



Phys. Chem. Chem. Phys.

Supporting Information for

Ozonolysis of 3-Carene in the Atmosphere. Formation Mechanism of Hydroxyl Radical and Secondary Ozonides

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Experimental Methods.

Figure S1. Time profiles of yields for POZ and Criegee intermediates in the reaction of 3-carene and O₃ at 298 K and 760 Torr from RRKM-ME calculation.

Figure S2. Fractional yields of the Criegee intermediates and the stabilized POZ from 243 K to 343 K at 760 Torr from RRKM-ME calculation.

Figure S3. The potential energy profiles of internal rotations at M06-2X level, (A-D) for Z-CI1, (E-H) for E-CI1, (I-L) for Z-CI2, and (M-P) for E-CI2. The dots are the calculated results, and the curves are the fit to the expansion of triangular functions.

Figure S4. The microcanonical rates of Criegee intermediates from RRKM theory. Four, one and none of the internal rotations are treated as hindered rotors for isomerizations to SOZs, VHPs, and Dioxiranes, respectively.

Figure S5. The formation of CIs* and their decay in the ozonolysis of 3-carene in the processes of 3-Carene + O₃ → POZ-A1/A2 → CI* → P, in which CI is Z-CI1, E-CI1, Z-CI2, or E-CI2, and P is SOZ, VHP, or Dioxirane. Four, one and none of the internal rotations are treated as hindered rotors for isomerizations to SOZs, VHPs, and Dioxiranes, respectively. All are plotted as the formation molar fraction with respect to 3-Carene consumed.

Figure S6. (A) The normalized internal energy distributions in Z-CI1* formed in the reaction of 3-Carene + O₃ → POZ-A1/A2 → Z-CI1* when subject to isomerization to SOZ, VHP, or Dioxirane at different reaction time (from RRKM-ME calculations), (B) The normalized internal energy distributions in Z-CI2* formed in the reaction of 3-Carene + O₃ → POZ-A1/A2 → Z-CI2* when subject to isomerization to SOZ, VHP, or Dioxirane at different reaction time (from RRKM-ME calculations)

Figure S7. ¹H NMR of 3-Carene secondary ozonide in CDCl₃.

Figure S8. ¹³C NMR of 3-Carene secondary ozonide in CDCl₃.

Figure S9. GC-MS of (A) total ion chromatogram (TIC), (B) extracted ion chromatogram (EIC, m/z=183) for the synthesized 3-carene-SOZ; (C) total ion chromatogram (TIC) and (D) extracted ion chromatogram (EIC, m/z=183) for the samples frozen downstream the gas phase mixture of 3-carene and O₃.

Figure S10. ¹H NMR of 3-Carene secondary ozonide in D₂O.

Experimental Methods:**1. Chemicals**

The (+)-3-Carene (90%) was purchased from Aldrich. Pentane (AR) and Mineral ether (AR) were acquired from Tianjin Damao Chemical Reagent Company, China. The phosphomolybdic acid (AR) were obtained from Tianjin Fuchen Chemical Reagent Company, China. O₂ (> 99.9999%) from Guangzhou Shengying Gas Co. LTD, China.

2. Instrumentation

Ozone is generated by an ozone sterilizer (HY-005-10A type, Guangzhou Jiahuan Electrical Technology Co, China).

GC-CI-MS Analysis: A gas chromatography coupled to a triple quadrupole mass spectrometer (Shimuzu GCMS-TQ8040) was used. The GC-oven program was: 50°C hold 1 min, ramp 1: 5°C min⁻¹ to 200°C, ramp 2: 20°C min⁻¹ to 250°C hold 4 min. Helium was used as carrier gas with controlled flow rate of 3.0 mL min⁻¹. Negative chemical ionization was used to ionize the sample. The ion source and the GC-MS interface was kept at 200°C.

FTIR Analysis: FT-IR spectra were recorded between 400⁻¹ and 4000 cm⁻¹ from KBr pellets on FT-IR Spectrometer (Tensor 27, BRUKE), which was utilized to measure the transmission of product and monitor special functional groups.

NMR: ¹H and ¹³C NMR spectra of the samples were recorded on AV 600Hz spectrometer (BRUKER) in CDCl₃(zg30) and in D₂O (noesygppr1d) solvent. Comparison of measured and calculated ¹³C chemical shift are listed below.

