Experimental Conditions and Secondary Organic Aerosol Formation in Chamber Experiments

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Abstract

The complicated processes involved in the formation of secondary organic aerosol (SOA) in the atmosphere can be studied during smog chamber experiments that enable isolation of systems of interest. Thus for the purposes of understanding the processes involved the reactions can be simplified and controlled. However, the conditions under which the experiments are performed are likely to impact on the results of the experiment. For example, in the ozonolysis of cycloalkenes, OH is removed from the experiment to prevent the OH oxidation of the cycloalkene competing with the ozonolysis. In this presentation, the effect of OH scavenger on SOA yield from the ozonolysis of cyclohexene is discussed. The simple mechanism presented in Keywood et al. (2004a) is used to explain discrepancies between results presented here and those presented by Docherty and Ziemann (2003) for the ozonolysis of \(\beta\)-pinene. This work confirms that the OH scavenger plays a role in SOA formation in alkene ozonolysis and the extent of this influence is dependent on the specific alkene. Acyloperoxy radicals play a central role of in SOA formation in the ozonolysis of alkenes and only by incorporating these in the simple model of radical chemistry discussed here could the observed trends in acid concentrations for the different scavenger be replicated. This work underscores the importance of gas-phase radical chemistry beyond the initial reaction.

**Keywords**: SOA, cyclohexene, biogenic, smog chamber, OH scavenger, reaction mechanism

1. Introduction

Secondary organic aerosol (SOA) is produced by the oxidation of a precursor hydrocarbon to form products with low vapour pressure that are able to partition from the gas to the particle phase. This is a very complicated process, dependent on many variables including the species of hydrocarbon, the oxidant, the presence of existing aerosol, environmental conditions such as temperature, pressure and relative humidity. This means that our understanding of their formation is limited, so that our ability to parameterise SOA in climate and pollution models is restricted. Despite this, SOA is ubiquitous in the atmosphere, being present in both the urban and remote atmosphere and hence is likely to contribute to adverse effects to human health, visibility degradation and climate change.

Much of our current understanding of SOA formation arises from the results of smog chamber experiments. Smog chamber experiments are invaluable, as they allow the isolation of systems of interest. However, the conditions under which the experiments are performed are likely to impact on the results of the experiment. For example, in the ozonolysis of cycloalkenes, OH is removed from the experiment, to prevent the OH oxidation of the cycloalkene competing with the ozonolysis. This is necessary as OH is a product of the initial reaction between cycloalkene and ozone. By adding an OH scavenger during the experiment, the potential exists for products of the scavenger-OH reaction to further participate in SOA formation.

A number of potential OH scavengers exist and the challenge remains to choose a scavenger which will have minimal effect on the SOA formation. Scavengers commonly used include cyclohexane, CO, alcohol, and aldehydes. Most investigations of ozone-alkene chemistry have had the goal of understanding the yield of OH, and so have been concerned primarily with the effect of the scavenger on the gas-phase chemistry (Paulson et al., 1999; Atkinson et al., 1993, Chew et al., 1996). Recently, it has been suggested that the OH scavenger can have an effect on the SOA yield...
itself (Docherty and Ziemann, 2003; Ziemann, 2003). For example, in the cyclodecene-ozone system, in the presence of propanol scavenger, Ziemann (2003) observed the formation of cyclic peroxymethylacetas, and while these products were not shown explicitly to result in an increase in aerosol yield we may suppose that these large cyclic peroxymethylacetas partition to the aerosol phase. In contrast to this, Docherty and Ziemann (2003) observed a reduction in SOA yield for the β-pinene ozonolysis when propanol scavenger was used, compared with cyclohexane as a scavenger.

This paper will review the current level of understanding on the effect of OH scavenger of cycloalkene ozonolysis, focusing on experiments carried out in the Caltech Indoor Chamber Facility, in which SOA yield from the ozonolysis of cyclohexene was investigated. For a detailed discussion of these experiments and analysis of the results, the reader is referred to Keywood et al. (2004a).

