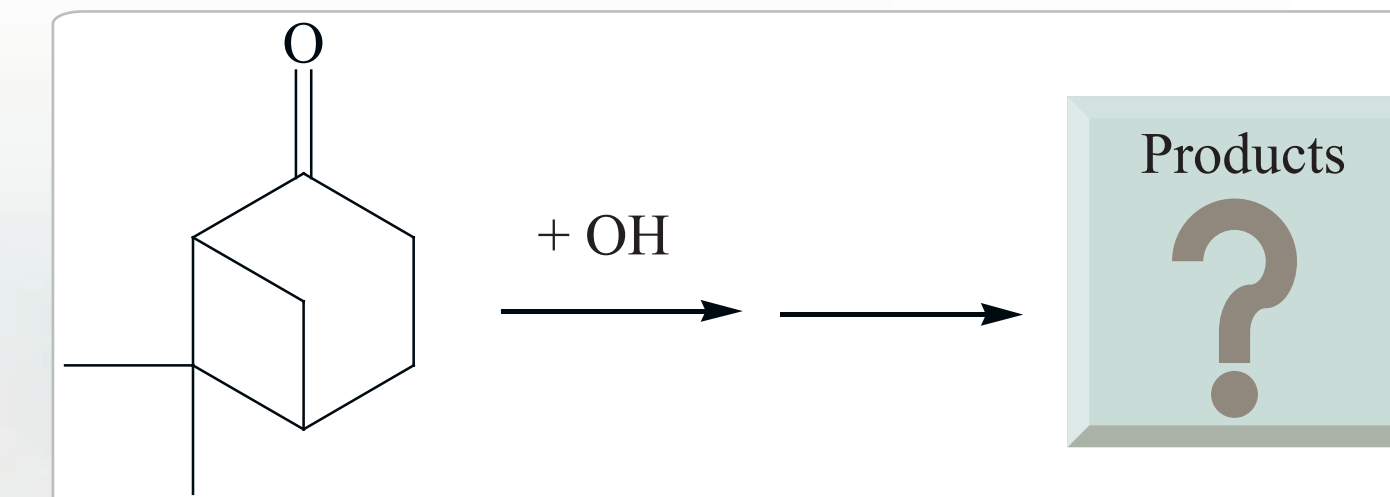


Carbonyl group containing products from nopinone oxidation

Introduction

Nopinone is a first generation product from the atmospheric β -pinene oxidation and was mainly investigated in kinetic studies in the past. Rate constants for OH (Atkinson and Aschmann, 1993; Calogirou *et al.*, 1999) and NO_3 reactions and few reaction products (Calogirou *et al.*, 1999) were reported. In this study nopinone oxidation was performed to investigate oxidation products in gas- and particle-phase by OH reaction.



Experimental

Chamber experiments:

