Organic acid formation in the gas-phase ozonolysis of α-pinene

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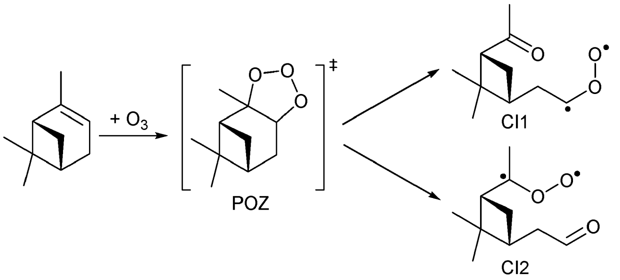
The mechanism of formation of pinonic and norpinonic acids from α-pinene ozonolysis has been investigated by studying the products of the ozonolysis of an enone derived from α-pinene using gas chromatography coupled to mass spectrometry.

In recent decades, there has been growing interest in the formation of secondary organic aerosols (SOA) in the atmosphere for reasons that have both local and global significance. SOA is the primary cause of photochemical smog, leading to a reduction in visibility;[1] particles can absorb or scatter solar radiation, serve as cloud condensation nuclei, hence directly or indirectly impacting on the Earth's radiation budget;[2–4] and they may be involved in heterogeneous chemistry in the atmosphere;[5] furthermore, the fine particles are likely to have severe health implications when inhaled.[6,7] The atmospheric oxidation of α-pinene is known to form low-volatility products which can be incorporated into SOA, and available evidence indicates that initiation by ozonolysis is the most efficient in this respect, while initiation by OH or NO_3 play relatively more minor roles.[8,9] Thus, a detailed understanding of the gas-phase ozonolysis of α-pinene, especially with regard to the generation of condensable species, is crucial in order to better understand atmospheric SOA formation.

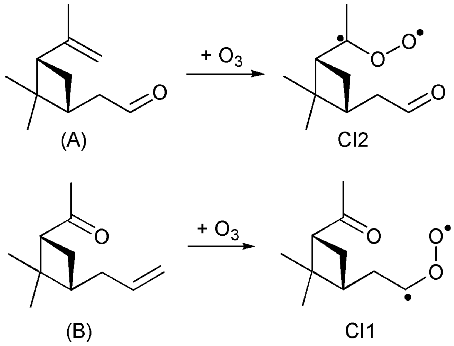
Various multifunctional oxygenated species have been detected in SOA, and products with acid functionalities feature highly.[10–18] The higher molecular weight organic acids, such as pinic acid and pinonic acid from α-pinene oxidation, have been suggested to be key compounds in aerosol creation,[10,12,19] and some have been detected in atmospheric aerosols.[20–24] A number of gas-phase mechanisms have so far been suggested for the formation of such products in α-pinene ozonolysis; however, to validate properly these mechanisms still remains a challenge. A particular difficulty is that the first step of the reaction gives two Criegee intermediates (CIs), as illustrated in Scheme 1.



Scheme 1

Both CIs can go on to decompose and/or react with other molecules, producing a variety of products. CI1 and CI2 have never been isolated and so it is difficult to determine which of these two intermediates generates which of the products that have been observed. One solution to this problem is to react ozone with compounds which are "cleaner" sources of either one or other of the two CIs: enal (A) and enone (B). As illustrated in Scheme 2, the enal only gives rise to the disubstituted CI2 when ozonised, while the enone only gives the monosubstituted CI1. An investigation of the products of the ozonolysis of these two compounds compared with products observed from α-pinene ozonolysis can then help to identify which of the CIs generates which products. We have previously reported the results of ozonolysis experiments on the enal (which was synthesised from α-pinene) with focus on the formation of *cis*-pinic acid and *cis*-pinonic acid, the two major acidic products in α-pinene ozonolysis.[25] Subsequent to publication of this earlier work, we have now successfully synthesised the enone, again starting from α-pinene;[26] a product study of its reaction with ozone was carried out which complements our previous results obtained from the enal experiments and gives an overall picture of the mechanism of formation of key acid products in the ozonolysis of α-pinene.

The procedure for the gas-phase ozonolysis experiments was described in our earlier paper. Briefly, experiments were carried out at atmospheric pressure (760 ± 10 Torr, 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



Scheme 2

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typically 5 ppmv less, in order to minimise secondary ozone reactions. 3000–4000 ppmv of cyclohexane was added to scavenge the $>95\%$ of any OH radicals formed in the reactions. Ozone was generated by passing oxygen through a Fischer ozone generator, its concentration being determined spectrophotometrically using its well-characterised absorption at λ = 254 nm. All reagents were added to the Teflon chamber by flushing with synthetic air from a vacuum line. Water vapor was introduced by passing the synthetic air through a series of bubblers containing deionized water. The reaction was started by adding ozone to the chamber, and allowed to occur long enough that it was simulated 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 carried out on the ozone–cyclohexene and ozone–α-pinene systems have shown that we were observing products formed as a result of gas-phase reactions, and that the yields were not significantly influenced by wall losses on the timescale that the experiments were performed. Reaction products were trapped onto a PTFE membrane filter (Schleicher and Schuell TE 36, 0.45 μm pore size) by pumping reactant–product mixtures through the filter. The filter sample was immediately 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 by quadrupole mass spectrometry (ThermoFinnigan, Trace MS).