3. Synthesis and purification of secondary ozonide of 3-carene in liquid phase

The SOZ was synthesized by cryo-ozonolysis of the 3-carene (0.3mL) dissolved in 50 mL pentane in a 200 ml impinger. The solution was kept at -45°C using acetonitrile/dry ice bath. O₃ was generated by corona discharge of pure O₂ with an Ozone sterilizer and bubbled through the reaction mixture for 3.5 h.

After the reaction, the mixture is brought to room temperature and then purged with N₂ to remove excess O₃ and to reduce the liquid volume to about 2 mL. Subsequently, the SOZ was purified by the use of chromatographic column, and the SOZ can be acquired by just using mineral ether to elute.

4. Ozonolysis of 3-carene in gas phase

Ozonolysis of 3-carene in the gas-phase was carried out in an Erlenmeyer flask with a few changes in flow rates and concentrations. Ozone was generated from discharge of pure O₂ at a flow of 114mL min⁻¹. 3-Carene vapor was introduced into the system by purging the headspace of liquid 3-carene with N₂ at a flow rate of 111 mL min⁻¹ in an impinger (100 mL). The two flows were then mixed to react and the products were collected by freezing -45°C with an acetonitrile/dry ice bath.

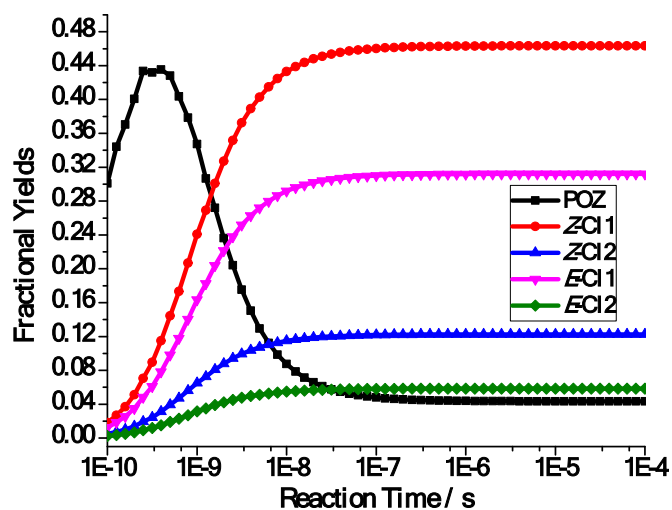


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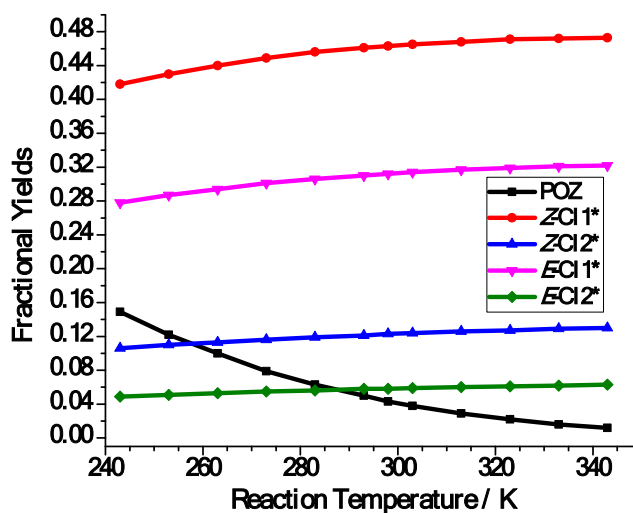