OH source: ozonolysis of TME

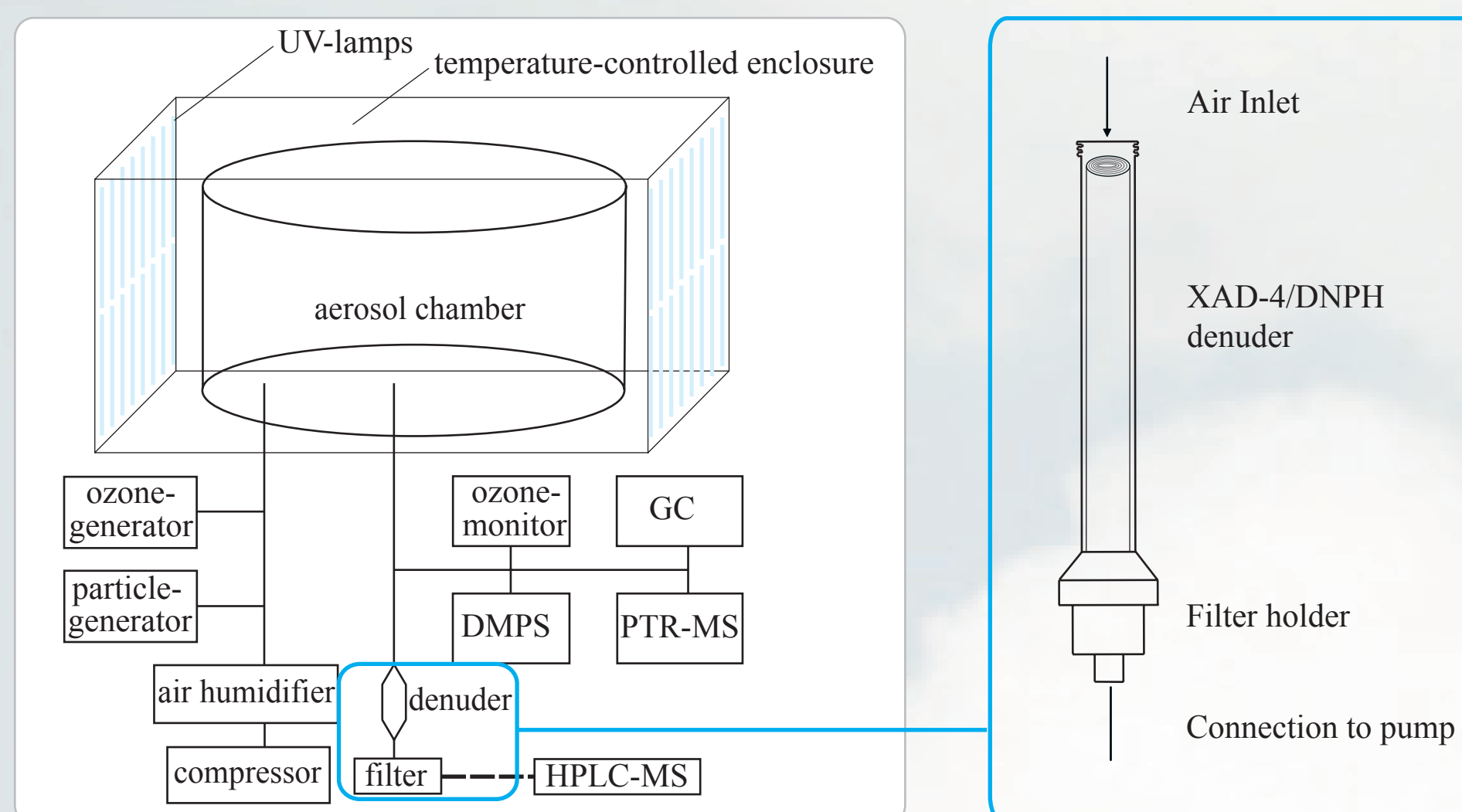
