# Secondary organic aerosol from limona ketone: insights into terpene ozonolysis *via* synthesis of key intermediates<sup>†‡</sup>

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Limona ketone was synthesized to explore the secondary organic aerosol (SOA) formation mechanism from limonene ozonolysis and also to test group-additivity concepts describing the volatility distribution of ozonolysis products from similar precursors. Limona ketone SOA production is indistinguishable from  $\alpha$ -pinene, confirming the expected similarity. However, limona ketone SOA production is significantly less intense than limonene SOA production. The very low vapor pressure of limonene ozonolysis products is consistent with full oxidation of both double bonds in limonene and furthermore with production of products other than ketones after oxidation of the *exo* double bond in limonene. Mass-balance constraints confirm that ketone products from *exo* double-bond ozonolysis have a minimal contribution to the ultimate product yield. These results serve as the foundation for an emerging framework to describe the effect on volatility of successive generations of organic compounds in the atmosphere.

# 1. Introduction

Limona ketone (4-acetyl-1-methylcyclohexene) is a potentially important intermediate in limonene ozonolysis<sup>1</sup> (Scheme 1). The system is both intrinsically important as a major atmospheric source of secondary organic aerosol (SOA) and chemically interesting as a model system and a tool to deconvolve multiple generations of oxidation in SOA formation.

Fine particulate matter plays a pivotal role in the atmosphere. It is typically defined as aerosol particles less than 2.5 microns in diameter (PM2.5). Fine particles strongly influence climate, most notably through the indirect effect, where their role as cloud condensation nuclei (CCN) controls the size distribution and total surface area of cloud droplets and thus cloud lifetimes and reflectivity.<sup>2,3</sup> Feedbacks associated with the indirect effect are one of the largest uncertainties in the climate system.<sup>4</sup> Fine particles also have severe negative health consequences, causing roughly 50 000 premature deaths each year in the United States alone<sup>5</sup> along with a host of chronic health effects. The mechanism responsible for these effects appears to be deposition in the deep lung followed by cardiopulmonary distress,<sup>6</sup> though other mechanisms including direct passage up olfactory nerves to the brain have been reported.7

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Roughly half of the  $PM_{2.5}$  mass consists of a vast mixture of organic compounds, known as organic aerosol (OA).<sup>8,9</sup> The rest are reasonably well-understood inorganic salts (principally ammonium sulfate and ammonium nitrate). The particles are generally either acidic or neutral. The organic fraction is of great interest because it is poorly understood, because organic composition strongly influences the properties described above, and because organics exhibit an extremely rich combination of chemical behaviors, including both gas- and condensed-phase oxidation chemistry and condensed-phase macromolecular chemistry.<sup>10</sup>

OA is traditionally divided into two categories with simple definitions: primary OA (POA), which are particles directly emitted into the atmosphere, most often from combustion sources, and the SOA mentioned above, which is condensedphase organic material formed during gas-phase chemical



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reactions in the atmosphere. SOA is known to be semivolatile,<sup>11</sup> and so SOA formation experiments typically seek to parameterize the vapor pressures of a large set of (typically unidentified) reaction products.<sup>12</sup> Recent experiments have demonstrated that a large fraction of POA is also semivolatile.<sup>13–15</sup> We thus now view all organic aerosol as a highly dynamic, evolving mixture subject to multiple generations of oxidation in both the vapor and condensed phases.<sup>10,15–17</sup>

Emissions, dilution, and chemistry will all alter the ambient volatility distribution over time. Now we must understand and describe multiple generations of oxidation of semi-volatile compounds, with reactions that transform the volatility distribution in either direction in a mixture containing hundreds of important compounds.

These issues pose a dilemma. On the one hand, the complexity of the system demands a simplified representation that still describes the range of behaviors and sensitivities occurring in the atmosphere. On the other hand, we must understand at least a subset of the system in detail in order to be able to frame and test that simplified representation. Good model systems are both intrinsically important to the atmosphere and suitable archetypes for broader behavior. Ozonolysis of limonene is one such system. Limonene has a significant flux into the atmosphere, and monoterpene ozonolysis is a major recognized SOA source. Because limonene is doubly unsaturated, it is also an excellent model system for multi-generational evolution of the vapor-pressure distribution. Ozonolysis of terpenoids is a major source of SOA.<sup>18,19</sup> and the selectivity of ozone to double bonds-and the wide range of ozone-alkene rate constants-makes the chemical mechanism vastly simpler than oxidation of large organic compounds by OH radicals.

