



Mechanisms for the formation of secondary organic aerosol components in the reaction of ozone with α -pinene

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The gas-phase mechanism of formation of a number of organic acids in the ozonolysis of α -pinene has been investigated using a static reaction chamber coupled to gas chromatography with mass spectrometry.

Secondary organic aerosol (SOA) is an important component of Earth's atmosphere for a variety of reasons. Formation of SOA follows the oxidation of large volatile organic compounds (VOCs), and available evidence indicates that initiation by ozonolysis is often more effective in this respect than initiation by OH or NO₃ reactions. Of the biogenic C₁₀ VOCs (terpenes), α -pinene is by far the most commonly emitted. 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. Pinic Acid for example has been proposed as a key nucleating species in SOA formation.¹ 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 different Criegee intermediates (CI). We have been able to overcome this difficulty by synthesising an enal derivative of α -pinene that only generates one of the CIs on ozonolysis.² In this way, we have been able to show which of the CIs generates pinic acid, confirming what has already been suggested.³ However, for pinonic acid, we find that there are two quite separate mechanisms for its formation — one dependent on relative humidity, the other not — each involving one of the CIs. By careful

choice of OH scavengers and other reagents in the ozonolysis of α -pinene and the enal derivative, we have been able to infer additional information about the yields and mechanisms of formation of pinic acid, pinonic acid, norpinic acid, norpinonic acid, pinalic acid, norpinalic acid, OH-pinonic acid, OH-pinalic acid, pinonaldehyde and norpinonaldehyde in these systems.⁴ We are able to construct mechanisms of formation of these compounds that are consistent with observations and are based — for the most part — on known chemistry. These mechanisms can be used to aid models such as the Master Chemical Mechanism.

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2. Y. Ma, T.J. Wilcox, A.T. Russell and G. Marston, 'Pinic and pinonic acid formation in the reaction of ozone with α -pinene.' *Chem. Comm.*, accepted for publication.
3. M. E. Jenkin, D. E. Shallcross and J. N. Harvey, *Atmos. Environ.*, 2000, **34**, 2837.
4. Y. Ma and G. Marston 'Multifunctional acid formation from the gas-phase ozonolysis of α -pinene', manuscript in preparation.