Supporting Information

Manuscript Title: Stoichiometry of Ozonation of Environmentally Relevant Olefins in Saturated Hydrocarbon Solvents
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Chemicals Used

The following chemicals were purchased and used in this work without further purification.
Reagents: undecylenic acid (Sigma Aldrich, 98%), oleic acid (Fisher Scientific, 98%), linoleic acid (Acros Organics, 99%), linolenic acid (Acros Organics, 99%), α-pinene (Acros Organics, 97%), β-pinene (Acros Organics, 98%), d-limonene (Acros Organics, 97%, stabilized with 0.03% Tocopherol)
Solvents: n-hexadecane (Acros Organics, 99%), n-nonane (Acros Organics, 99%), cyclohexane (Fisher Scientific, HPLC grade, 99.9%), cyclopentane (Acros Organics, 99%), carbon tetrachloride (Acros Organics 99%), methanol (Fisher Scientific, HPLC grade, 99.9%), glacial acetic acid (EMD, 99.7%), compressed oxygen (Airgas, UHP grade), compressed helium (Airgas, UHP grade)
GCMS standards: cyclohexanone (Sigma Aldrich, 99.8%), cyclohexanol (Acros Organics, 99%), cyclopentanone (Acros Organics, 99%), cyclopentanol (Acros Organics, 99%), 1-octanol (Sigma Aldrich, 99%)

Reactions in Participating Solvents

Figure 1S. Double bond to ozone (DB:O_3) reaction stoichiometry for oleic acid ozonolysis measured in different solvents at room temperature. The measured DB:O_3 ratios were somewhat less reproducible in participating solvents compared to linear alkane solvents. However, they were reproducibly well in excess of DB:O_3 ratios measured for linear alkane solvents.