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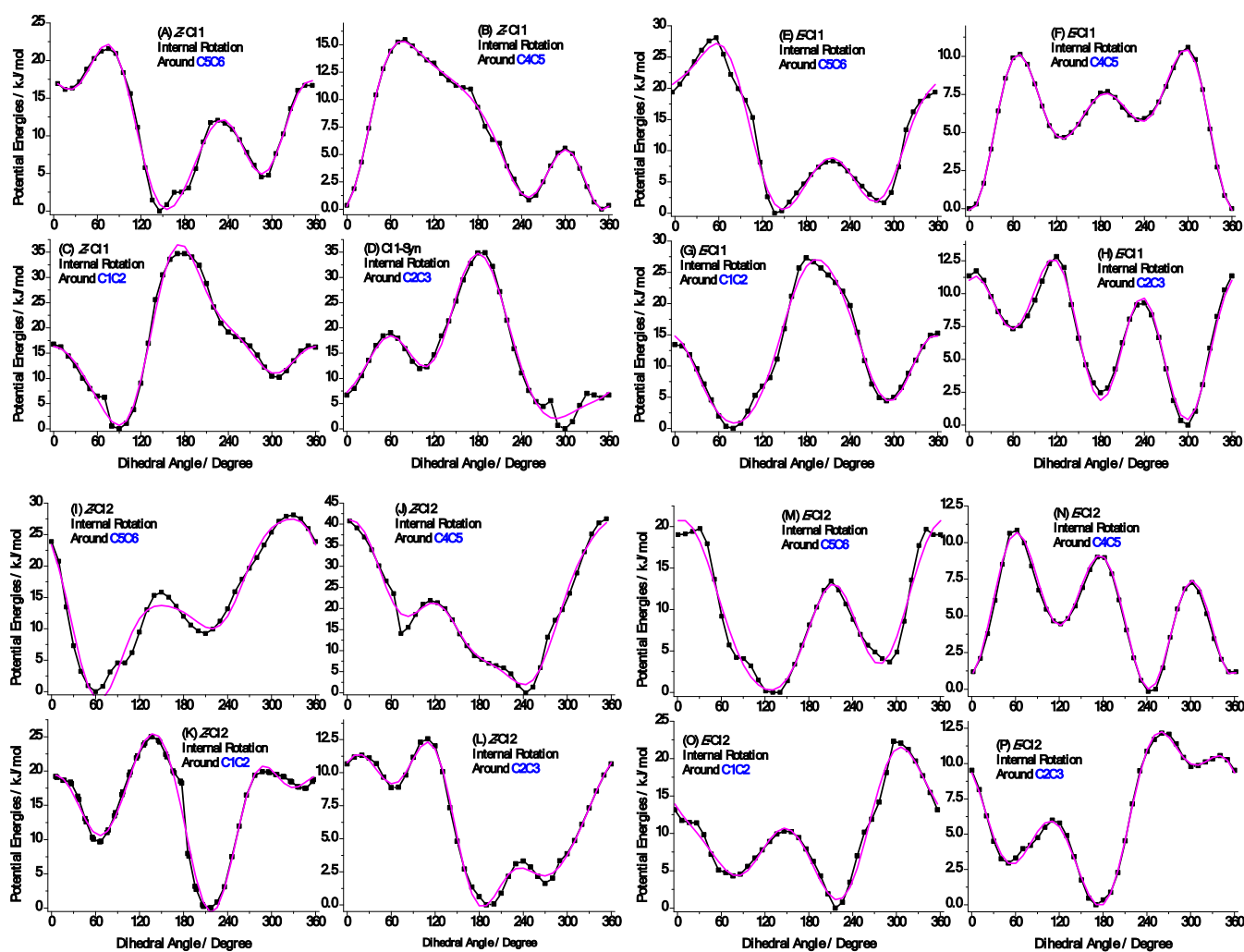


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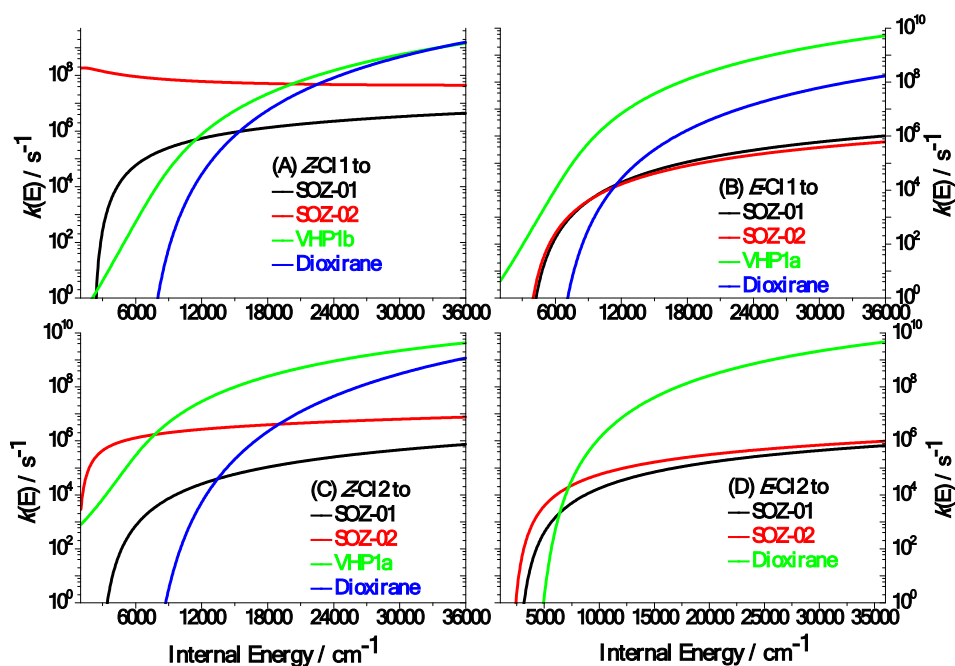