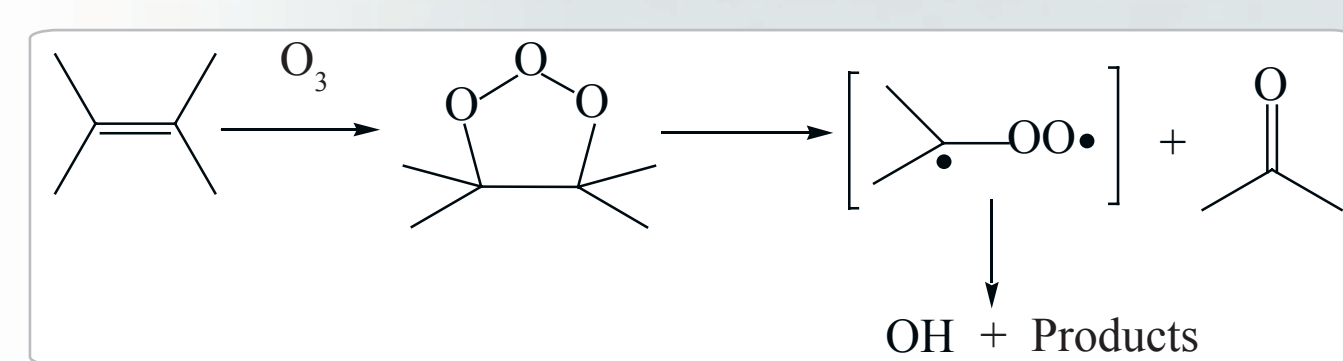