Methods

Ozonolysis of cyclohexene in the presence of different OH scavengers (cyclohexane, 2-butanol, and CO) and in the absence of OH scavenger was carried out in the Caltech Indoor Chamber Facility. Cyclohexene is a very well studied compound and its structure may be viewed as a building block on which many of the more complicated biogenic hydrocarbons are based. Details of Caltech Indoor Chamber Facility have been described in detail elsewhere (Cocker et al., 2001) and details of the experimental methods employed in these experiments are described in Keywood et al. (2004b). In short, the experiments were carried out in the presence of (NH₄)₂SO₄ seed, and the volume of SOA was determined by scanning electrical mobility spectrometers (SEMS). Temperature and RH within the chambers were measured continuously; temperature of operation of the chambers was 20±2 °C and the RH was <10%. Concentration of the parent hydrocarbon was determined by gas chromatography flame ionization detection.

The OH scavengers, cyclohexene, 2-butanol, and CO, were injected at sufficient concentration so that the reaction rate of OH radicals with the scavenger exceeded that of the OH with the cycloalkene by a factor of 100, into a glass bulb and gently heated as a stream of clean air was passed through the bulb, vaporizing the scavenger and carrying it into the chamber. Microliter syringes were used to inject known amounts of liquid cyclohexene into the chambers using the same method. The reaction was initiated with the injection of ozone. Ozone was generated using a UV lamp ozone generator, and continuously measured. The total concentration of ozone injected was sufficient to exceed the parent hydrocarbon concentration by a factor of 3.

Results

SOA Yield

Figure 1 shows the SOA yields from the ozonolysis of cyclohexene as a function of aerosol mass produced (ΔM₀) when the different OH scavengers, cyclohexane, 2-butanol, and CO, are used. Also shown are the SOA yields in the absence of scavenger. ΔM₀ was determined from the change in aerosol volume (measured by the SEMS) and assuming a particle density of 1.4 g cm⁻³, as determined by Kalberer et al. (2000) for the cyclohexene-ozone system. Measured particle number concentrations were corrected for size-dependent wall loss (Keywood et al., 2004b). SOA yield (Y) can be defined as the ratio of organic aerosol mass concentration produced (ΔM₀, µg m⁻³) to the mass concentration of hydrocarbon consumed (ΔHC, µg m⁻³), Y = ΔM₀ / ΔHC. The error bars in Figure 1 are computed based on propagation of uncertainties arising in the ΔHC and ΔM₀ measurements (Keywood et al., 2004b).

The use of cyclohexane as an OH scavenger results in the smallest aerosol yield. 2-butanol scavenger results in a higher SOA yield than that of cyclohexane. When no scavenger is used, the SOA yield is similar to that when 2-butanol is used; finally, the use of CO as a scavenger results in the greatest yield (as well as the greatest uncertainty in the measurement).

Scavenger Chemistry

The reaction between cyclohexene and ozone is initiated by the addition of ozone to the double bond. This forms a primary ozonide which stabilizes or decomposes to an excited bifunctional Criegee intermediate that has two isomers (Ziemann, 2003).
How this intermediate then goes on to form SOA has been discussed extensively (Ziemann, 2003; Kalberer et al., 2000; Ziemann, 2002). The predominant low molecular weight SOA products identified in the cyclohexene-ozone system are dicarboxylic acids and hydroxylated dicarboxylic acids (Kalberer et al., 2000). Hydroxyl radicals can be produced from various reactions in the alkene ozonolysis mechanism. The dominant pathway of OH formation is by the alkyl group of the syn isomer interacting with the terminal oxygen (Fenske et al., 2000; Gutbrod et al., 1997).

How does the OH scavenger affect the SOA yield? One possible explanation lies in reactions of the stabilized Criegee intermediate (SCI) with the scavenger, which could potentially form different low-volatility products. However, in the case of cyclohexene ozonolysis, such reactions probably do not occur to an appreciable extent, as there is very little SCI formed. A more likely explanation for the observed effect of the scavenger on SOA yield may lie in the differing radical products formed in the OH-scavenger reactions. Docherty and Ziemann (2003) showed that different scavengers lead to differences in HO$_2$/RO$_2$ ratios, which may have an effect on the subsequent radical chemistry. In the case of the CO scavenger, only HO$_2$ is produced:

\[ \text{OH} + \text{CO} (+ \text{O}_2) \rightarrow \text{HO}_2 + \text{CO}_2 \]