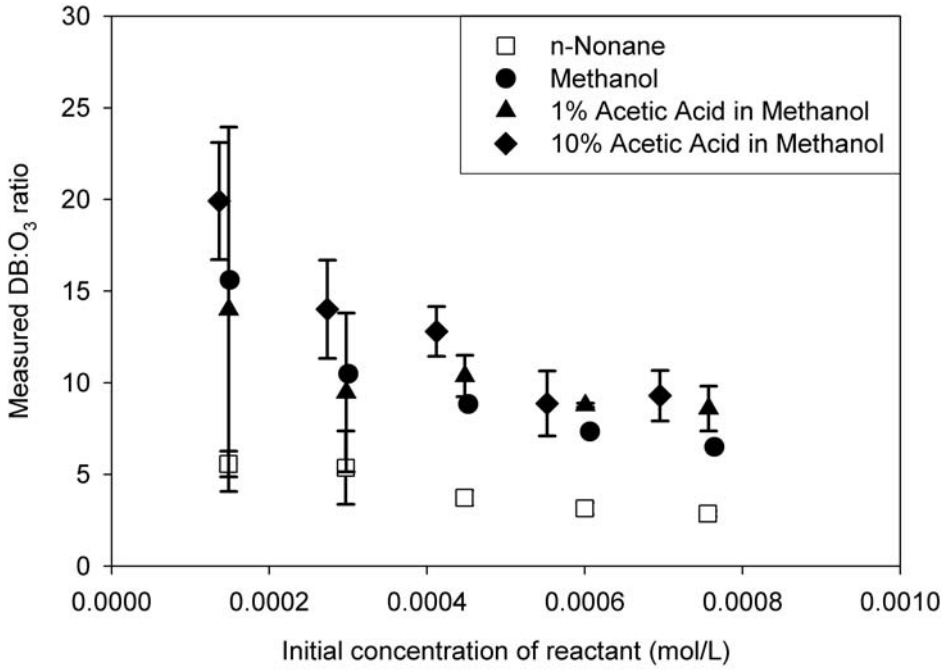
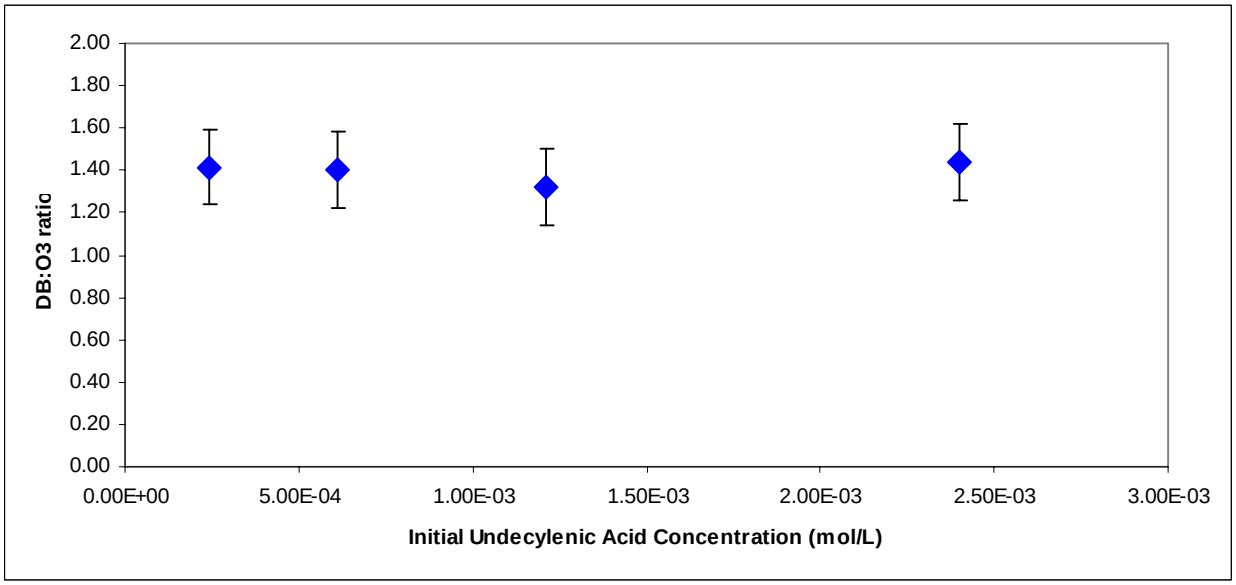
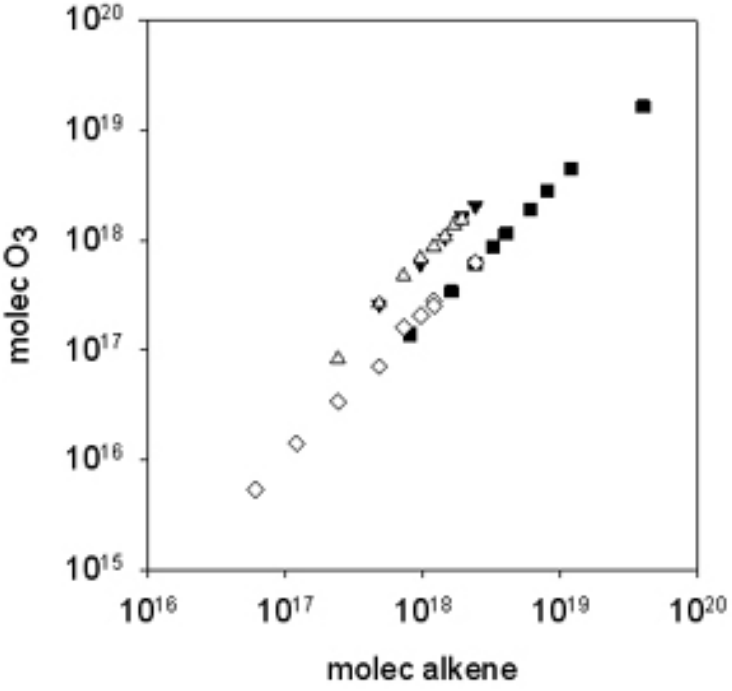


Figure 2S. A sample measurement of DB:O_3 reaction stoichiometry for undecylenic acid ozonolysis in CCl_4 at room temperature.



Reproducibility Tests

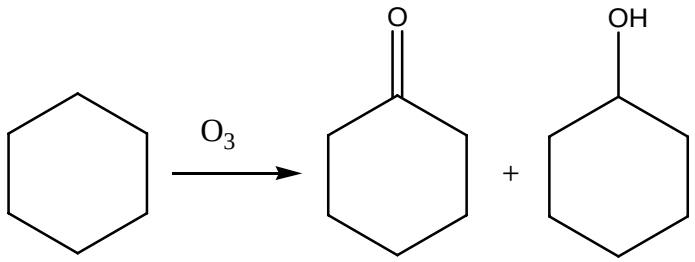
Figure 3S. Sample reproducibility tests. In the first example, stoichiometry for ozonation of β-pinene (△,▼) was measured on two separate days for the same ozone concentration. In the second example, stoichiometry for ozonation of undecylenic acid was measured with different ozone concentrations (◇=6×10^{15}, ■=6×10^{16} molec/cm^3), and over a wide range of reactant concentrations. The x-axis shows the number of reactant molecules injected in the reaction vial, and the y-axis shows the number of ozone molecules consumed by the injection.