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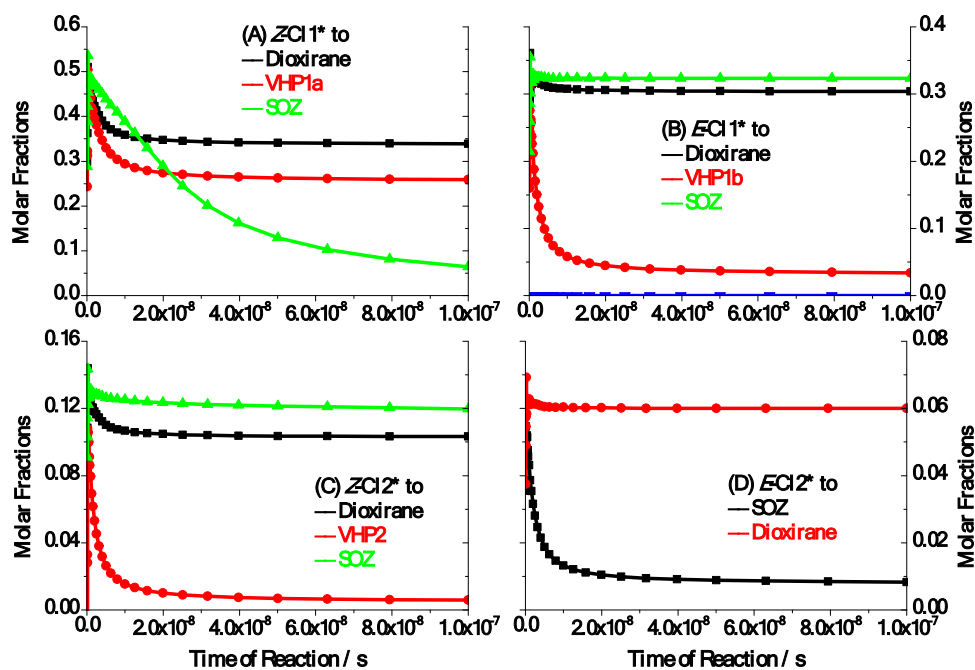


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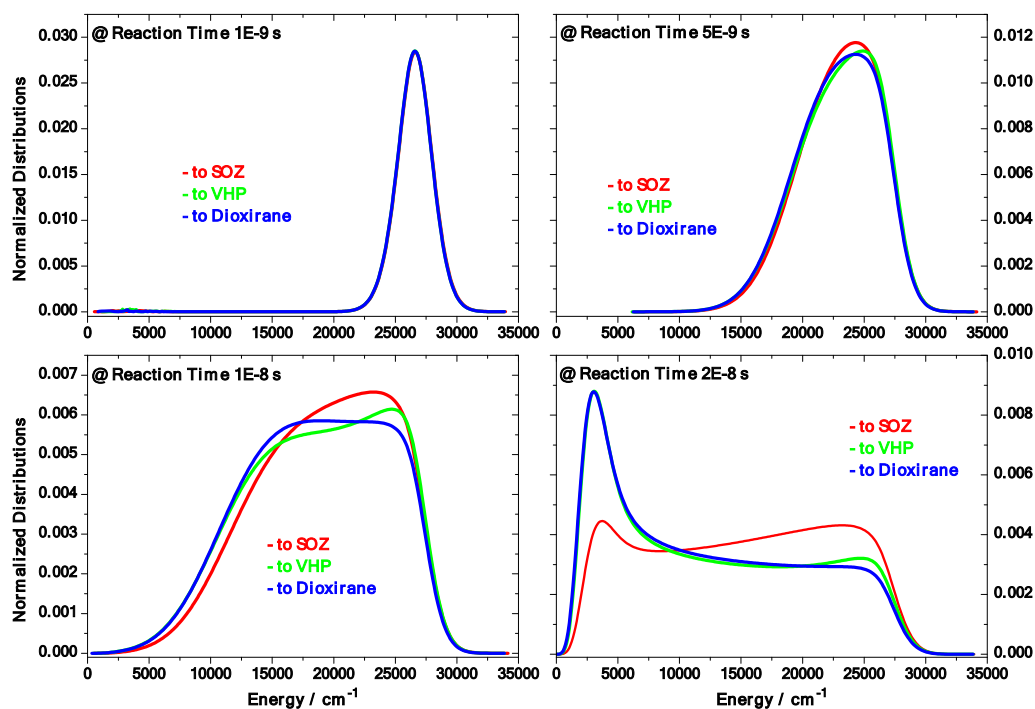


