

SOA Formation from Acid Catalysed Rearrangement Reactions

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INTRODUCTION

The influence of acidic seed particle on SOA formation has been received a significant attention in the past decade since Jang et al. (2002) have presented evidence for multifold increases in SOA formation through acid catalysed particle phase reaction. The enhanced SOA formation is attributed to the formation of accretion compounds from acid catalysed reaction of carbonyl compounds, peroxy compounds, or the formation of organosulphates from alcohols and epoxides.

Reactive uptake of gas-phase semi-volatile organic compounds has been reported to be an important pathway leading to the formation of organosulfates, and enhanced SOA formation (e.g. Iinuma et al., 2009; Surratt et al., 2010), though it does not explain increases in SOA production for some of VOC oxidation experiments in which no organosulphate formation is observed (e.g. α -pinene ozonolysis). In this study, we present a formation of highly reactive VOCs from acid catalysed multiphase reactions of monoterpene oxides. Subsequent oxidation of the highly reactive VOCs forms significantly more SOA than the precursor VOCs. The process involves both gas- and particle- phase reactions and likely plays a role in SOA formation in the ambient atmosphere.

EXPERIMENTAL

Table 1 summarises experimental conditions used in the present study. Resulting SOA was sampled with Teflon coated borosilicate filters for subsequent UPLC/ESI-TOFMS analysis (Ultra Performance Liquid Chromatography coupled with Electrospray Ionisation Time-of-Flight Mass Spectrometry). SOA formation was monitored using a DMPS system (Differential Mobility Particle Sizer) during the course of chamber experiments.

Table 1. Chamber experiment conditions used in this study.

	α -Pinene oxide	β -Pinene oxide
Initial HC Conc. [ppbv]	100	100
Initial Ozone [ppbv]	0, 60	0, 60
RH%	50	50
Temp [°C]	20	20
Reaction Time [h]	~ 3	~ 3
Sampling [h]	1 (1.8 m ³)	1 (1.8 m ³)
Seed Particle	pH 0, 7	pH 0, 7

SOA FORMATION

Figures 1A and 1B show the SOA mass increases as a function of experimental time for α -pinene oxide and β -pinene oxide, respectively. For both VOCs, almost no SOA mass increase was observed in the case of neutral seed aerosol experiments regardless of the ozone concentrations. On the other hand, significant increases in the SOA mass were observed for both VOCs in the presence of acidic seed aerosol and ozone. In the case of β -pinene oxide, acidic seed aerosol is sufficient to promote significant SOA formation from a reactive uptake process that forms organosulfates (Iinuma et al., 2009).

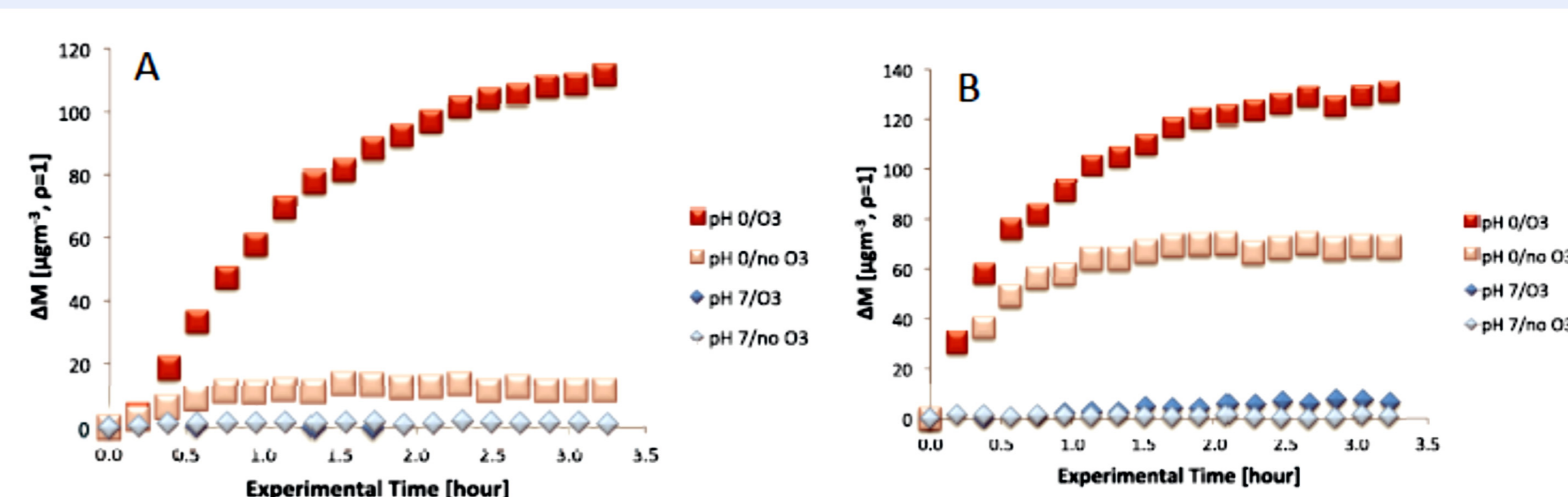


Figure 1. SOA mass increase as a function of experimental time for (A) α -pinene oxide and (B) β -pinene oxide.

