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Models of Terpene Interactions with Ozone and NO_x

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ABSTRACT

Terpenes are a common ingredient among household items, but can cause health issues when in the presence of ozone and NO_x. Terpenes are very volatile and can be reactive given certain conditions and time. Products of reactions between terpenes and ozone or NO_x include carcinogens and particulate matter, both posing serious health risks.

This study looks at creating models to hypothesis how certain terpenes interact with both ozone and NO_x using reaction rates and chemical characteristics found from other studies performed. These models will help influence the finalized physical experiment that Dr. Clack's laboratory will conduct. The final models showed that α -Terpinene and Terpinolene may be very reactive with ozone in a short period of time while D-Limonene, Eucalyptol, and α -Pinene present little to no reactivity with ozone or NO_x within the 30-minute time frame.

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1.0 INTRODUCTION

Many common household products, including cleaners, personal care, and air fresheners, have a component called a terpene within their list of ingredients. A terpene is an organic compound that comes from plants and insects that creates the smells that give many products their names. Terpenes are found in products with pine and citrus smells as well as in many, if not all, essential oils. While terpenes do create a pleasant odor, they also have a negative impact on human health when in the presence of common air pollutants⁶.

Dr. Herek Clack developed a non-thermal plasma reactor (NTP reactor) in which electrical discharge is used to inactivate aerosolized viruses. Figures 1 and 2 show the NTP reactor schematic at different perspectives. The NTP reactor is an alternative to traditional screen filters. Instead of a physical barrier that is made useless if a room is not entirely sealed, the NTP reactor lets air flow through the device freely and inactivates viruses instead of trapping them in a physical barrier⁸.