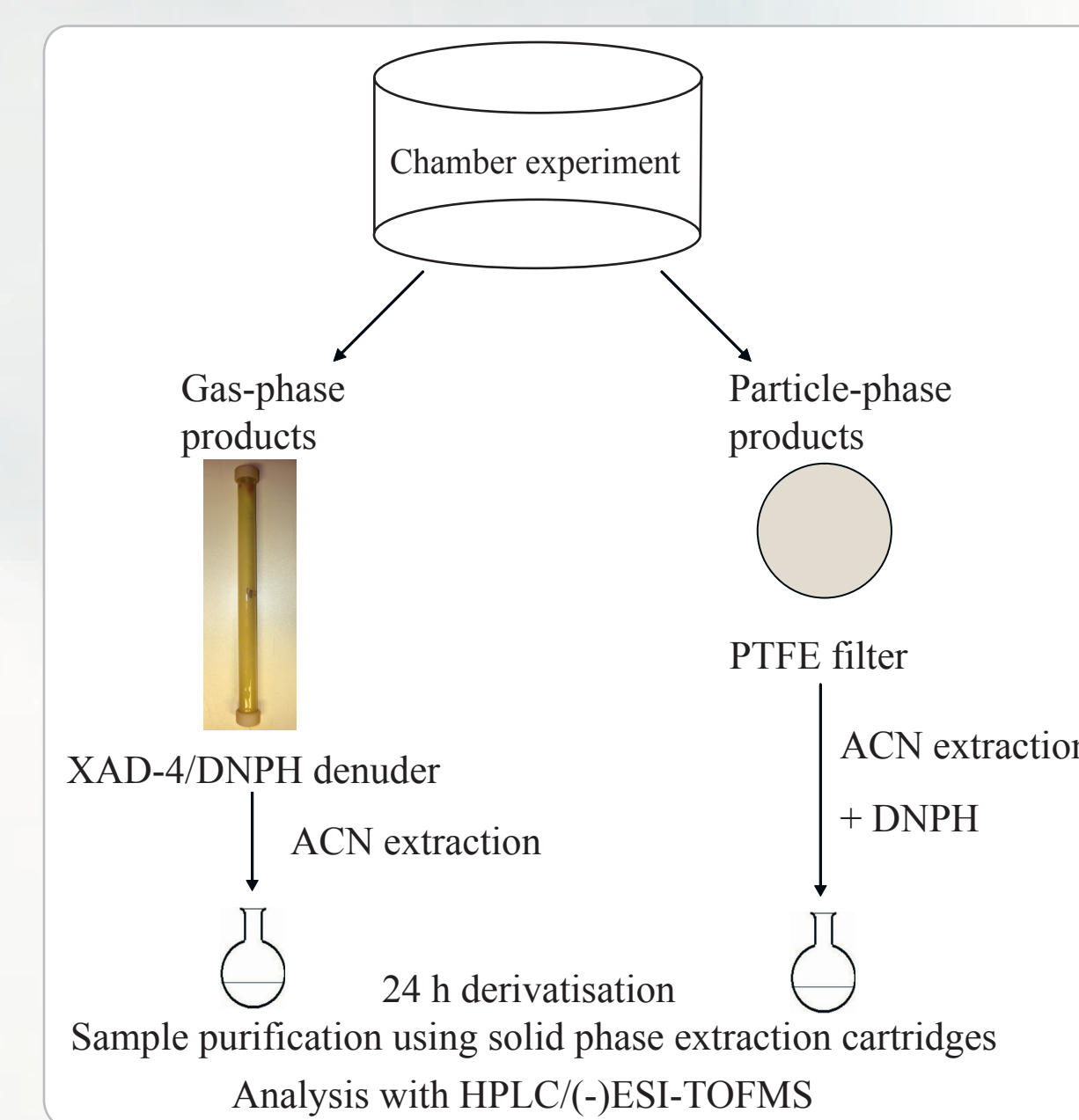