O₃ CONSUMPTION

Figures 2A and 2B show the changes in O₃ mixing ratios as a function of experimental time. Higher O₃ consumption was observed in the presence of acidic seed particles for both α -pinene oxide and β -pinene oxide, indicating the formation of reactive VOC species in the presence of acidic particles. These are consistent with the SOA mass increases shown in Figures 1A and 1B.

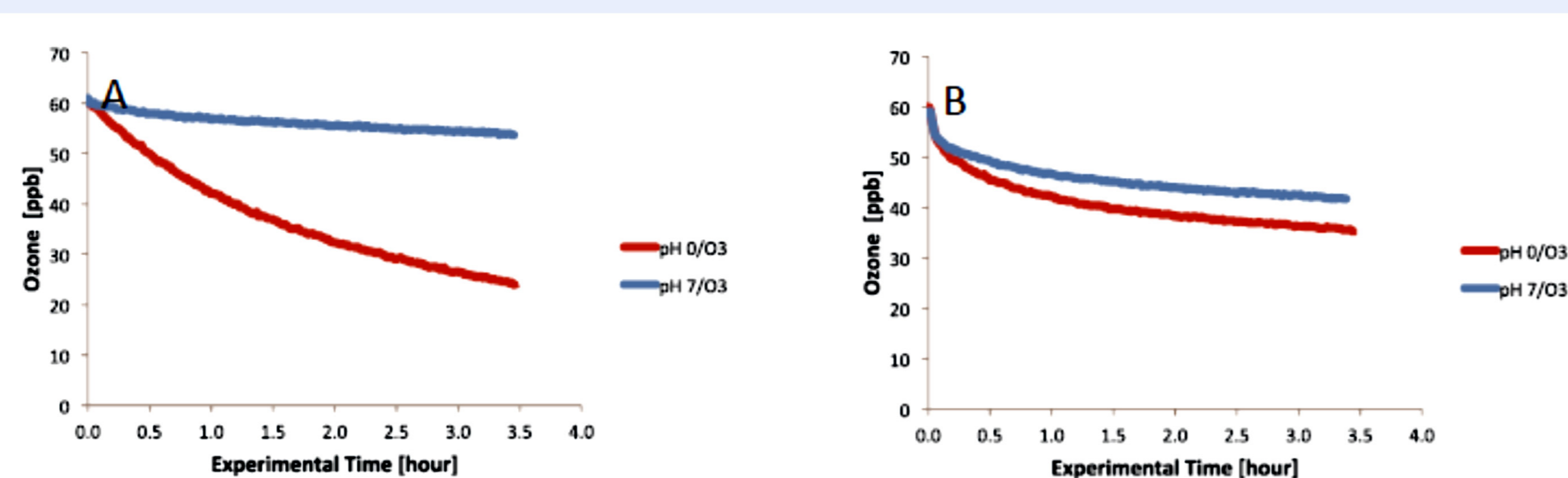
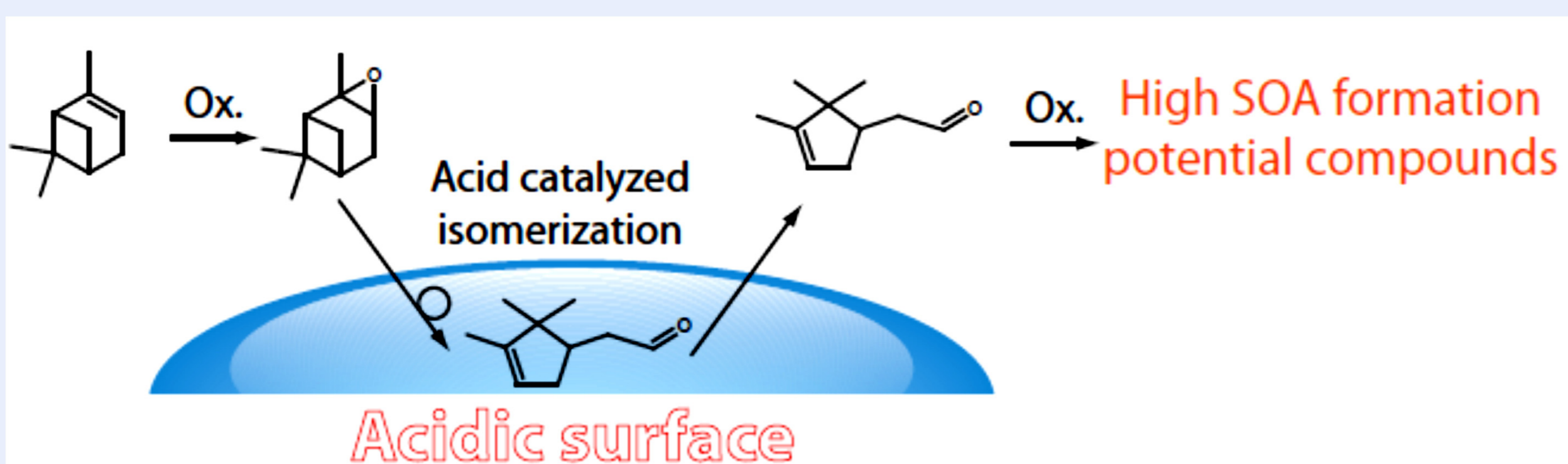