By contrast, when cyclohexane is used as a scavenger, the radical product is an alkylperoxy radical:

\[ \text{OH} + \text{C}_6\text{H}_{12} \rightarrow \text{HO}_2\text{-C}_6\text{H}_{10} + \text{H}_2\text{O} \]

Some HO$_2$ production is expected by the OH-cyclohexane reaction due to reactions of the cyclohexylperoxy radical. Self-reactions form alkoxy radicals which may further react to form HO$_2$ although the amount formed is expected to be small. The intermediate case is the reaction of OH with 2-butanol, which may form either HO$_2$ or RO$_2$:

\[ \text{OH} + \text{C}_4\text{H}_{10} \rightarrow \text{HO}_2\text{-C}_4\text{H}_8 + \text{H}_2\text{O} \]

The expected trend in the HO$_2$/RO$_2$ ratios from each scavenger, CO>2-butanol>cyclohexane, matches that of the aerosol yields observed here, suggesting that increased concentrations of HO$_2$ and/or decreased concentrations of RO$_2$ promote aerosol formation. This conclusion is in contrast to that reached by Docherty and Ziemann (2003), who argue that for β-pinene ozonolysis, increased HO$_2$/RO$_2$ ratios instead inhibit aerosol formation.

A simple chemical reaction scheme or mechanism used to understand the role that differences in scavenger chemistry may have on the ozonolysis reaction system, and why β-pinene and cyclohexene exhibit opposite trends in SOA formation, has been presented in Keywood et al. (2004a). The mechanism predicted the ozone and cyclohexene concentrations as well as radical production for the chamber experiments discussed here. As expected, radical production was dependent on the scavenger used. For example, HO$_2$ concentration was maximum for CO and minimum for cyclohexane. Alkylperoxy radicals displayed the opposite trend. The mechanism assumed SOA was represented by organic acids since these are the most abundant low-molecular weight products found in SOA from cyclohexene ozonolysis (Kalberer et al., 2000). The simple mechanism predicted that most organic acids were formed when cyclohexane was used as the scavenger, and least with CO, however when the direct formation of acylperoxy radicals was included in the mechanism (as suggested by Aschmann et al., 2003, and Ziemann 2002 in order to rationalise products observed in chamber experiments), the predictions of organic acid formation were more in line with the experimental results presented here.

The simple mechanism can be used to explain the discrepancy between the observations presented here and those of Docherty and Ziemann (1), where SOA yield from the ozonolysis of β-pinene in the presence of cyclohexane were greater than in the presence of propanol. Notably, the additional source of acylperoxy radicals does not play a role in the ozonolysis of β-pinene, as the Criegee formed in that case has no vinylic hydrogens so cannot form acyl radicals.

Recently, Jenkin (2004) modelled SOA formation from the ozonolysis of α-pinene and β-pinene using the Master Chemical Mechanism (version 3), and reported the same sensitivity of β-pinene to OH scavenger type as presented in Docherty and Ziemann and suggested by the simple mechanism presented here. The insensitivity of α-pinene to the species of OH scavenger was explained in terms of the structure of α-pinene, specifically the bicyclic nature and presence of an alkyl substitution at the double bond which differs significantly from the structure of cyclohexene.
Implications

The results presented here confirm those of Docherty and Ziemann (2003) that the OH scavenger plays a role in SOA formation during alkene ozonolysis. However, the extent and direction of this influence are dependent on the specific alkene. The main influence of the scavenger arises from its independent production of HO₂ radicals, with CO producing the most HO₂. The reactions of HO₂-acylperoxy and RO₂-acylperoxy in particle formation; instead, acids are formed by OH scavenger reactions do not participate directly of HO₂ radicals, with CO producing the most HO₂, scavenger arises from its independent production of specific alkene. The main influence of the direction of this influence are dependent on the extent and different studies. However, based on the very recent modelling results presented in Jenkins (2004), the insensitivity to OH scavenger of SOA yield from ozonolysis of α-pinene, the SOA yields for the biogenic endocyclic alkenes at least, presented in Griffin et al (1999) may be unaffected by the OH scavenger type.

Regardless, in order for ozonolysis to be isolated, an OH scavenger must be employed, and until one that results in a chain-termination step can be identified, the scavengers currently used (cyclohexene and 2-butanol) are the most suitable. Highlighted here is the importance of understanding the chemistry of the scavenger itself.

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References


