

Introduction

(3Z)-hexenyl acetate, also known as leaf acetate, is a volatile organic compound emitted by green foliage as a result of leaf cutting or wounding. The atmospheric fate of (3Z)-hexenyl acetate is dominated by gas-phase reactions with the hydroxyl radical (OH), nitrate radical (NO₃) and ozone (O₃). The aim of this work is to investigate the ozonolysis of (3Z)-hexenyl acetate and use a variety of analytical techniques to determine the chemical composition of the secondary organic aerosol (SOA) formed during the reaction. Analytical efforts were focussed on the identification of oligomers and polymers as these species are believed to play a major role in SOA formation.

Experimental

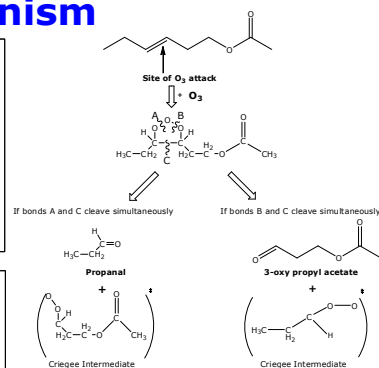
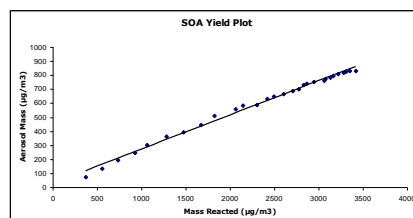
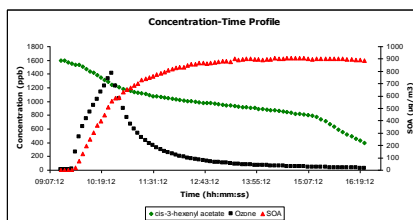
Experiments on the O₃ initiated oxidation of (3Z)-hexenyl acetate were performed in a 3910 L indoor simulation chamber in our laboratory in Cork.



Fig 1. Atmospheric Simulation Chamber

The chamber is equipped with GC-MS and in-situ FTIR for chemical analysis. A Scanning Mobility Particle Sizer (TSI 3034) is used for aerosol measurements. SOA was analysed using Gas Chromatography with Time of Flight Mass Spectrometry (GCxGC-TOF/MS) and Reverse phase Liquid Chromatography with Electrospray Ionisation and Ion Trap Mass Spectrometry (LC-ESI-MS/MS).

SOA Yield & Reaction Mechanism



**SOA Yield
23%**

Small Molecules

Low molecular weight products identified by GCxGC-TOF/MS

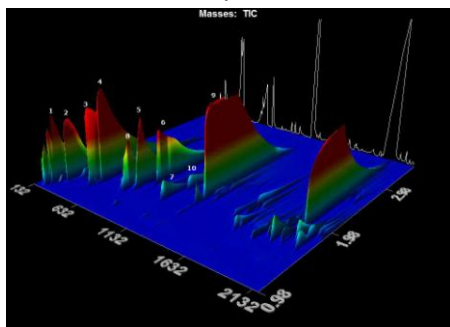


Fig 2. 3-dimensional total ion chromatogram

Product	Mass	GCxGC Peak Number	Structure
Propanal	58	1	<chem>CCC=O</chem>
Propenal	56	2	<chem>CC=CC=O</chem>
Acetic Acid	60	3	<chem>CC(=O)O</chem>
Ethyl acetate	88	4	<chem>CC(=O)OCC</chem>
Propanoic acid	74	5	<chem>CCC(=O)O</chem>
Propyl acetate	102	6	<chem>CCC(=O)OCC</chem>
1,2-ethanediol monoacetate	104	7	<chem>CC(=O)OCCO</chem>
2-methyl furan	82	8	<chem>CC1=CC=CO1</chem>
3-oxo-propyl acetate	116	9	<chem>CCC(=O)OCC(=O)C</chem>
2-epoxy-propyl acetate	116	10	<chem>CC1(O)CC(=O)OCC1</chem>

Oligomer Formation

Oligomers identified by LC-ESI-MS/MS

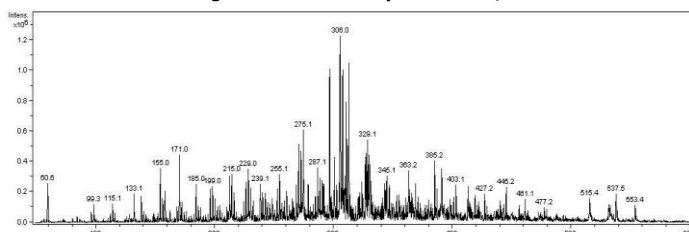


Fig 3. Averaged mass spectra of the water soluble extract of (3Z)-hexenyl acetate ozonolysis secondary organic aerosol.

Product	Mass	Structure
3-oxo-propyl acetate	116	<chem>CCC(=O)OCC(=O)C</chem>
3-acetoxy-propanoic acid (ACP)	132	<chem>CCC(=O)OCC(=O)O</chem>
3-acetoxypropane peroxy acid	148	<chem>CCC(=O)OCC(=O)OO</chem>

Table 2. Three most abundant small reaction products in the (3Z)-hexenyl acetate SOA.

Product	Mass	Structure
2-hydroxyethyl 3-acetoxypropanoate	176	<chem>CCC(=O)OCC(O)CC(=O)C</chem>
2-(3-oxo-propyl)ethyl 3-acetoxypropanoate	232	<chem>CCC(=O)OCC(=O)OCC(=O)C</chem>
2-(2-(3-acetoxypropoxyloxy)ethoxy)acetic acid	234	<chem>CCC(=O)OCC(=O)OCC(=O)OCC(=O)C</chem>
2-(2-(3-acetoxypropoxyloxy)ethoxy)propanoic acid	248	<chem>CCC(=O)OCC(=O)OCC(=O)OCC(=O)C</chem>
5-acetoxy-3-oxopentyl-3-acetoxypropanoate	274	<chem>CCC(=O)OCC(=O)OCC(=O)OCC(=O)C</chem>
Ethane-1,2-diyl bis(3-acetoxypropanoate)	290	<chem>CCC(=O)OCC(=O)OCC(=O)OCC(=O)C</chem>
3-(2-(3-acetoxypropoxy)ethoxy)-3-oxopropyl-3-acetoxypropanoate	348	<chem>CCC(=O)OCC(=O)OCC(=O)OCC(=O)OCC(=O)C</chem>

Table 3: Seven of the most abundant heterogeneous reaction products.

- The 7 oligomers identified in table 3 contain ester and ether linkages and all contain the (APA) unit.

- The smallest oligomer, 2-hydroxyethyl-3-acetoxypropanoate appears to be a building block for larger oligomers.

- In addition to those shown here, a further 10 oligomers were also identified.