Recent experiments on the photoxidation of isoprene have shown that SOA can be formed as a second-generation product from oxidation of first-generation methacrolein (MAK).<sup>20</sup> Though only a very small fraction of the mass of oxidized isoprene winds up as SOA, this may well be important due to the enormous biogenic isoprene flux.<sup>21</sup> However, monoterpenes have twice as many carbons as isoprene, and consequently tend to yield products with much lower vapor pressures<sup>22</sup> when they are oxidized. Oxidation of terpenes is thus a major, well-known source of SOA, but in almost all cases only a single generation of oxidation has been considered in chamber experiments. In one recent study, though, multiply-unsaturated terpenes were shown to exhibit more complicated SOA-formation behavior than singly-unsaturated terpenes, with continued SOA formation even after complete terpene consumption.<sup>23</sup> This behavior was observed in both 'photooxidation' experiments, in which both ozone and OH radicals are formed during photochemical oxidation of hydrocarbons in an illuminated chamber, and pure ozonolysis experiments, in which a 'HO<sub>x</sub> conditioner' (*i.e.*, 2-butanol) was added to an ozone + terpene mixture in order to convert OH radicals generated in the ozonolysis reaction.<sup>23</sup>

## 2. Background

We need to understand how organic reaction products partition between the vapor and a condensed phase consisting of a complex mixture of thousands of individual organic compounds. For several reasons we follow the total mass concentration of organic aerosol particles,  $C_{OA}$ , typically in  $\mu g m^{-3}$ . Atmospheric levels range from 1  $\mu g m^{-3}$  in the remote atmosphere<sup>24</sup> to 100  $\mu g m^{-3}$  in very polluted urban settings.<sup>25,26</sup> The corresponding total mass concentration of a compound (in all phases) is  $C_i$ . The vapor pressure can be converted into an *effective saturation concentration*,  $C_i^*$ . This subsumes nonideality such as activity coefficients; derivations and extensive discussions are presented elsewhere,<sup>11,12,15</sup> though in some cases  $C^*$  is presented as a partitioning constant,  $K = 1/C^*$ .<sup>11,12</sup>

Given these values, one can then find a partitioning coefficient,  $\xi_i$ . This is the fraction of compound *i* found in the condensed phase at equilibrium

$$\xi_i = \frac{1}{1 + C_i^* / C_{\text{OA}}}$$
(1)

Eqn (1) is an expression of Raoult's law. It is a simple saturation curve, of the same form as a Langmuir–Hinshelwood isotherm or a Lindemann–Hinshelwood pressure falloff curve in kinetics. The interpretation is simple as well: when the mass concentration of organic aerosol is equal to the saturation concentration of some compound, that compound will be evenly divided between the condensed and vapor phases ( $\xi_i =$ 0.05). However, if  $C_{OA}$  greatly exceeds  $C_i^*$ , then almost all of that compound will be in the condensed phase ( $\xi_i \simeq 1$ ), and at the other extreme almost none of that compound will be in the condensed phase ( $\xi_i \simeq 0$ ). The total aerosol concentration is in fact derived iteratively from all of the individual concentrations and partitioning coefficients

$$C_{\rm OA} = \sum_{i} \xi_i C_i. \tag{2}$$

It is important to note that coexistence demands that if there is a condensed phase, some amount of any compound will be in it, and of course there will always be some vapor pressure even for 'non-volatile' compounds. This can be important in either direction, with gas-phase oxidation of low-volatility material<sup>17</sup> and condensed-phase processing of volatile monomers<sup>20,27</sup> potentially playing an important role in the atmosphere by altering volatility and mass distributions of semi-volatile organics.