Figure S6. (A) The normalized internal energy distributions in Z-CI1* formed in the reaction of 3-Carene + O₃ → POZ-A1/A2 → Z-CI1* when subject to isomerization to SOZ, VHP, or Dioxirane at different reaction time (from RRKM-ME calculations)

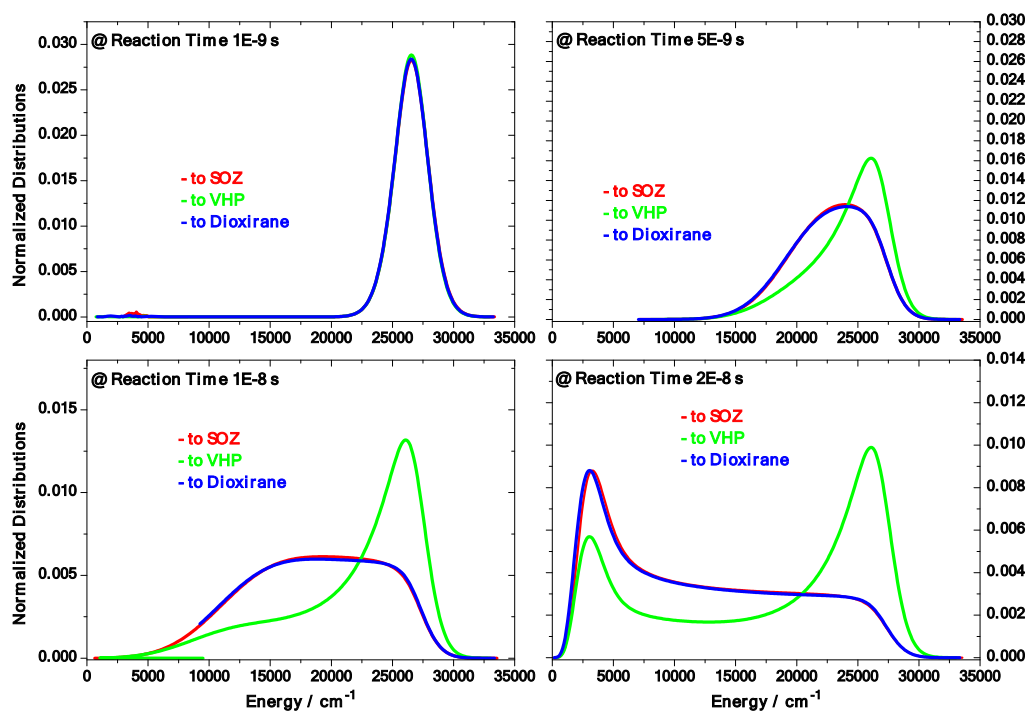


Figure S6. (B) The normalized internal energy distributions in Z-CI2* formed in the reaction of 3-Carene + O₃ → POZ-A1/A2 → Z-CI2* when subject to isomerization to SOZ, VHP, or Dioxirane at different reaction time (from RRKM-ME calculations)

