Pinic and pinonic acid formation in the reaction of ozone with α-pinene

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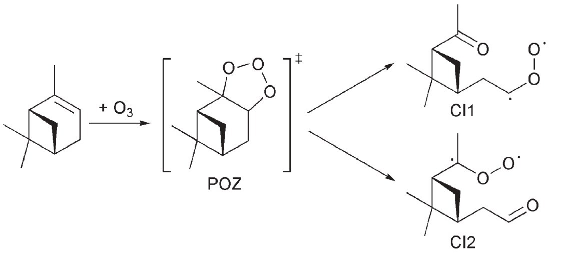
The mechanism of formation of key compounds in atmospheric secondary aerosol (SOA) has been investigated by studying the products of the ozonolysis of an enal derived from α-pinene using gas chromatography coupled to mass spectrometry.

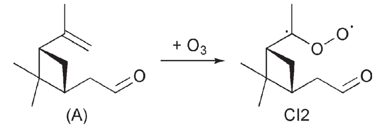
Secondary organic aerosol (SOA) is an important component of Earth's atmosphere for a variety of reasons. It is the primary manifestation of photochemical smog, impacting on urban visibility;[1] particles are easily inhaled, inducing various health problems;[2,3] they can impact on the atmospheric radiation budget directly and indirectly by acting as cloud condensation nuclei;[4–6] and they may act as surfaces catalysing heterogeneous reactions in the atmosphere.[7] The atmospheric oxidation of both large and small volatile organic compounds (VOCs) is an important source of SOA, and available evidence indicates that initiation by ozonolysis is often more effective in this respect than initiation by OH or NO_3 reactions.[8,9] Of the biogenic C_{10} VOCs (terpenes), α-pinene is by far the most commonly emitted.[10] Thus, the ozonolysis of α-pinene is a key process in the formation of SOA and understanding the reaction mechanism is an essential part of understanding atmospheric SOA formation.

Various multifunctional oxygenated species have been detected in SOA, and products with acid functionalities feature highly.[11–19] Christoffersen *et al.* were the first to suggest that pinic acid could be the compound leading to aerosol nucleation.[11] However, while there have been a number of suggested mechanisms for the formation of such products in α-pinene ozonolysis, properly validating the mechanisms is very difficult. A particular difficulty is that the first step in the reaction can occur in two ways, to give two Criegee intermediates (CI), as illustrated in Scheme 1.

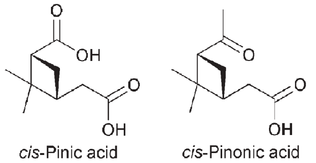
The two CIs, CI1 and CI2, have never been isolated and so there is a problem deciding which of these two intermediates gives rise to the various products that have been observed. In order to overcome this problem, we have synthesised an enal (A) derived from α-pinene[20] that can only give rise to CI2 when ozonised; see Scheme 2. An investigation of the products of ozonolysis of this compound compared with products obtained from the ozonolysis of α-pinene can then identify which of the CIs generates which products. A wide range of acidic products were observed in the ozonolyses, and will be reported fully elsewhere. For the purposes of this communication, we focus on *cis*-pinic and *cis*-pinonic acids, which have been identified in SOA, are the major acidic products and were the main thrust of our original investigation.



Scheme 1



Scheme 2



Ozonolysis experiments were carried out at atmospheric pressure (synthetic air) at a temperature of 295 ± 4 K in an 80 L collapsible Teflon chamber. Concentrations of the unsaturated compounds were on the order of 15–20 ppmv, with ozone concentrations being typically 5 ppmv less in order to limit secondary reactions. Experiments were carried out in the presence of *ca.* 3000–4000 ppmv cyclohexane in order to scavenge any OH radicals (>95%) formed in the reactions. Ozone was generated using a Fischer (Model 502) ozoniser, and was trapped onto silica gel at 225 K, before being desorbed into a Pyrex bulb. Its purity was checked by measuring its ultraviolet absorption at 254 nm. Reagents were added to the Teflon chamber by flushing with synthetic air from a vacuum line. The air used could be admitted dry or wet by passing through a series of bubblers; by varying the fraction of dry to wet air it was possible to control the relative humidity of the reaction mixture. Reaction was allowed to occur long enough that it was estimated to be more than 95% complete, but not so long that subsequent slower heterogeneous processes could significantly affect the results. A variety of diagnostic experiments on the ozone–cyclohexene and ozone–α-pinene systems were carried out before the main study; these included looking at the time dependence of product yields, measuring products on the walls of glass vessels and varying the surface-to-volume ratio of the reaction vessel. These experiments showed that we were observing products formed as a result of gas-phase