We have recently proposed that organic aerosol can be described by a 'semi-volatile basis set',  $\{C_i^*\}$ . Individual compounds are lumped into volatility bins and each bin is separated by an order of magnitude in saturation concentration

$$C_i^* = \{0.01, 0.1, 1, 10, 100, 1000, 10^4, 10^5, 10^6\} \ \mu g \ m^{-3}$$
(3)

For reference,  $1 \ \mu g \ m^{-3}$  is roughly  $10^{-7}$  Torr. We then reduce a complex reaction, such as ozonolysis, to

$$Precursor + O_3 \rightarrow \alpha_1 p_1 + \alpha_2 p_2 + \dots$$
 (4)

where  $\alpha_1$  is the mass yield of products  $p_1$  with saturation concentration  $C_1^* = 0.01 \ \mu g \ m^{-1}$ , *etc.* Our objective is to identify the volatility distribution of the products  $\{\alpha\}$ , where  $\Sigma \alpha_i > 1$  because the oxidation reactions typically add mass to the products. This greatly simplifies representation of the aerosol and of SOA formation chemistry when dealing with multiple reactions and multiple generations of oxidation chemistry.<sup>17</sup>



**Fig. 1** The fraction of material in the condensed phase for different bins in the semi-volatile basis set for  $C_{OA} = 1 \ \mu g \ m^{-3}$  (arrow). Lower-volatility material is almost completely in the condensed phase ( $\xi = 1$ ), while higher-volatility material is almost completely vapor-ized ( $\xi = 0$ ). If the aerosol loading were higher, for example  $C_{OA} = 10 \ \mu g \ m^{-3}$ , the curve would be shifted 1 decade to the left, with the  $C^* = 10 \ \mu g \ m^{-3}$  bin showing 50–50 partitioning.

The bins at 1000  $\mu$ g m<sup>-3</sup> and above represent 'intermediate volatility organic compounds' (IVOC), which are not significantly partitioned into the condensed phase in the atmosphere but which have a large mass concentration compared with typical  $C_{OA}$ . These derive from combustion emissions<sup>14</sup> as well as first-generation oxidation of 'traditional SOA' precursors. The IVOC are a potentially potent source of SOA.<sup>17</sup> Traditional SOA precursors such as monoterpenes have  $C^*s$  of  $10^8 \,\mu$ g m<sup>-3</sup> and above.

The great value of the basis set is that it allows us to describe partitioning without identifying all of the compounds forming the organic aerosol solution, and this lets us define chemical transformations that alter saturation concentrations and partitioning without either identifying all of the material or writing an essentially unknowable complete chemical mechanism.<sup>15</sup> For example, Fig. 1 shows how material will partition for  $C_{OA} = 1 \ \mu g \ m^{-3}$  (indicated on the figure with an arrow). The basis set also underscores the importance of designing experiments spanning the atmospheric range of aerosol concentrations. To enhance signal to noise, many experiments have been conducted at elevated aerosol levels (often >1000  $\mu g \ m^{-3}$ ), where partitioning will be completely different than in the atmosphere. This is a serious mistake.

It is very easy to fit data from both SOA experiments<sup>28–30</sup> and primary-emissions dilution experiments<sup>14</sup> using eqn (1) and (2). One obtains meaningful parameters spanning the basis set (for example product yields in SOA experiments and a flux distribution in emissions experiments) though parameters are only constrained if the actual  $C_{OA}$  range of the experiment falls near the C\* for a given bin. In this paper we shall use basis-set fits of SOA production from limona ketone + ozone as well as limonene + ozone to constrain the atmospheric mechanism for oxidation of the *exo* double bond in limonene. Gas-phase ozonolysis of the *endo* double bond in limonene is approximately 30 times faster than the *exo* double bond,<sup>31</sup> but by studying limona ketone we can effectively 'preselect' one of the two possible pathways for the *exo* ozonolysis (pathway 2b in Scheme 1)—the only pathway in which the large reaction fragment is a stable molecule rather than a Criegee intermediate (CI).