Figure 1: Schematic diagram and instrumentation of the Ift aerosol chamber.

Table 1: Experimental conditions.

Chamber experiment	
Initial HC [ppb]	50
RH [%]	50
T [°C]	21
Reaction Time [min]	70
Sampling Volume [m ³]	0.6
Sampling Time [min]	60
Seed particles	Na ₂ SO ₄ (pH = 7)

Workflow:



The PTR-MS was operated in scan mode from m/z 21-250 (dwell time: 2s) that resulted in a cycle time of about 8 min. Higher time resolved measurements were performed using the selected ion mode.

Results and Discussion

Gas-phase:

PTR-MS measurements

Figure 2 shows a time series of a nopinone/OH experiment that was recorded in selected ion mode by PTR-MS.

Only two compounds were detected at m/z 153 and 155. Unlike α - or β -pinene oxidation (data not shown) that typically show a number of m/z .

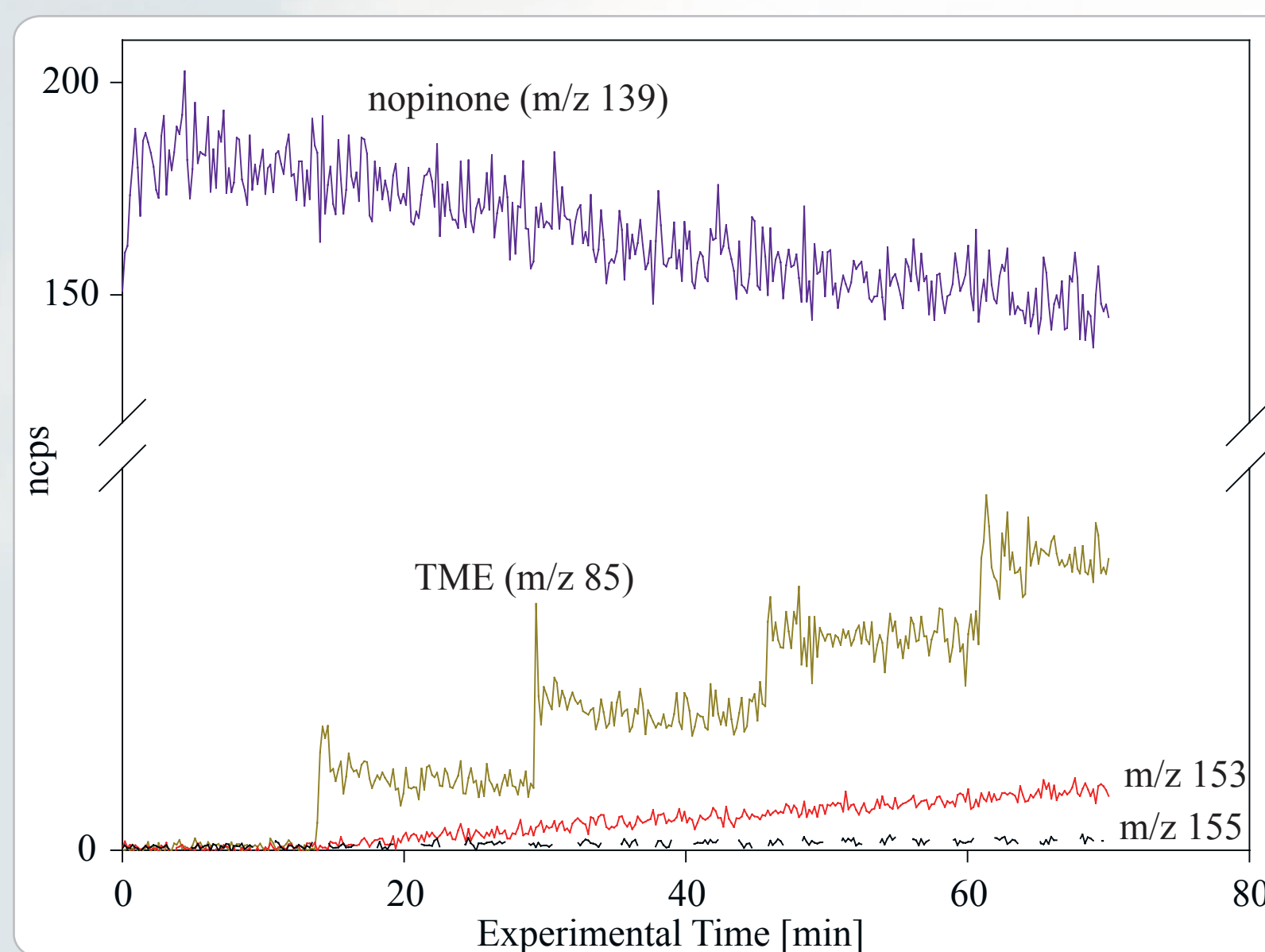


Figure 2: PTR-MS time resolved measurement of nopinone, the OH source TME and products from nopinone oxidation.

Denuder samples

Denuder extracts were analyzed for further product identification and compared with blank experiments (see Figure 3).