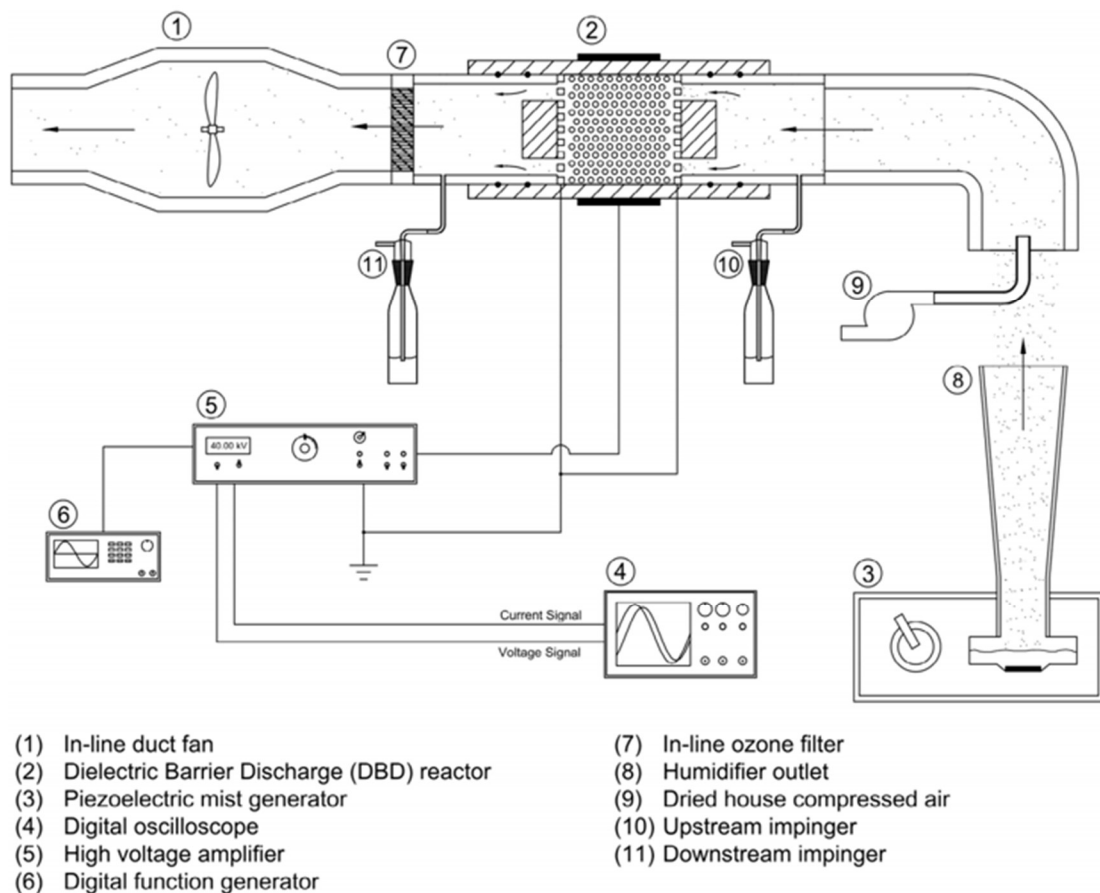


Figure 1. Overall NTP Reactor schematic⁸

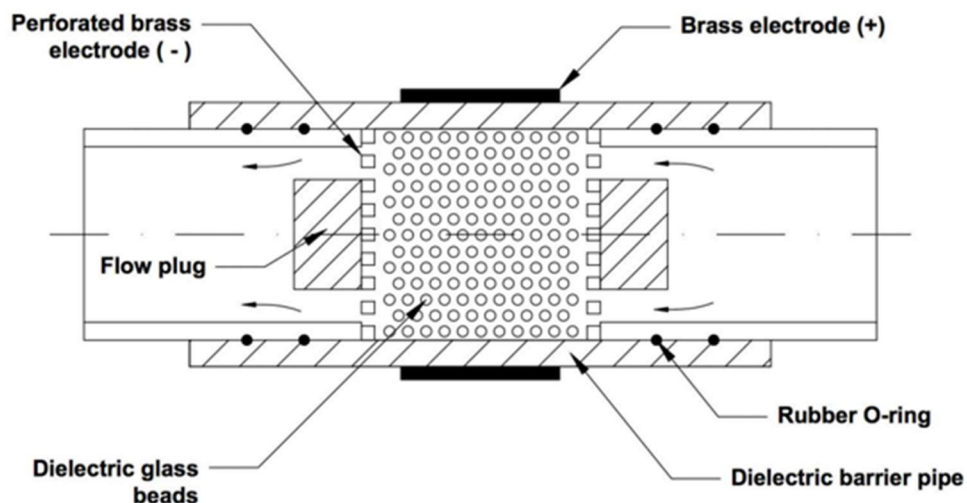


Figure 2. Schematic of Dielectric Barrier Discharge (DBD) Reactor⁸

Terpenes are very volatile and reactive, especially with ozone (O_3). Ozone is a common constituent of indoor air. The terpenes that react with ozone within the scope of this study all have a carbon-carbon double bond ($C=C$). Ozone attacks this double bond to form a primary ozonide (O_3^-). The ozonide is extremely unstable and decomposes quickly into carbonyls and Criegee biradicals (CB). The CB then go on to form carbonyls, hydroxyl carbonyls, dicarbonyls, carboxylic acids, and oxocarboxylic acids⁷. One of the carbonyl products generated is formaldehyde with minor products including acetaldehyde, propionaldehyde, glyoxal, and methyl glyoxal⁷. The ozone/terpene reaction also creates particulate matter that can cause serious respiratory illness with exposure⁵. A similar reaction occurs with NO_x and terpene interactions.

The NTP reactor has many potential applications within different industries and locations, especially where numerous people are in one condensed area. This could include travel, especially air travel and trains, hospitals and other medical facilities, and entertainment venues. The dominant stable oxidants of the NTP reactor, depending on the power settings it is set to, are NO_x and ozone. Using the NTP reactor in an area with scented cleaning products could potentially be a health issue from the ozone-terpene reactions and the NO_x -terpene reactions. This study looks at exactly how ozone and NO_x interaction with different common terpenes in order to determine any potential risks associated with using the NTP reactor in areas with scented products.