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reactions, and that the yields were not significantly influenced by wall losses on the timescale that the experiments were performed. Acid products were trapped onto a PTFE membrane filter (Schleicher and Schuell TE 36, 0.45 μm pore size) by pumping product mixtures through the filter. The filter was then methylated using 14% BF_3–methanol to generate the methyl esters of the acids, which were extracted with hexane and then separated using gas chromatography (ThermoFinnigan, Trace GC) and detected using quadrupole mass spectrometry (ThermoFinnigan, Trace MS). *cis*-Pinic acid and *cis*-pinonic acid were identified as methyl esters by comparison of the GC retention times and mass spectra with those of the methylated authentic standards. Quantification was performed using the calibration of the relevant standards by GC-MS. Under dry conditions and in the presence of cyclohexane as OH scavenger, yields of pinic acid and pinonic acid are measured to be 2.85 ± 0.31% and 1.86 ± 0.31% respectively, in the range of the results from other studies.[12,13,15,19]

Illustrated in Fig. 1 are plots of pinic acid and pinonic acid yields as a function of relative humidity in the presence and absence of acetic acid.

In the absence of acetic acid, pinonic acid shows a fairly strong dependence on RH, while pinic acid shows a much weaker dependence. This is consistent with the suggestion that water catalyses the rearrangement of CIs to acid functionalities, probably *via* a hydroxyalkylhydroperoxide.[21–24] No such mechanism is expected for the formation of pinic acid. However, pinonic acid also has a significant source that is not dependent on RH. One possible explanation is that the acid is formed in the well-known ester channel,[25] and we shall return to this point later.

In the presence of acetic acid—a well known SCI scavenger—the dependence of the pinonic acid yield on RH has been removed, consistent with acetic acid competing more effectively for CI than water.[26]

Fig. 2 illustrates similar results to Fig. 1, except that these are for the ozonolysis of the enal illustrated in Scheme 2 rather than α-pinene. The first thing to note is that the yields of pinic acid are similar to those for α-pinene ozonolysis and in both cases are—at most—mildly affected by the presence of water vapour or acetic acid. This is entirely consistent with the generally held view that this acid species is generated *via* the decomposition of CI2.[13,19,23] However, these experiments are the first to show conclusively that pinic acid is generated predominantly through CI2. The pinonic acid experiments are also interesting. Three sets of experiments give very similar results (α-pinene in the presence of acetic acid; enal in the presence of acetic acid; and enal in the absence of acetic acid), while one set (α-pinene in the absence of acetic acid) is very different. What these experiments show is that there are two routes to pinonic acid. Water can react with CI1 to generate pinonic acid in a route that is fairly well known in ozone chemistry. However, in addition there is a further route that occurs *via* CI2 and does not involve reaction with water. Thus it can be concluded that the ester channel illustrated in Scheme 3 is not a major source of pinonic acid.

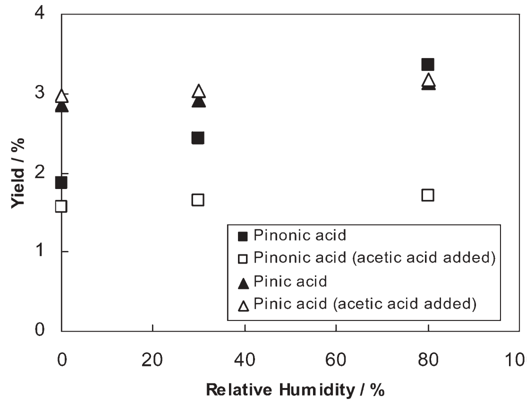


Fig. 1 Acid yields from the ozonolysis of α-pinene under various conditions.