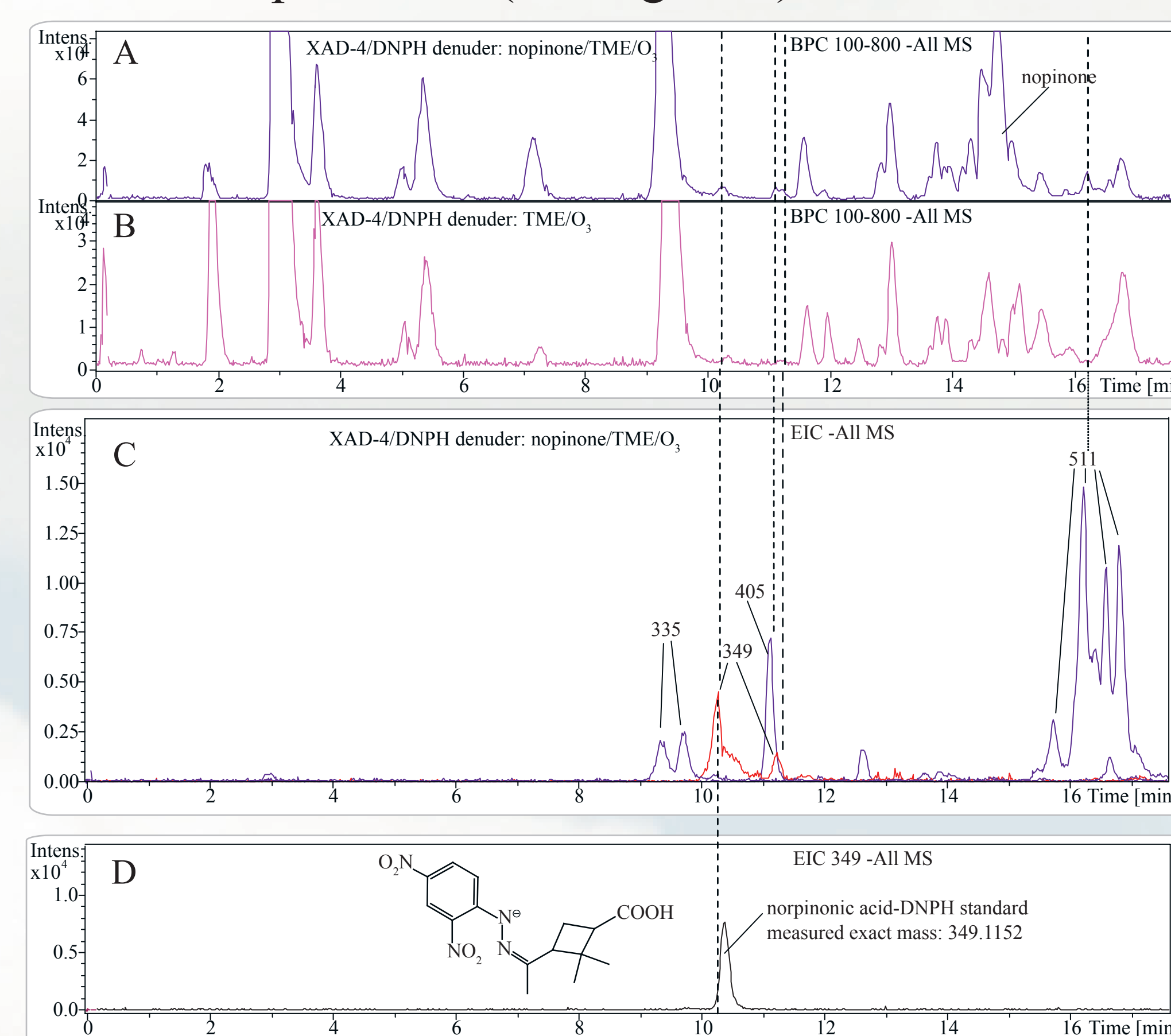


Figure 3: HPLC(-)ESI-TOFMS analysis of denuder extracts. Top part compares Base Peak Chromatograms (BPC) (A) of a nopinone experiment with (B) a TME/O₃ blank reaction. (C) Shows the Extracted Ion Chromatograms (EIC) that were compared with norpinonic acid-DNPH standard m/z 349.

Detected m/z 511 compound from denuder samples

A complex mixture of oxo-nopinones were detected at m/z 511 with no apparent favor of one isomer.

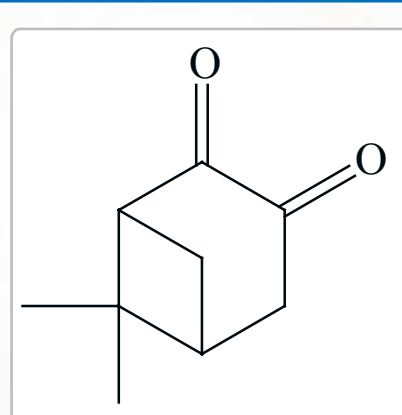


Figure 4: Oxo-nopinone with the keto-groups in 2,3 position.