# 3. Limona ketone synthesis

Limona ketone was synthesized using a Diels–Alder reaction of isoprene and methyl vinyl ketone on dry silica gel.<sup>32</sup> SiO<sub>2</sub> was dried in an oven overnight. Equimolar amounts of isoprene and methyl vinyl ketone were added on top of the dried SiO<sub>2</sub> in a round bottom flask and stirred overnight in a water bath at 55 °C. The product was extracted from the reaction flask with methanol. After washing the organic phase with water, it was dried over MgSO<sub>4</sub>. A yellow-colored oil was collected after thorough rotary evaporation down to 50 mbar.

We analyzed the collected product with H- and C-NMR. The spectra are shown in the supporting information, along with simulations. H-NMR analysis of the product shows the requisite unsaturated proton at 5.3 ppm and two methyl groups at 1.65 and 2.15 ppm in both the experimental and simulated spectra. Isomerization of the product with one major and one minor compound appears as splitting at 1.65 and 2.16 ppm, revealing the presence of a 4-acetyl-2-methyl-cyclohexene Diels–Alder isomer. In the C-NMR spectra, the major isomer's unsaturated carbons appear at 119 and 134 ppm, with the ketone carbon found at 210 ppm. The ring carbons and methyl groups are found between 23 and 50 ppm, with the experimental data matching the simulation nicely.

The major and minor isomers were structurally elucidated by heteronuclear multiple-bond coupling (HMBC) long-range coupling experiments. The ratio of limona ketone to the 4-acetyl-2-methylcyclohexene isomer was determined to be approximately 3:1 by integration of the methyl proton peaks. HMBC analysis initially shows coupling of the 1-methyl protons at 1.64 ppm in the 1-D H-NMR with both isomers' vinylic tertiary C-NMR carbons at 119 and 121 ppm. The major isomer's methyl protons couple with the major vinylic tertiary carbon peak seen in the spectrum at 119 ppm while the minor proton peak couples with the minor vinylic C-NMR peak at 121 ppm. After determining which tertiary vinylic carbon was associated with the major compound, long-range coupling shows that the 119 ppm major tertiary vinylic carbon couples with the proton on the acetyl bound carbon. The minor vinylic carbon does not show this association as it is out of range, three carbons away. The minor isomer's proton, found adjacent to the acetyl substituent, shows a slight coupling with the 134 ppm quaternary vinylic carbon. This proves that the minor isomer has the acetyl substituent 2 carbons away from a quaternary unsaturated carbon in the meta position, while the major product has a para substituted acetyl group to C-1. From this analysis, we conclude that the major product is limona ketone while the minor product is the meta substituted isomer, 4-acetyl-2-methylcyclohexene.

From GC/MS analysis, the strongest elution shows m/z of 138 and a retention time consistent with limona ketone. This peak contains approximately 98% of the eluted material based

on GC peak-height integration. All in all, the calculated limona ketone yield was approximately 70%, with 25% 4-acetyl-2-methylcyclohexene secondary product. The hypothesis under consideration here is that mono-unsaturated monoterpenes with a 1-methylcyclohexenyl functionality should all give similar SOA product yields, with respect to volatility. Specifically, we wish to determine whether limona ketone and  $\alpha$ -pinene ozonolysis products show similar volatility. Confirmation of this hypothesis is not impeded by the mixture of isomers we obtained and so we continued with SOA experiments using the product as synthesized.

# 4. Experimental

We measure a mass partitioning coefficient by oxidizing a known mass of a precursor (limona ketone,  $\Delta C_{\rm lk}$ ) and observing the mass of organic aerosol produced ( $\Delta C_{\rm OA}$ ). The resulting aerosol mass fraction is

$$\xi = \frac{\Delta C_{\text{OA}}}{\Delta C_{\text{lk}}} \tag{5}$$

We measure  $\Delta C_{lk}$  using both proton transfer reaction mass spectrometry (PTRMS) and gas chromatography, and we measure aerosol volume using ion mobility with a scanning mobility particle sizer (SMPS). The volume is converted to a normalized mass ( $\Delta C_{OA}$ ) with a nominal density of 1 g cm<sup>-3</sup>; to indicate this we represent the normalized aerosol mass fraction as  $\xi$ . These normalized values can be converted easily to absolute masses after later experiments determine the SOA density.