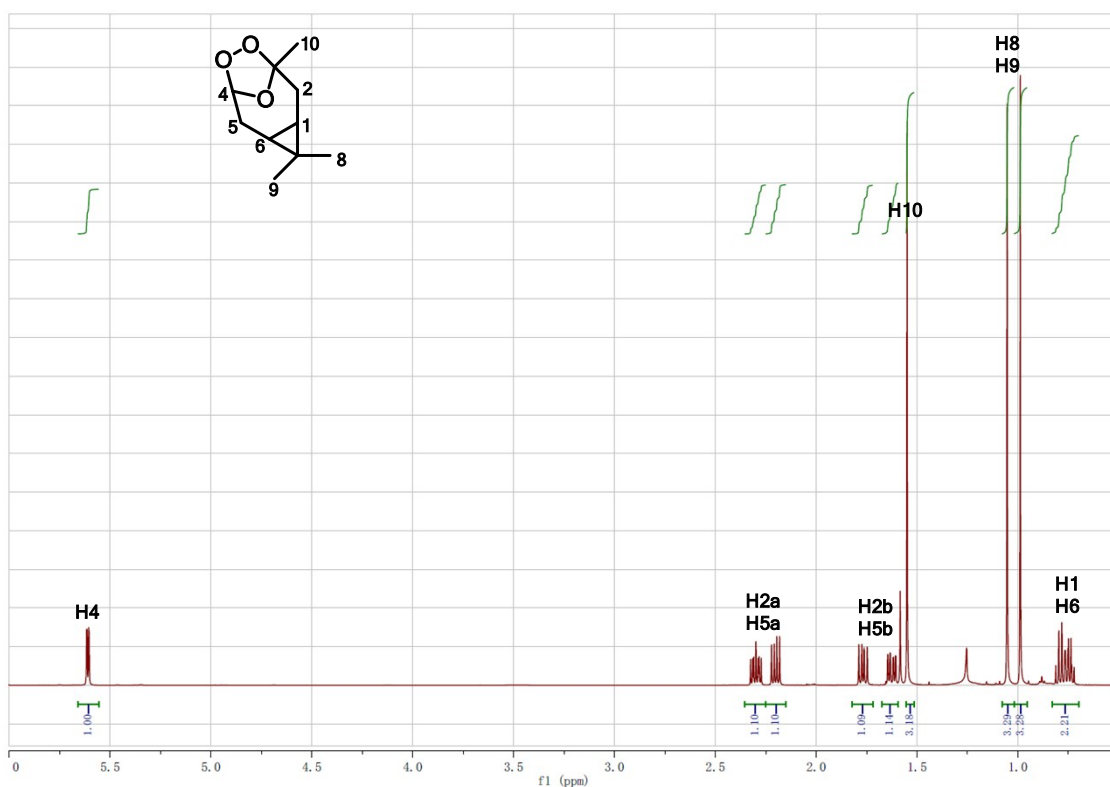


Figure S7. ^1H NMR of 3-Carene secondary ozonide in CDCl_3 .