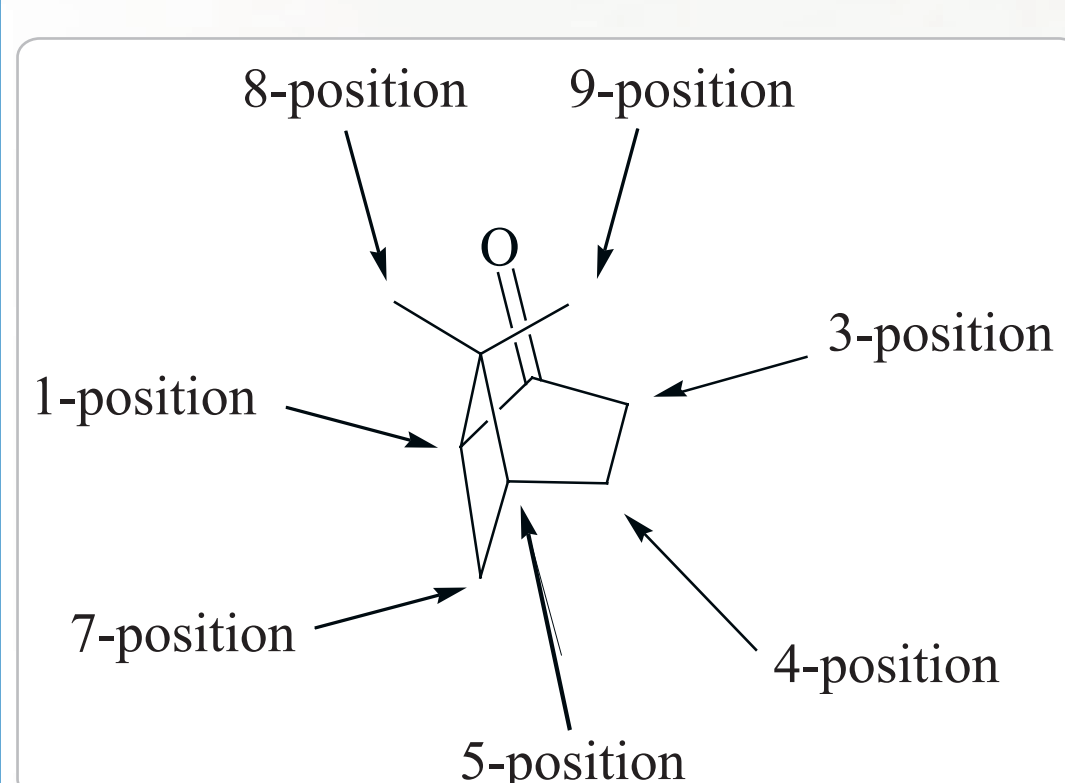


Figure 5: Possible positions of initial H-abstraction from nopinone OH oxidation.

A modelling study suggested the C3-position as favored location for the initial H-abstraction (Lewis *et al.*, 2005) where the C-H bond was calculated to have the lowest energy barrier.

Due to the neighbouring carbonyl-group, the weak C α -H bond is preferred for the OH attack.

Formed 3-nopinonyl radical can react further e.g. with O₂ to form oxo-nopinone (see Figure 6).

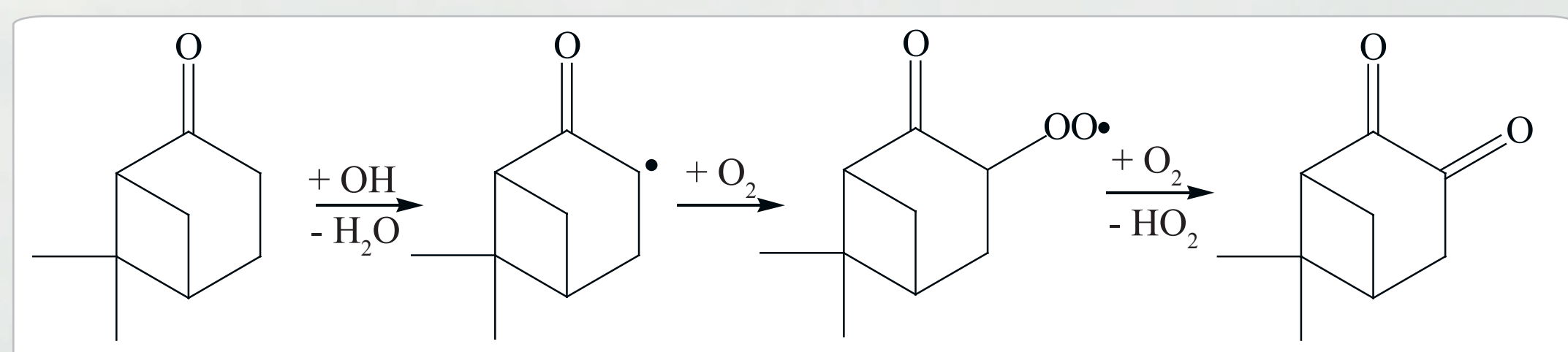


Figure 6: One possible mechanism for oxo-nopinone formation.

Table 2: List of detected compounds as their hydrazone derivatives and their obtained accurate mass data from HPLC(-)ESI-TOFMS measurements.