2.0 METHODS

For this research, only the following terpenes are discussed:

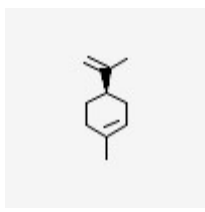
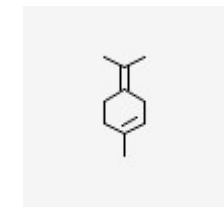
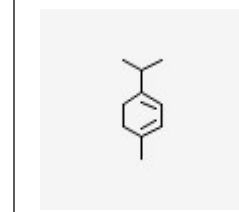

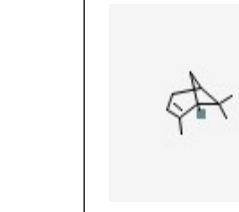

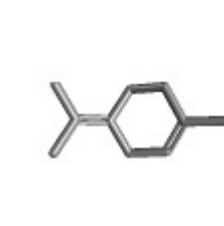
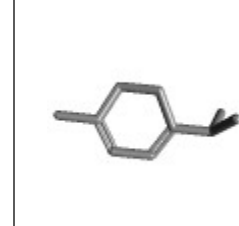

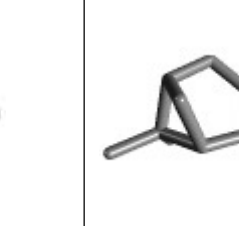
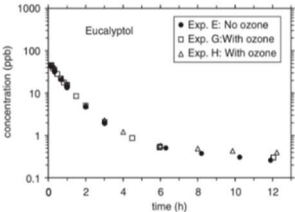
- D-Limonene
- Terpinolene
- α -Terpinene
- Eucalyptol

- α -Pinene

These terpenes were chosen because of how common they are within household products as well as because of previous research conducted on their reactions with air pollutants, especially ozone.

Table 1 shows the chemical makeup of each terpene and its reaction rates with both ozone and NO_x that were compiled from literature reviews.

Table 1. Terpene characteristics and reaction information

Chemical Name	D-Limonene	Terpinolene	α -Terpinene	Eucalyptol	α -Pinene
Chemical Formula	C ₁₀ H ₁₆	C ₁₀ H ₁₆	C ₁₀ H ₁₆	C ₁₀ H ₁₈ O	C ₁₀ H ₁₆
Chemical Structure (2D)*					
Chemical Structure (3D)*					
Chemical Safety*	Flammable, Irritant, Health & Environmental Hazard	Flammable, Irritant, Health & Environmental Hazard	Flammable, Irritant, Health & Environmental Hazard	Flammable, Irritant, Health & Environmental Hazard	Irritant
Reaction Rate With Ozone (@ 23 degC)	5.1 E -6 [1/ppb*s] ²	Exocyclic: 120E-17 [cm ³ /molecule*s] ¹	2110 E -17 +/- 770 [cm ³ /molecule*s] ³	<p>No reaction?⁶</p> 	2.1 E -6 [1/ppb*s] ²
	2 E -16 [cm ³ /molecule*s] ⁴	Endocyclic: 43E-17 [cm ³ /molecule*s] ¹			
Reaction Products With Ozone	carbonyls, hydroxyl carbonyls, dicarbonyls, carboxylic acids, and oxocarboxylic acids	6-oxo-3-(propan-2-ylidene)heptanal, 4-methylcyclohex-3-en-1-one ¹			carbonyls, hydroxyl carbonyls, dicarbonyls, carboxylic acids, and oxocarboxylic acids
Reaction Rate with NO ₂	2 E -16 [cm ³ /molecule*s] ⁴				

*Note: Chemical structure images and safety information from U.S. National Library of Medicine National Center for Biotechnology Information PubChem

The reaction rates for each terpene reaction were converted so all reaction rates are in units of $\text{m}^3/\text{ug}\cdot\text{s}$. This process is different depending on the original units and the calculations for this can be found in Appendix A. There is no specific importance to the reaction rate units chosen. No model was performed for eucalyptol since there does not appear to be reactive in the presence of ozone or NO_x . The blank sections of the table are topics still under research or there were no clear results found within literature reviews.

The reaction rates listed are indicative that these are second order reactions ($1/\text{concentration}\cdot\text{time}$). This information provides a specific equation for modeling the reaction. The equation found below manipulates the data into forming a linear relationship. If the models formed are not linear, it is indicative of an issue within the data or the model itself.