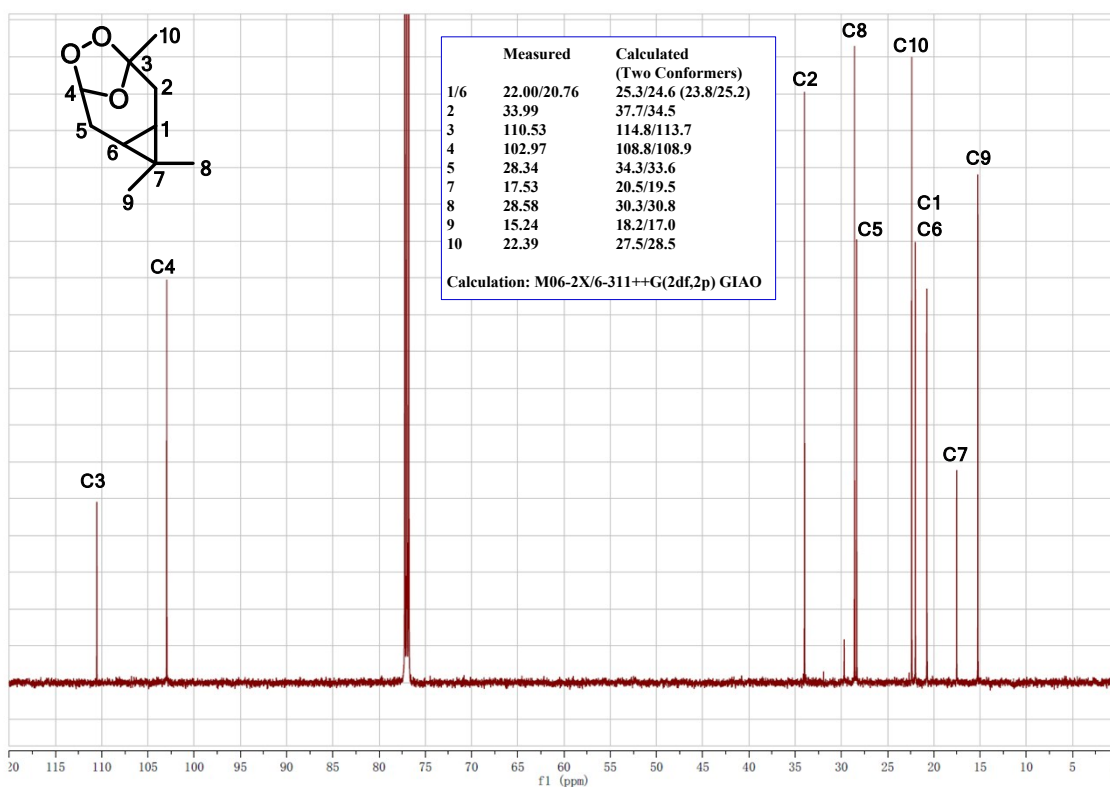


Figure S8. ^{13}C NMR of 3-Carene secondary ozonide in CDCl_3 .