RT [min]	Measured exact mass	Elemental composition	Error [ppm]	Sigma	Carbonyl compound	Mw
9.3	335.1016	C ₁₄ H ₁₅ N ₂ O ₆	-5.8	0.0102	C ₈ H ₁₂ O ₃ (1 carbonyl group)	156
9.7	335.0995	C ₁₄ H ₁₅ N ₂ O ₆	0.6	0.0137	C ₈ H ₁₂ O ₃ (1 carbonyl group)	156
10.3	349.1150	C ₁₅ H ₁₇ N ₂ O ₆	1.1	0.0083	C ₉ H ₁₄ O ₃ (1 carbonyl group)	170
11.2	349.1149	C ₁₅ H ₁₇ N ₂ O ₆	1.2	0.0080	C ₉ H ₁₄ O ₃ (1 carbonyl group)	170
11.1	405.0549	C ₁₅ H ₁₉ N ₂ O ₈	0	0.0029	Fragile compound	-
15.7	511.1322	C ₂₁ H ₁₉ N ₂ O ₈	1.8	0.2445	C ₉ H ₁₂ O ₂ (2 carbonyl groups)	152
16.2	511.1321	C ₂₁ H ₁₉ N ₂ O ₈	1.9	0.0090	C ₉ H ₁₂ O ₂ (2 carbonyl groups)	152
16.3	511.1318	C ₂₁ H ₁₉ N ₂ O ₈	2.1	0.2178	C ₉ H ₁₂ O ₂ (2 carbonyl groups)	152
16.5	511.1320	C ₂₁ H ₁₉ N ₂ O ₈	2.3	0.0583	C ₉ H ₁₂ O ₂ (2 carbonyl groups)	152
16.7	511.1325	C ₂₁ H ₁₉ N ₂ O ₈	1.5	0.0137	C ₉ H ₁₂ O ₂ (2 carbonyl groups)	152

Particle-phase:

The compounds with m/z 335, 349 and 511 were also detected in the particle-phase.

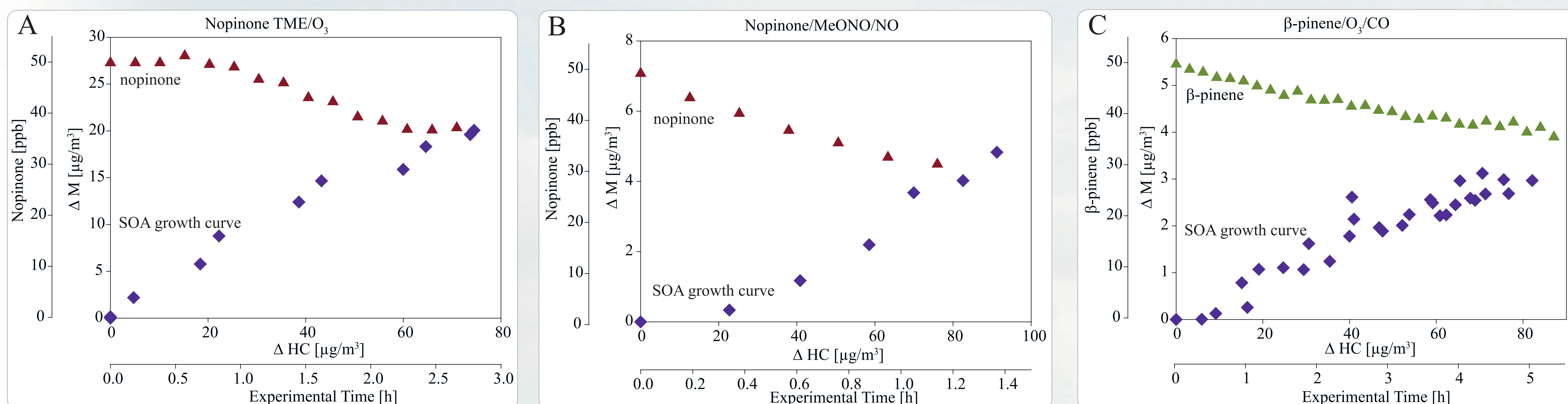


Figure 7: SOA growth curves for nopinone/OH reaction (A) without NO (B) in the presence of NO and (C) β -pinene ozonolysis. Note that the axis have different scales.

The observed SOA growth curve (see Figure 7A) indicates that the first OH oxidation leads to the formation of low volatile compounds that form SOA (Ng *et al.*, 2006).

In comparison to OH reaction in the presence of NO (Figure 7B) and β -pinene ozonolysis (Figure 7C), particle formation starts at very low hydrocarbon conversion.

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