GCMS Experiment

The following is a description of the procedure used to measure the yields of cyclohexanone and cyclohexanol produced by reaction between O_3 and cyclohexane solvent. A similar procedure was used in experiments on ozonolysis of cyclopentane.

Figure 4S: Major primary stable products of ozonation of cyclohexane.



Step 1: Preparation of Internal Standard Stock Solution

- Dilute 50 μL of 1-octanol (measured with a 50 μL Hamilton syringe) with cyclohexane in a 5 mL volumetric flask
- Take 0.5 mL of the above solution and dilute with cyclohexane in a 5 mL volumetric flask. This is your internal standard; you will be adding 50 μL of your internal standard to every sample that you run on GC/MS.

Step 2: Preparation of Calibration Standard Stock Solution

- Dilute 50 μL of cyclohexanone and 50 μL of cyclohexanol (measured with a 50 μL Hamilton syringe) with cyclohexane in a 100 mL volumetric flask.
- Take 10 mL of the above solution and dilute with cyclohexane in a 100 mL volumetric flask.

Step 3: Preparation of Calibration Solutions

- Prepare five 5-mL vials with calibration solutions (see table below) using appropriate volumetric pipettes.
- Transfer 1 mL of each solution into a GC/MS vial with a volumetric pipette.
- Add 50 μL of internal standard stock solution to every GC/MS vial (this should result in 3.16×10^{-4} M concentration of internal standard if it was prepared as described above).

Table 1. Molecular weight and density of calibration chemicals

Chemical	Density	Molecular weight
Cyclohexanone	0.9478 g/mL	98.15 g/mol
Cyclohexanol	0.962m/mL	100.16 g/mol
1-octanol	0.824 g/mL	130.23 g/mol

Table 2. Concentrations of cyclohexanone and cyclohexanol in calibrations solutions.

Vial	Calibration stock (mL)	Cyclohexane (mL)	[Cyclohexanone] (mol/L)	[Cyclohexanol] (mol/L)
A	1	4	9.66E-5	9.60E-05
B	2	3	1.93E-4	1.92E-04
C	3	2	2.90E-4	2.88E-04
D	4	1	3.86E-4	3.84E-04
E	5	-	4.83E-4	4.80E-04

Step 4: Sample preparation

- Generate an ozone/oxygen flow (20 sccm) and let it go through the bypass of the setup shown in Figure 1 of the manuscript until the ozone concentration in the outgoing flow is stable.
- Bubble the ozone/air mixture through 5 mL of cyclohexane at 20 sccm for 5-60 min. Record the ozone concentration in the outflow as a function of oxidation time.
- After the ozone exposure, transfer 1 mL of the oxidized solution into a GC/MS vial with a graduate pipette.
- Add 50 μL of internal standard stock solution to this GC/MS vial.

Step 5: GS/MS Parameters

- Run all 5 calibration standards and samples on GC/MS using the same method.
    - Column: Restek Rtx-65
    - Purge gas @ flow rate: He @ 50 mL/min
    - Injector Port Temp: 230°C
    - Injection volume: 1 μL
    - Initial Temperature: 35°C @ 1 min hold
    - Ramp 1: 5°C/min until 100°C
    - Ramp 2: 30°C/min until 225°C @ 2 min hold
    - MS: on at 3 min (to avoid cyclohexane peak)

Step 6: Data Analysis

- Assign peaks to the internal standard, cyclohexanone, and cyclohexanol. See sample chromatogram below as an example.
- Construct a calibration plot, and calculate the concentration of cyclohexanone and cyclohexanol in oxidized sample.
- Calculate the number of cyclohexanone + cyclohexanol molecules formed in solution
- Calculate the number of ozone molecules that were lost in solution using Eq. (5) in the main body of the manuscript.
- Calculate the reaction yield by dividing these two numbers.