Our previous results showed that pinic acid and pinonic acid are generated from the ozonolysis of α-pinene and the enal, indicating that both these acids can be formed from CI2.[25] Results from the enal experiments also indicated that CI1 should contribute to pinonic acid formation. By comparison of the GC retention time and mass spectrum with those of the methylated authentic standard, it was confirmed in the present study that no pinic acid is formed from enone ozonolysis in the presence or absence of water vapour. This provides conclusive evidence that pinic acid is generated exclusively from CI2 and not from CI1 in the ozonolysis of α-pinene, consistent with our recent results[25] and inferences from previous studes.[12,18,19] *cis*-Pinonic acid was positively identified in the collected enone ozonolysis products as its methyl ester, confirming that pinonic acid can be generated from CI1.[25] Its formation yield was quantified using the calibration of the methylated standard by GC-MS. Under dry conditions, the measured yield of pinonic acid from the enone was 0.18%, which rose to 1.36% at 80% RH. Fig. 1 illustrates the yields of pinonic acid from enone ozonolysis at different relative humidities (RH), together with results from our previous studies of the ozonolysis of α-pinene and the enal. In addition, the sum of the yields from the enal and enone experiments are also shown.

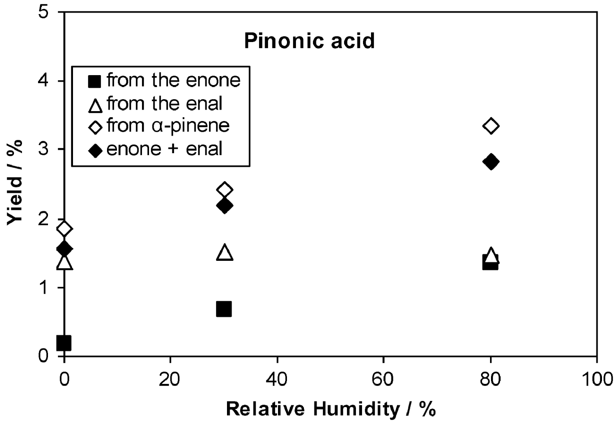
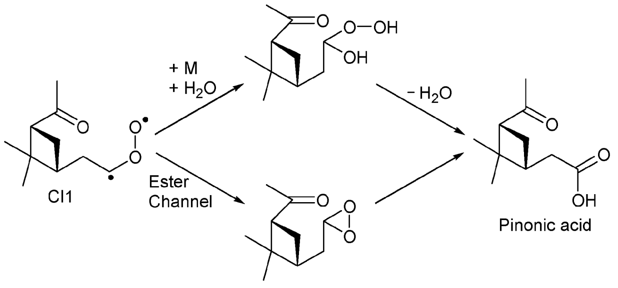


Fig. 1 Pinonic acid yields from the ozonolysis of the enone precursor, the enal precursor and α-pinene at different relative humidities.

The pinonic acid yield from the enone–O_3 reaction shows a clear dependence on RH, which is very similar to that observed previously for α-pinene ozonolysis. This strongly supports the suggestion that water can react with CI1 to generate pinonic acid, probably *via* a hydroxyalkylhydroperoxide intermediate as illustrated in Scheme 3.[19,27–29] It is also noted that a small amount of pinonic acid was observed from the ozonolysis of the enone in the absence of water vapour, indicating that there is an additional route *via* CI1 that does not involve reaction with water. One possible explanation is that the acid is formed from the rearrangement of CI1 through the well-known ester channel,[30] as also shown in Scheme 3. Combining the observations on pinonic acid formation from α-pinene, the enal and the enone, it can be concluded that the RH-dependent formation of pinonic acid in the α-pinene ozonolysis is due to CI1, while the RH-independent formation is mainly due to CI2, and in a small fraction to CI1.

In addition to pinonic acid, norpinonic acid was tentatively identified as its methyl ester in the ozonolysis of the enone. The assignment was made on the basis of an observed electron impact (70 eV) mass spectrum identical to that reported by Koch *et al.*[12] for this compound. Due to the lack of authentic standard, norpinonic acid was semi-quantified using pinonic acid as the surrogate. Norpinonic acid was also observed from the ozonolysis of α-pinene, but not from the ozonolysis of the enal. These findings show clearly that its route of formation is *via* CI1. Yields of norpinonic acid from the enone compared with those from α-pinene are depicted in Fig. 2 as a function of relative humidity.

