals; reactions with olefinic products are not competitive. Alkyl radical reactions with ozone proceed by oxygen-atom transfer, forming a chemically activated alkoxy radical that subsequently decomposes by C–H and C–C scissions.[34] For larger linear and cyclic radicals, C–C fissions dominate owing to smaller barriers, as we demonstrated for the analogous reaction with oxygen atoms.[35,36] Hence, this type of reaction is not expected to produce precursors for nucleation, because species of rather higher volatility are formed.

Much more likely are reactions of the comparably stable peroxy and alkoxy (RO) radicals, which are among the most abundant radical species in the atmosphere.[37] In ozonolysis experiments, RO_2 radicals are produced from O_2 addition to alkyl radicals, and alkoxy radicals are formed from the self reaction of peroxy radicals.[37,38] In the MCHe and MCHa oxidation mechanism, RO/RO_2 reactions are assumed to be involved in several steps.[16]

Recent studies elucidated the complex chemistry of large RO radicals[39] and their potential role in SOA formation.[40] In smog-chamber experiments, Bonn et al.[27] detect peroxy radicals as organic compounds formed during alkene ozonolysis, the reactions of which with product species of low volatility and freshly formed aerosols lead to growth of aerosol particles to detectable sizes. On the basis of their proposal, the removal of RO_2 radicals coupled to fast ozone removal as well as ozone reactions in the RO/RO_2 system may explain the nucleation suppression. One such ozone reaction might be $RO + O_3 \rightarrow RO_2 + O_2$. No direct kinetic data is available for this type of reaction, but for the analogous reaction $C_2H_5O + NO_3 \rightarrow C_2H_5O_2 + NO_2$, Ray et al. report a high rate constant of $k = 2 \times 10^{12}\ \mathrm{cm^3\,mol^{-1}\,s^{-1}}$.[41] The analogy of oxygen transfer to C_2H_5 radicals by O, O_3, and NO_3 has been studied in detail by Hoyermann et al.[34] If O-atom transfer by ozone to large RO radicals is competitive to RO decomposition and reactions with O_2, the following chain is established:

$$R + O_2 \rightarrow RO_2 \tag{1}$$

$$RO_2 + RO_2 \rightarrow RO + RO + O_2 \tag{2}$$

$$RO + O_3 \rightarrow RO_2 + O_2 \tag{3}$$

This chain raises RO_2 concentrations, because the loss channel via alkoxy decomposition (forming smaller carbonyl products and smaller radicals by C–C decomposition) is significantly suppressed as long as ozone is present in the reaction system. Such a mechanism may contribute to the observed effect of ozone removal.

Assuming a similar time scale of secondary chemistry for MCHe and MCHa, justified by their comparable oxidation mechanisms,[16] the much faster removal of O_3 from the reactive system in the case of MCHe would lead to decreased RO_2 radical concentrations at much lower alkene excesses and consequently to the suppression of particle formation. In other words, when ozone consumption and particle formation occur on similar time scales, the quasi-steady-state assumption (QSSA) largely applies for RO_2 or other transient species involved in particle formation, and no suppression can be observed. This assumption is valid for standard smog-chamber or reactor experiments with low reactant concentrations. Under the conditions of our experiments, we cause a breakdown of QSSA conditions for transient species by fast ozone removal, thus suppressing nucleation.

We constructed a simplified, qualitative kinetic model that is capable of predicting the suppressed nucleation (see the Supporting Information). This exemplary model includes the formation, decomposition, and stabilization of the Criegee intermediates and the formation of a secondary ozonide (SOZ) using lumped species. We described lumping in detail for heptylperoxy isomers in reference [30]. The formation of nucleating species is represented by RO_2 addition to the SOZ; RO_2 is formed by a representative unimolecular reaction step from the Criegee intermediate as well as by the reaction chain involving RO_2 described above. For the modeling, all the reaction rates are kept constant, except that the rate constant for MCHe/MCHa + O_3 is adjusted.

The model predictions (lines) are shown together with the experimental results in Figure 3. Especially for the experiments with lower ozone consumption rates, our simple model nicely captures the experimental data. For the experiments with MCHe and 5 ppm ozone, the model overpredicts relative particle formation at moderate concentrations; similar overprediction is found for MCHa only at extreme alkene excess. However, the experiments with the reversed filling sequence (Figure 3, triangles) indicate that this effect is probably due to higher excess alkene concentrations during initial mixing. We also found that the model is robust to changes of the used reaction rates, which are assumed to be in the range of available data for unimolecular and bimolecular reactions of stabilized Criegee intermediates (SCI).[42,43] The successful and robust modeling of the suppressed nucleation suggests that the particle formation mechanism involves reactions of transient species such as RO_2.

We also tested an alternative mechanism involving direct SCI and hydroperoxide reactions.[28] However, to achieve the suppression of nucleation under alkene excess, a fast SCI scavenging reaction by the alkene must be included. However, SCI scavenging by alkenes has not been reported to be competitive.[42] Including SCI scavenging, we still could not reproduce our results owing to the high sensitivity of scavenging to absolute alkene concentrations. At this point we have strong indications for the relevance of transient-species reactions in organic particle formation during ozonolysis.

The hypothesis that RO_2 radicals are indeed involved is supported by the study of Burkholder et al.,[13] who report that the usage of N_2 as bath gas instead of synthetic air leads to the absence of nucleation events for the whole range of experimental conditions in their study of the ozonolysis of α- and β-pinene. The significantly diminished abundance of peroxy radicals formed by $R + O_2$ in the absence of O_2 can explain their results. Using MCHe, we also tested N_2 as bath gas. Particle formation was reduced by a factor of two for an ozone concentration of 5 ppm, while a factor of eight was observed for a concentration of 2.5 ppm, and the suppression was seen at a much smaller alkene excess. These findings indicate that the nucleation threshold is at much higher O_3 concentrations with N_2. At high ozone concentrations, RO_2 could be formed by traces of oxygen as well as by the sequence $R + O_3 \rightarrow RO + O_2$ and $RO + O_3 \rightarrow RO_2 + O_2$. On the other hand, Berndt et al. showed that the substitution of synthetic air by N_2 had no effect on the nucleation rate when a different nucleation mechanism applies. They studied particle formation from the ozonolysis of α-pinene in the presence of SO_2.[44]

In summary, we report the suppression of particle formation under excess alkene concentrations in laboratory ozonolysis experiments. The effect has been discovered with the new approach of kinetically controlled ozone removal. The presented method is complementary to studies focusing on product analysis, because it is sensitive to the chemistry of transient species by exploiting effects of time-scale separation. Our results support the hypothesis that peroxy radicals are involved in organic nucleation and particle-growth mechanisms.[27] The presented approach is expected to provide valuable reference data for studying transient-species chemistry involved in organic particle formation.

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