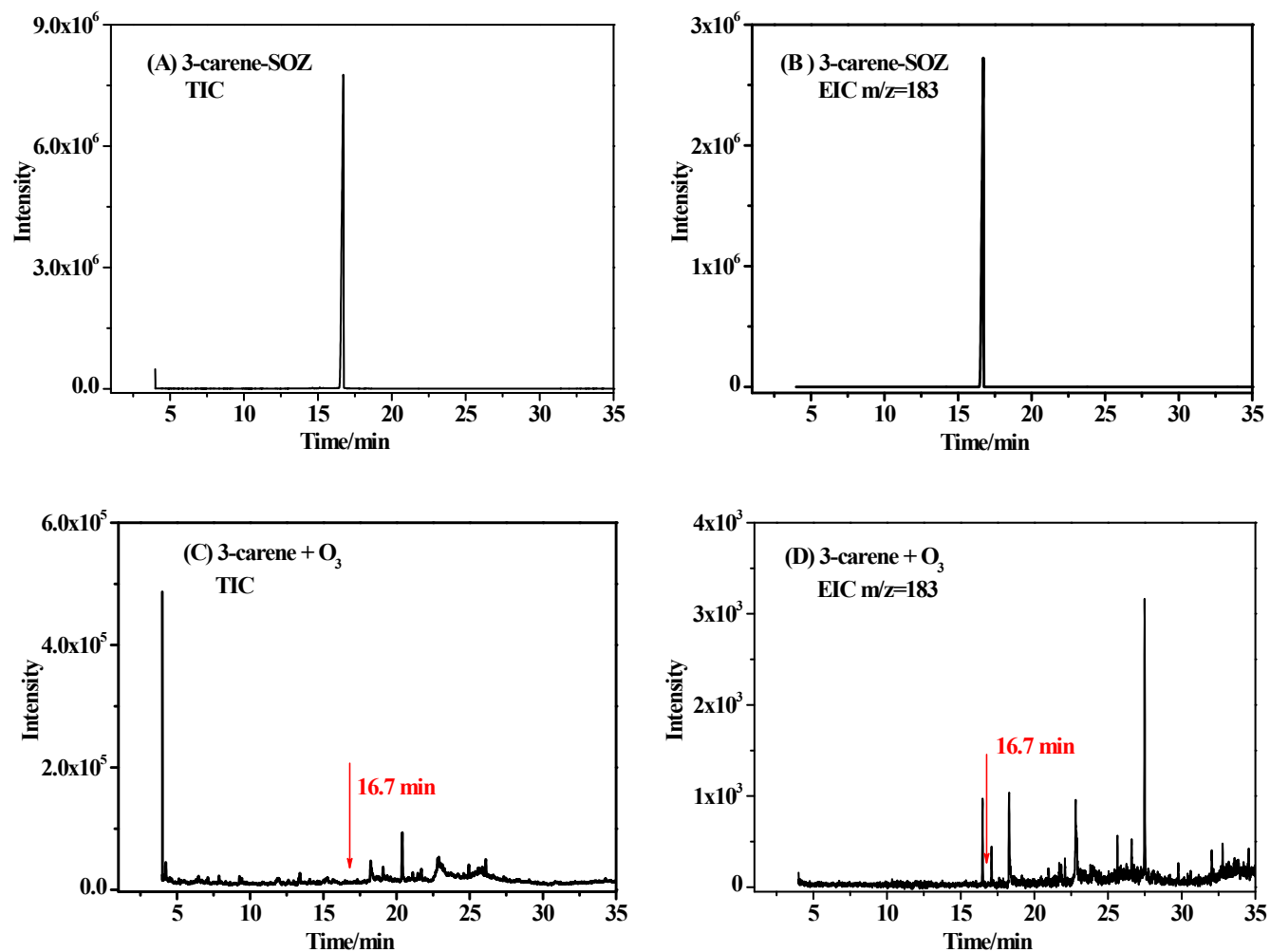


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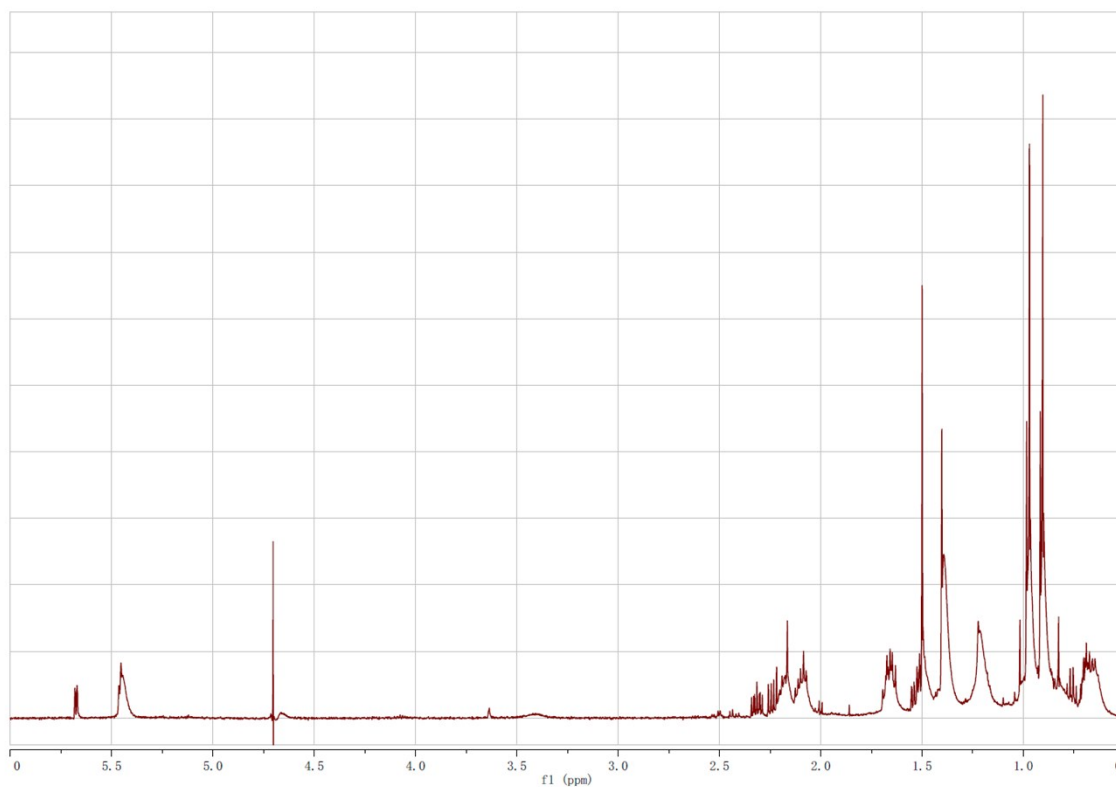


Figure S10. ^1H NMR of 3-Carene secondary ozonide in D_2O