The yields observed for norpinonic acid from the ozonolysis of α-pinene and the enone are indistinguishable. This observation is interesting in terms of what it tells us about the yields of CI1 in the two sets of experiments. Generally, ozonolysis leads to higher yields of the more substituted CI (Jenkin *et al.*[19] propose a 40 : 60 ratio for the yield of CI1 to CI2). For α-pinene, CI1 is the less substituted CI, while for the enone, it is the more substituted (the other CI being CH_2OO); *i.e.* a higher yield of norpinonic acid is expected for the enone



Scheme 3

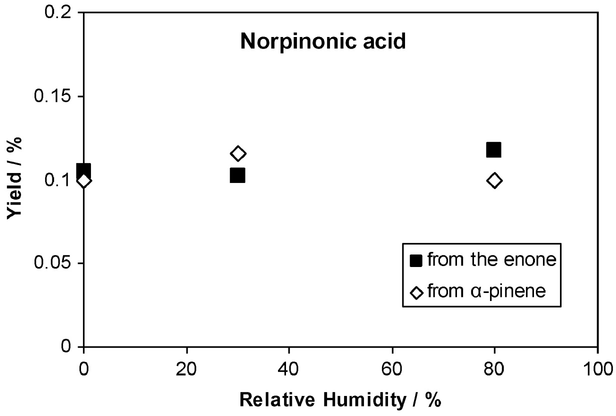
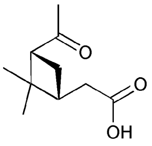


Fig. 2 Norpinonic acid yields from the ozonolysis of the enone precursor and α-pinene at different relative humidities.

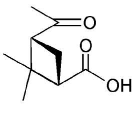
experiments. The most likely explanation is that the branching ratio for CI1 in both systems is close to 0.5. Indeed, there is evidence that for double bonds attached to long chains, there is little differentiation in yield between the two possible CIs.[31] A recent theoretical study in our laboratory suggests that ozonolysis of α-pinene results in equal yields of CI1 and CI2.[32] Assuming that CI1 and CI2 are formed with equal yields from α-pinene, the enal and the enone, allows the pinonic acid yields from α-pinene to be compared with the sum of those from the enal and the enone. Fig. 1 shows that there is reasonable agreement (within 20%) between the two.

It is also worth noting that in both systems, the norpinonic acid yield shows no clear dependence on the water vapour concentration. This would suggest that the pathway leading to its formation does not involve the interaction of CI with water; thus a possible formation mechanism is through the radical mediated decomposition of CI1. However, to date, no plausible mechanism has been proposed to explain the direct formation of norpinonic acid in the gas-phase ozonolysis of α-pinene.

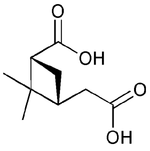
Based on the mass spectra and GC retention time information, a range of other organic acids, including pinalic acid, norpinic acid, norpinalic acid, OH-pinonic acid and OH-pinalic acid, were tentatively identified from the ozonolysis of α-pinene and the enal, but none of these were observed from the ozonolysis of the enone. This gives evidence that all of these acids are generated exclusively from CI2 during α-pinene ozonolysis. A systematic study of the detailed mechanisms of formation of pinic acid, norpinonic acid and other acids is underway and will be reported fully elsewhere.



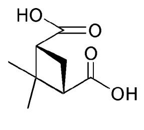
Pinonic acid



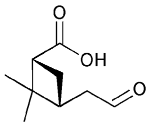
Norpinonic acid



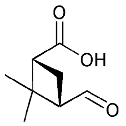
Pinic acid



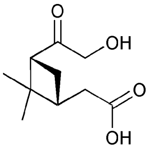
Norpinic acid



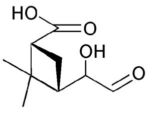
Pinalic acid



Norpinalic acid



OH-pinonic acid



OH-pinalic acid

In summary, the results presented here show conclusively, for the first time, that pinonic acid and norpinonic acid are formed in the ozonolysis of α-pinene *via* CI1. For pinonic acid, there is a channel with a strong dependence on RH, and a minor source that is independent of RH; from our previous experiments, we know that there is also a more important RH-independent channel *via* CI2. For norpinonic acid, the only channel is *via* CI1, and the close agreement between yields from α-pinene and the enone strongly suggests that the branching ratio for CI1 from both compounds is 0.5.

The results of the experiments described here and in our previous paper have significantly improved our understanding of the mechanism of the early stages of the ozonolysis of α-pinene and can be used in detailed atmospheric chemistry models such as the Master Chemical Mechanism.[33] In addition, the experimental approach of generating and studying the Criegee intermediates individually in separate experiments is clearly very useful for understanding alkene ozonolysis mechanisms. It is worth noting that the concentration of reactants used here is very much greater than those encountered in the atmosphere—as is the case in the majority of laboratory studies. Nevertheless, the results are applicable to conditions where the fate of peroxy radicals is to react with RO_2 or HO_2, rather than NO_x; *i.e.* the results apply to the chemistry of the rural, unpolluted atmosphere.

Acknowledgements

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