There are numerous experimental details vital to obtaining accurate mass fractions, all of which have been described in a succession of papers treating our own experimental chamber.<sup>28,31,33,34</sup> The salient features are that we perform experiments in a cleaned 10 m<sup>3</sup> Teflon reactor enclosed in a temperature-controlled room and filled with dried, filtered air at relative humidities of 5–15%. Cleaning includes overnight purging with filtered 40 °C air containing >1 ppm ozone under UV illumination.

During these experiments, with ozone between 0.5 and 2 ppm, the limona ketone was completely removed (3 e-folds) in 3–15 min. Suspended particles are lost *via* deposition to the chamber walls with a timescale of ~2 hr. When the deposition timescale is sufficiently longer than the precursor oxidation timescale (as it is here), the suspended aerosol volume can be adjusted for wall losses with a simple first-order correction, which typically adds 10–20% to the maximum observed aerosol mass.<sup>33,35</sup> As with  $\alpha$ -pinene,<sup>33</sup> the SOA shows no sign of aging, instead settling down to a constant modal size after the aerosol growth period. Repeatability is of order ±10%, with an added absolute uncertainty of approximately ±0.01 µg m<sup>-3</sup>, while comparison with the literature suggests that an uncertainty of approximately ±15% is appropriate for similar experiments.

We routinely add 10 ppm of 2-butanol as an OH radical scavenger.<sup>33,36</sup> Ozone–alkene reactions are a source of OH radicals in the gas phase, and these OH radicals would otherwise react with the limona ketone and interfere with the target chemistry. Differences in SOA formation with

different scavengers have been observed, but for endocyclic alkenes such as limona ketone the primary effect appears to be associated with HO<sub>2</sub> production from the scavenger, with 2-butanol showing relatively high HO<sub>2</sub> formation (which is desirable).<sup>36</sup> We use 2-butanol for consistency in all of our experiments. Also, in roughly 2/3 of the experiments we use a small mass of ammonium sulfate seeds to promote condensation of organic vapors.<sup>30</sup> We see no systematic dependence on the presence of inorganic seed aerosol. In all other respects it is assumed that the target chemistry remains constant as we vary both limona ketone and ozone concentrations.

# 5. Results

The results of twelve individual experiments are reported in Table 1 and plotted in Fig. 2, showing the aerosol mass fraction,  $\xi'$ , versus the mass of aerosol produced,  $C_{OA}$ . This form of presentation was first proposed by Odum et al.<sup>12</sup> to emphasize how the partitioning of semi-volatile compounds depends on the total condensed-phase mass available for an ideal solution. This form also enables direct fitting under the volatility basis set.<sup>15,28</sup> For example, we see here that the condensed-phase products amount to around 5% by mass of the consumed limona ketone at 1  $\mu$ g m<sup>-3</sup> total aerosol concentration, but upwards of 20% by mass at 100  $\mu$ g m<sup>-3</sup>. The cumulative mass yield of products with saturation vapor pressures less than or equal to  $1 \ \mu g \ m^{-3}$  is thus no more than 0.1 or so, while the cumulative mass yield of products with saturation vapor pressures less than or equal to 100  $\mu$ g m<sup>-3</sup> is roughly 0.3. In fact, a basis-set fit to the data using the basis set shown in eqn (3)  $(0.01-1000 \ \mu g \ m^{-3})$  gives mass yields of

$$\alpha_i = \{0.004, \ 0.005, \ 0.08, \ 0.05, \ 0.09, \ 0.18\}$$
(6)

and indeed we see a cumulative yield of 0.09 at 1  $\mu$ g m<sup>-3</sup> and 0.23 at 100  $\mu$ g m<sup>-3</sup>. Details of the fitting procedure are described in Presto and Donahue.<sup>28</sup> A 63% confidence interval is shown with dashed lines in Fig. 2—it is meaningless to quote uncertainties for any single yield because of covariance amongst the fit parameters, but the overall confidence of the AMF values over the range covered by the data is of order 20%.