Figure 5S: Sample GC/MS chromatogram of cyclohexane after it was ozonized at room temperature for 15 min with a 20 sccm flow of O_3/O_2 mixture containing ~6×10^{16} molec/cm^3 ozone. Peaks at 7.20, 8.62. and 11.05 min correspond to cyclohexanol, cyclohexanone, and internal standard 1-octanol, respectively. Small peaks corresponding to products containing two oxygen atoms were also observed (estimated yield < 10%).

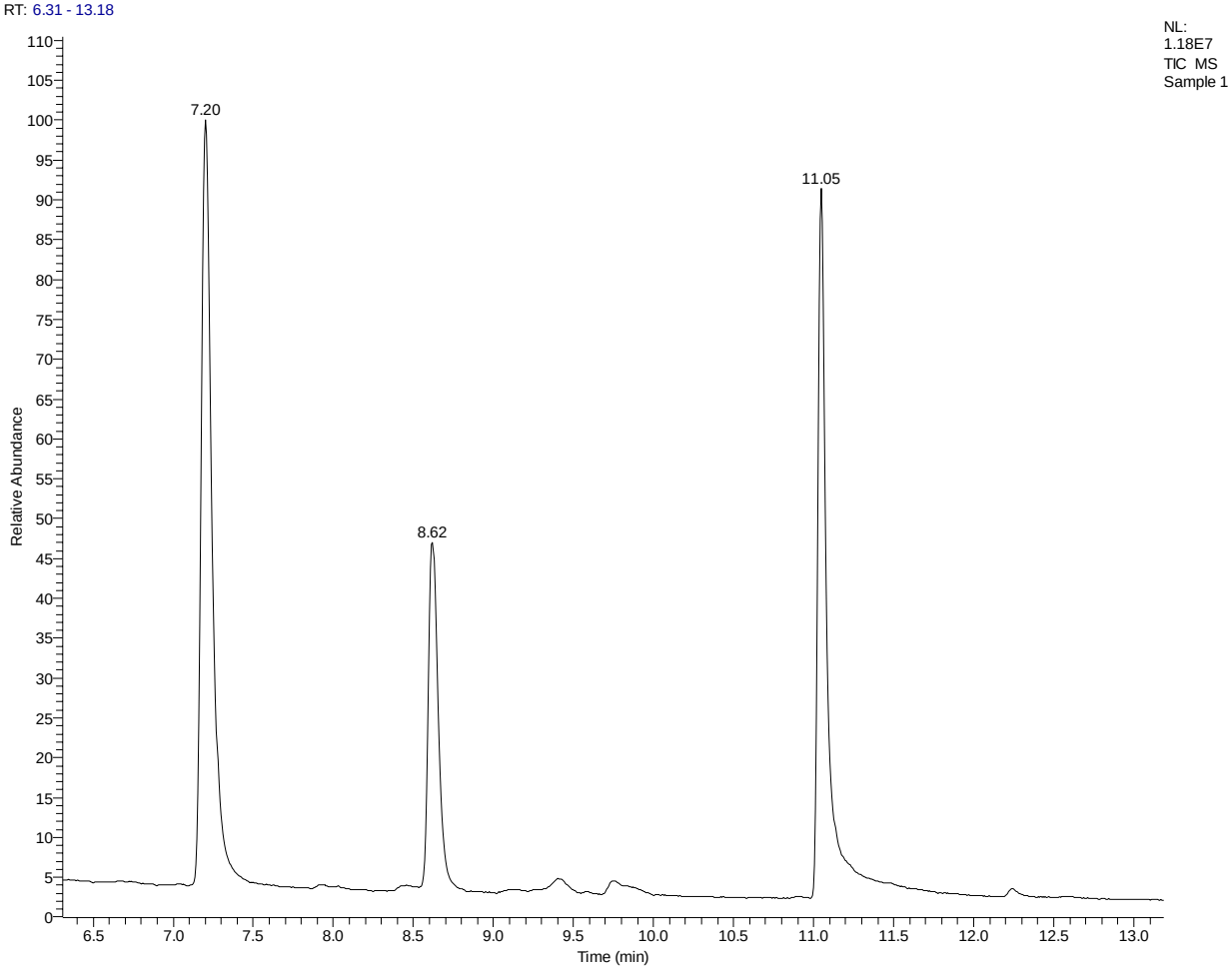


Figure 6S. Measured relative yields of cyclohexanone and cyclohexanol in oxidation of cyclohexane by ozone as a function of ozone bubbling time.