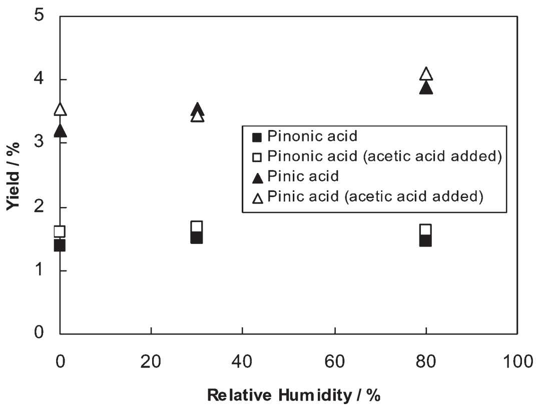
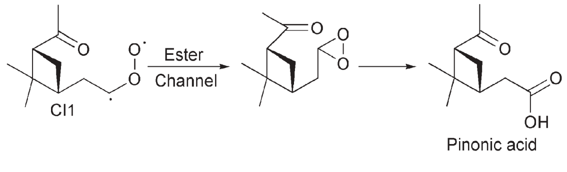


Fig. 2 Acid yields from the ozonolysis of the enal under various conditions.

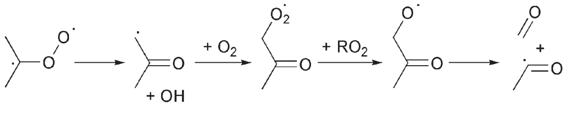
A number of comments can be made about the mechanism for this channel. It is generally believed that doubly alkyl-substituted CIs decompose with high efficiency to give the OH radical and a co-radical, which is then converted to the peroxy then alkoxy radical followed by carbon–carbon bond fission, as illustrated for the dimethyl CI (Scheme 4).

Pinonic acid cannot be generated *via* this (or part of this) process; addition of O_2 to the initially formed radical introduces functionality at two carbon centres, while carbon fission reduces the number of carbon atoms in the product molecule. A possible route to pinonic acid is that a small fraction of CI2 isomerises (possibly *via* an alkyl-bisoxy radical intermediate), abstracts the aldehydic hydrogen from the other end of the molecule, releases OH and then leads to the acid as shown in Scheme 5.

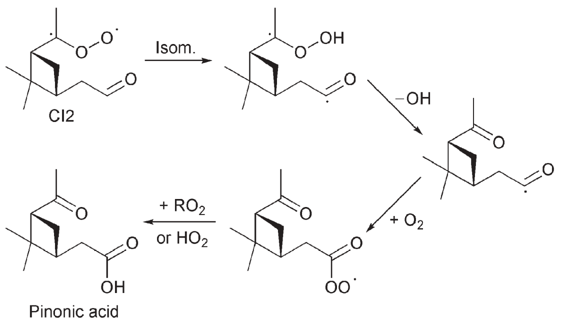
The first isomerisation step in this scheme has not previously been suggested, but is similar to those postulated to explain pinic



Scheme 3



Scheme 4



Scheme 5

acid formation from α-pinene[23] and the proposed reaction step for the CI formed in cyclohexene ozonolysis.[27,28] Furthermore, some kind of rearrangement of this type is required in order that the acid moiety can be generated at the opposite end of CI2 from the original CI centre. The other steps in this mechanism are consistent with known chemistry.

In summary, we have provided, for the first time, conclusive evidence that pinic acid is formed *via* CI2 in the ozonolysis of α-pinene; this observation is consistent with inferences from previous studies. On the other hand, we have shown that pinonic acid is formed *via* both CI1 and CI2. Formation *via* CI1 is RH-dependent and our observations are consistent with previous studies that suggest monosubstituted CIs can react with water to give organic acids. Formation *via* CI2 is unexpected and is not dependent on RH; a plausible mechanism for formation of pinonic acid *via* this route is proposed. The results are important for atmospheric chemistry because they provide mechanistic information that can be used in detailed models such as the Master Chemical Mechanism. It is worth noting that the concentration of reactants used here is very much greater than those observed in the atmosphere—as is the case in the majority of laboratory studies. Nevertheless, the results are applicable under conditions where the fate of peroxy radicals is reaction with RO_2 or HO_2 rather than NO; *i.e.* the results apply to the chemistry of the rural, unpolluted atmosphere.

In addition to the acids described here, information was also obtained about a range of other products, including norpinic acid, norpinonic acid, pinalic acid, norpinalic acid, OH-pinonic acid, OH-pinalic acid, pinonaldehyde and norpinonaldehyde. Further information was obtained on the mechanisms of formation of pinic acid and the other compounds through examining the dependence of product yields on a variety of conditions. Results from these studies will be published elsewhere.

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