During one experiment with relatively low ozone concentrations (85 ppb) we measured limona ketone decay using the PTRMS, following 2.5 e-folds of log–linear decay over 400 s to

Table 1 Aerosol production results

$\chi_{lk}$ (ppb)	$\Delta C_{\rm lk}/\mu { m g}~{ m m}^2$	$^{-3} \Delta C_{\rm OA}/\mu {\rm g \ m}^{-3}$	<sup>3</sup> χ <sub>O3</sub> (p <sub>1</sub>	ob) <i>T</i> /°C	$C_{\rm seed}/\mu {\rm g}~{\rm m}^{-3}$
112.13	636.0	109.00	0.50	25	2.00
59.07	333.0	42.00	0.98	22	15.20
23.60	133.0	10.04	1.00	24	2.30
11.80	66.7	10.74	1.50	25	1.50
1.18	6.7	0.32	1.70	25	2.68
176.53	1000.0	168.90	1.50	25	2.18
142.00	800.0	184.50	1.50	25	2.94
35.50	200.0	52.49	0.70	24	2.00
35.50	200.0	63.04	0.83	24	0.00
35.50	200.0	61.29	1.20	24	0.00
35.50	200.0	58.62	0.85	23	0.00
124.00	700.0	130.42	0.91	24	0.00





**Fig. 2** Aerosol mass fractions  $\xi' = \Delta C_{OA}/\Delta C_{lk}$  for the limona ketone + ozone reaction, plotted *vs.* the organic aerosol mass concentration ( $C_{OA}$ ). SOA formation from limona ketone is similar to that from  $\alpha$ -pinene (lower dashed curve), but a factor of four less intense than from limonene (upper dashed curve).

give a second-order rate constant at 298K for the ozone + limona ketone reaction of  $2.7 \times 10^{-16}$  cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>, in good agreement with other compounds containing the 1-methylcyclohexenyl moiety.<sup>37</sup> There are numerous potential sources of systematic error in rate constant determinations based on slow decay in a smog chamber; our best estimate based on experience for alkenes with well-known rate constants is an accuracy of order 30%.

The bottom line for these experiments is that limona ketone behaves kinetically and mechanistically very much like  $\alpha$ -pinene, consistent with our hypothesis.

#### 6. Discussion

The most obvious feature of the data shown in Fig. 2 is the comparison with AMF values for limonene and  $\alpha$ -pinene shown as dashed curves. Limona ketone generates SOA with an efficiency that is statistically indistinguishable from  $\alpha$ -pinene (where  $\alpha_i = \{0.004, 0, 0.05, 0.09, 0.12, 0.18\}^{28}$ ), but is much lower than limonene.

We can draw two general conclusions from this. First, the common features for limona ketone and  $\alpha$ -pinene are consistent with a common mechanism for the endocyclic ozonolysis—this is presumably shared by the endocyclic double bond in limonene as well. Second, the greatly enhanced SOA formation for limonene indicates that additional oxidation of the *exo* double bond in limonene generates products with substantially reduced vapor pressures; this means that ketone production from *exo* ozonolysis is at best a minor pathway. We shall discuss these conclusions in turn.

#### Endo oxidation

There is every reason to believe that the basic mechanism for compounds with a 1-methylcyclohexenyl moiety does not change much with distant substitutions, including the 4–6 bridge of  $\alpha$ -pinene. A nominal mechanism is shown in Scheme 2.

This includes pathways 1a and 1b in Scheme 1 for limonene. The mechanism applies to gas-phase ozonolysis, where the CI is formed with an enormous amount of internal vibrational energy ( $\sim 200 \text{ kJ mol}^{-1}$ ).<sup>38</sup> This is a representative pathway for low-NO<sub>x</sub> conditions; we use it only to place a reasonable constraint on the expected product mass. For the sake of simplicity we show a single reaction pathway, with several steps subsumed in the second arrow including isomerization and prompt dissociation of the 'hot' CI, subsequent thermalization of the resulting organic radical followed by addition of molecular oxygen to form an organo-peroxy radical (RO<sub>2</sub>), and finally reaction of that RO<sub>2</sub> with HO<sub>2</sub> to form the peroxide shown.