Figure 2. O₃ consumption as a function of experimental time for (A) α -pinene oxide/O₃ and (B) β -pinene oxide/O₃.

SUMMARY

- Pinene oxides readily isomerise on the acidic surface.
- An isomerisation product reacts rapidly with O₃, leading to low volatile SOA compounds.
- This mechanism partly explains the increased SOA formation in the presence of acidic particles.



VOC AND SOA PRODUCTS

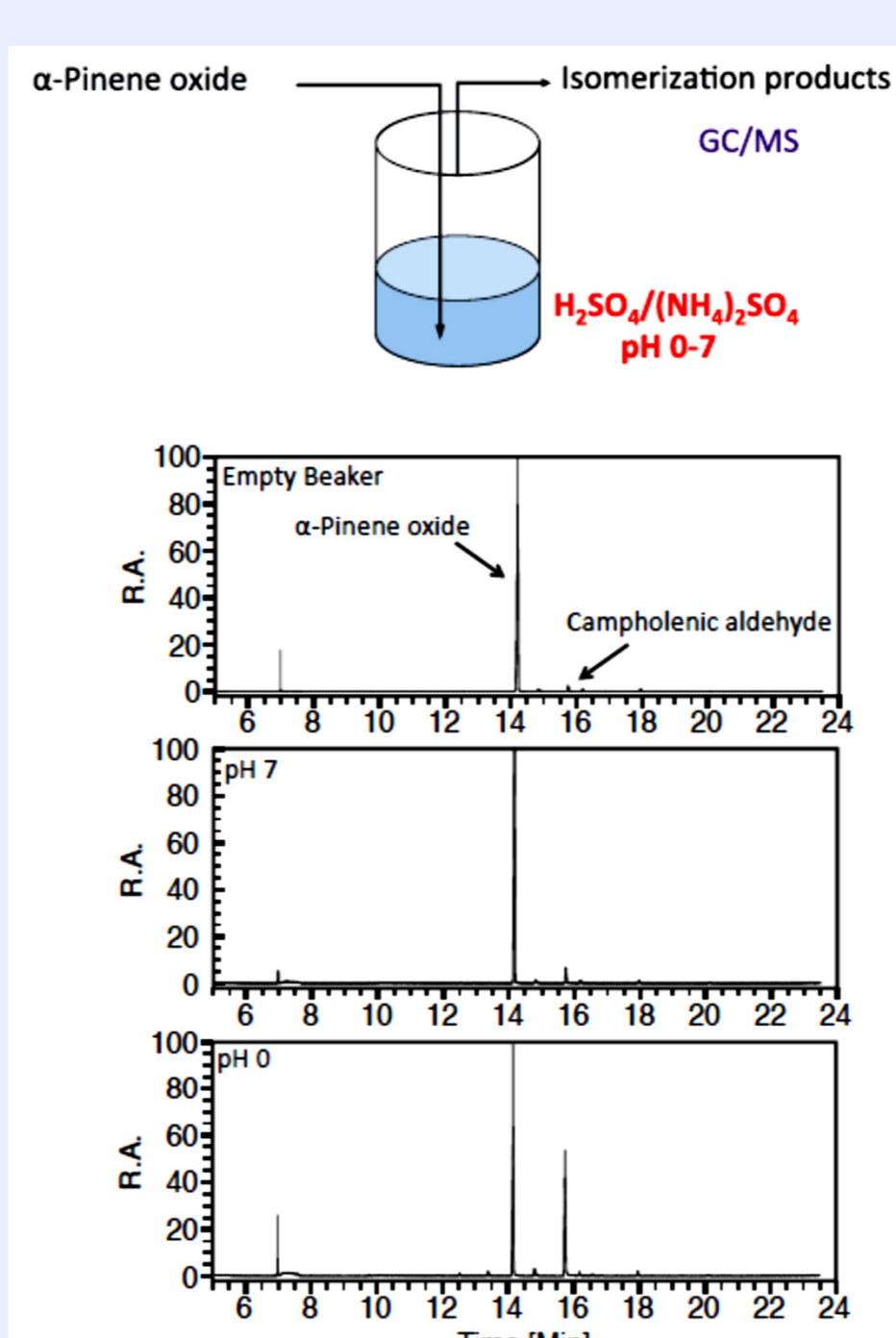


Figure 3. GC/MS chromatograms obtained from laboratory beaker experiments.

A series of simple beaker experiments were performed to determine gas-phase VOC species responsible for the enhanced SOA formation. Figure 3 shows GC/MS chromatograms from