The actual *endo* mechanism almost certainly involves many reaction products—the wide range in  $C^*$  values needed for the basis-set fit suggest this, and several analytical studies on terpene oxidation products confirm it.<sup>39–41</sup> This general pathway is also consistent with the large observed OH yields from cyclohexene,  $\alpha$ -pinene and limonene.<sup>42,43</sup> However, the details of the gas-phase mechanism remain uncertain; this is one of several reasons why we use the volatility basis-set formalism in order to represent the vapor-pressure distribution in spite of ill-defined reaction products.

Finally, group additivity relationships developed to describe vapor-pressure changes with substitution suggest that replacing the vinyl  $CH_2$  in limonene with a carbonyl in limona ketone should have at most a modest influence on the vapor pressure.<sup>22</sup> All of the available indicators thus suggest a similar vapor-pressure distribution for the ozonolysis products of limona ketone and  $\alpha$ -pinene, as well as many  $C_{10}$  compounds containing a 1-methyl-cyclohexene moiety. This is consistent with our observations.

#### Exo oxidation

The second issue is the branching of the reaction between ozone and the *exo* double bond (pathway 2a *vs.* 2b in Scheme 1). If the reaction occurs in the gas phase, this branching ratio should not depend strongly on whether pathway 1 or pathway 2 occurs first. In fact,  $k_1 \simeq 30 k_2^{31}$  so pathway 1 predominates in limonene ozonolysis. However, we



Scheme 2 Endocyclic gas-phase mechanisms without  $NO_x$ .

can use limona ketone ozonolysis as a surrogate to probe half of the possible second-generation products following pathway 1a and 1b (in essence simply substituting the terminal  $CH_2$  with an O).

Because ozonolysis of limonene yields significantly lessvolatile products than either limona ketone or  $\alpha$ -pinene, we can quickly conclude that limona ketone itself is a minor product in limonene ozonolysis.

We can develop stronger constraints with a mass balance. There is strong evidence that for SOA from limonene ozonolysis (at low NO<sub>x</sub>), both double bonds have been oxidized.<sup>29</sup> Our basis-set fits from limona ketone and limonene reveal the mass in each volatility bin in each case. For example, the mass yields of products from complete limonene oxidation (plotted as a dashed grey line in Fig. 2) are  $\alpha_i^{\text{Lim}} = \{0, 0.03, 0.29, 0.31, 0.30, 0.60\},^{29}$  so  $\alpha^{\text{Lim}} = \sum_i \alpha_i^{\text{Lim}} = 1.53$ . This is broadly consistent with complete oxidation of C<sub>10</sub> limonene leading to a C<sub>9</sub>O<sub>7</sub> product ( $\alpha^{\text{Lim}} \simeq 1.65$  for all products containing more than 1 carbon) where almost all of this mass is accounted for at  $C^* \leq 1000 \,\mu\text{g m}^{-3}$ .

If the ozonolysis of limonene consists of pathway 1 and pathway 2 in Scheme 1 in succession, if the branching ratio of each pathway does not depend on the order, and if the reactions occur in the gas phase, we can use the limona ketone to close the mass balance. Specifically, we shall assume that the volatility distribution of the ultimate products does not depend on whether the *endo* or *exo* double bond is oxidized first. Furthermore, because the *endo* ozonolysis products are tethered, we shall assume that the ultimate volatility distribution is determined by the products of pathway 2 in Scheme 1.

Products from pathway 2a we label  $\alpha^{\text{LCI}}$  and products from pathway 2b we label  $\alpha^{\text{LK}}$ . From our fit to the limona ketone data,  $\alpha^{\text{LK}} = 0.41$  for  $C^* \leq 1000 \ \text{\mu g} \ \text{m}^{-3}$ , with a 'nominal product' formula (neglecting H) of C<sub>9</sub>O<sub>5</sub>. The branching ratio toward pathway 2a is  $\beta$ . In general, branched terminal alkenes have been observed to slightly favor the more substituted carbonyl oxide ( $\alpha^{\text{LCI}}$ ), with  $\beta \simeq 0.65$ –0.80.<sup>44,45</sup>