such experiments. In the presence of pH 0 sulfate solution, campholenic aldehyde was found to be the major product from the acid catalyzed isomerisation reactions.

From UPLC/ESI-TOFMS analysis, m/z 229 (C₁₀H₁₃O₆⁻) was found to be one of the important compounds in α -pinene oxide/O₃ SOA (Figure 4). The analysis of campholenic aldehyde/O₃ SOA shows the m/z 229, indicating that campholenic aldehyde is the VOC responsible for the enhanced SOA formation in the α -pinene oxide/O₃/pH0 seed experiment.

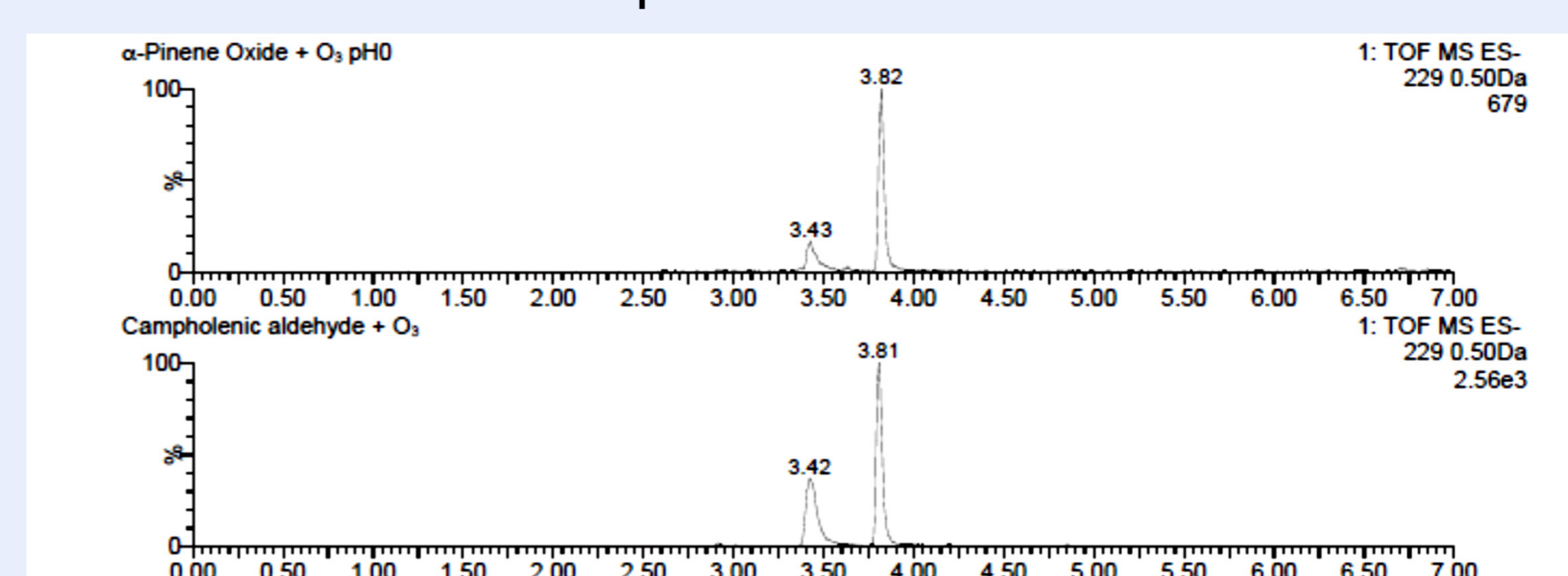


Figure 4. UPLC/ESI-TOFMS extracted ion chromatograms (EICs) of m/z 229 for α -pinene oxide/O₃ SOA (top) and campholenic aldehyde/O₃ SOA (bottom).