With our mass-balance constraints, the total mass yield from limonene ozonolysis ( $\alpha^{Lim}$ ) is

$$\alpha^{\text{Lim}} = \beta \alpha^{\text{LCI}} + (1 - \beta) \alpha^{\text{LK}}$$
(7)

where  $\alpha^{\text{LCI}}$  and  $\beta$  are the unknowns. Eqn (6) can be trivially solved for  $\alpha^{\text{LCI}}$  as a function of  $\beta$ 

$$\alpha^{\rm LCI} = \frac{1}{\beta} \alpha^{\rm Lim} - \frac{1-\beta}{\beta} \alpha^{\rm LK} \tag{8}$$

so the observed SOA from limonene could be explained by a number of different combinations of  $\alpha^{\text{LCI}}$  and  $\beta$ , as shown in Fig. 3. However, it is difficult to imagine a mass yield ratio much greater than 1.7—a C<sub>9</sub> O : C of nearly 1 : 1, meaning that  $\beta \ge 0.85$ .

One other significant possibility exists—we have shown that the *exo* double bond in limonene is oxidized by rapid heterogeneous uptake of ozone onto fresh, unsaturated SOA particles, at least under low- $NO_x$  conditions such as those employed in this study.<sup>31</sup> In a solution where essentially all of the organic compounds contain at least one carbonyl moiety (the fresh SOA), it is very likely that any CH<sub>2</sub>OO produced following condensed-phase ozonolysis of a terminal



Fig. 3 Constraints on the limona ketone formation branching ratio from ozonolysis of the *exo* double bond in limonene ( $\beta = 1$  is complete branching toward the carbonyl oxide on the limonene residue).

double bond would lead to rapid secondary ozonide formation. The end result might be a  $C_{10}O_7$  substituted secondary ozonide, rather than limona ketone products. This would have a similar mass to our 'nominal product' as well as a very low vapor pressure.

In the end we can determine what fraction of the *exo* double bond does *not* resemble limona ketone oxidation, either because the primary ozonide of the terminal double bond favors pathway 2a, or because any  $CH_2OO$  is scavenged within the aerosol to form a secondary ozonide. In all likelihood a combination of these factors is responsible for what we observe. Either way, there is very little gas-phase production of ketones from the terminal double bond in limonene ozonolysis.

# 7. Conclusions

The work presented here establishes constraints on the branching of the second oxidation step in limonene ozonolysis. This is one piece of a challenging analytical problem convolving the difficulties of sampling and measuring very low levels of products ( $<10 \ \mu g \ m^{-3}$ ) with the complex and poorly constrained gas-phase Criegee mechanism. The findings lead to two important insights into the oxidation behavior of terpenes. First, the volatility distributions following oxidation of similar precursors are likewise similar. Specifically in this case, limona ketone and  $\alpha$ -pinene share a 1-methylcyclohexene functionality and their ozonolysis products show very similar aerosol volatility distributions. Second, multiple oxidiation steps of poly-unsaturated terpenes can generate high yields of very low vapor pressure products. This is not prima facie obvious, as complete oxidation will ultimately lead to volatile CO2.16

Two possibilities remain viable. First, the regio chemistry of the large terminal alkenes in the gas phase may favor leaving the Criegee moiety on the larger, more substituted fragment. This would also explain, for example, why ozonolysis of  $\beta$ -pinene gives only slightly less SOA than  $\alpha$ -pinene. Alternately,

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if the terminal double bond is in fact oxidized in the condensed phase the ketone could still be an important intermediate product, only to be lost to SOZ formation. These are not exclusive; what we know with certainty is that ketone production is very small.

This work represents a step toward solution of the 'generation problem'<sup>16</sup> in atmospheric organic aerosol chemistry. The problem is how to represent the complex, multi-generation chemistry associated with the complex mixture that comprises atmospheric organic aerosols. This work reveals clearly that ozonolysis, at least, can lead to highly oxidized products from terpenes with a large carbon number and an O : C ratio approaching unity, and that the effect of the oxidation chemistry on similar precursors shares common features. The next question is whether continued oxidation of these products (presumably by OH radical attack) will continue to reduce the vapor pressures of the products, or whether fragmentation will drive the vapor pressures back up as the products head toward complete oxidation.

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