The governing equation for second order reactions is:

$$\frac{1}{A} = k * t + \frac{1}{A_0}$$

Where “A” is the concentration at a given time [ug/m^3], “ A_0 ” is the initial concentration [ug/m^3], “t” is the time elapsed [s], and “k” is the reaction rate [$\text{m}^3/\text{ug}\cdot\text{s}$]. It is assumed that ozone or NO_x is in excess and will not decrease with time and there is no air exchange rate impacting the reaction. The models have a maximum time of 30 minutes to reflect the intended experiment design.

The results of these simplified models helped impact the process of designing a physical experiment using terpenes and ozone within the NTP reactor. A physical experiment delving into ozone-terpene and NO_x -terpene relationships is currently being discussed within the laboratory and the details of this are found in section 5.

3.0 RESULTS AND CONCLUSIONS

The simplified models for each of the terpenes can be found in Appendix B. Each terpene reacted differently within the simplified models. D-Limonene proved to be not very reactive with either ozone or NO_x within the 30 minutes timeframe whereas α -Terpinene and Terpinolene were very reactive with ozone within the 30 minutes. α -Pinene was also not very reactive with ozone within the 30 minutes.

The results from these models will be used to help solidify the design for the physical experiment. Each terpene-gas interaction happens at different rates and creates different specific products. All the models yielded R^2 values of >0.90 except for the α -Terpinene value. The R^2 value for α -Terpinene is 0.57. The R^2 value is important because it shows how close to a perfect linear relationship the data is with 1.0 being a perfect fit and 0.0 being definitively not a fit. An R^2 value of above 0.90 in this instance shows that the relationship is linear. If the R^2 value is less, as it is for α -Terpinene, this shows that the reaction may not be second order or there is an issue within the process. The α -Terpinene graph appears to have the shape of an exponential decay rather than linear (hence the low R^2 value). This could be because of an error in the model or an

error in the calculation or interpretation of the reaction rate. The models are from the same template so an error in the model seems unlikely.

4.0 WORK TO BE DONE

Before a comprehensive experiment can be conducted, the gaps in knowledge of the reactions between the selected terpenes and NO_x needs to be filled. This could be done a few different ways including conducting experiments to conclude a reaction rate or further literature reviews. Using this information, a COMSOL model will be created to mimic a physical experiment and discover if the simplified models are close to the actual chemical interactions. Creating a COMSOL model can also help identify the issue with the α -Terpinene simplified model.

The design for the physical experiment has been in process for months. There are design issues that the laboratory is facing when approaching this experiment. Firstly, the container in which the experiment is held has to be completely sealed off from the outside atmosphere in order to prevent any unaccounted mixing or contamination. This is proven difficult when brainstorming materials for the tank to be composed of and sealed with. Secondly, the air sampling tool used within the laboratory samples at a rate of 1 liter/minute and needs to be used for 30 minutes. The container currently within the design is only 40 liters and using the air sampler would create a major pressure issue within the container by removing 30 liters within the sampling time frame.

The plan for the experiment, if the 40-liter tank is used, is to aerosolize the viruses within a humidifier set up and insert the aerosolized viruses into the tank at the same time as the ozone or NO_x gas. The mixture would sit for approximately 30 minutes and once sampling begins the respective gas would flow into the tank while the air sampler is taking air out. Adding the gas once sampling begins would prevent any implosion issues within the tank.

5.0 REFERENCES

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Appendix A: Unit Conversions

*When Reaction Rate in Units 1/ppb*s:*

$$k_0 [1/ppb*s]$$

$$I = \frac{MW}{10^9 * 0.0224} * 10^6 \rightarrow \text{Converting ppb}_v \text{ to g/m}^3 \text{ to ug/m}^3$$

$$k_2 = \frac{k_0}{I}$$

MW: molar weight [g]

I: intermediate

k₂: reaction rate in units [m³/ug*s]

*When Reaction Rate in Units [cm³/molecule*s]:*

$$k_0 [cm^3/molecule*s]$$

$$I_1 = k_0 * 6.022E23 \rightarrow \text{Original rate times Avogadro's Number [molecules/mole]}$$

$$I_2 = \frac{I_1}{MW * 10^6} \rightarrow \text{Converting moles to grams and grams to micrograms}$$

$$k_2 = \frac{I_2}{(10^2)^3} \rightarrow \text{Converting cm}^3 \text{ to m}^3$$

MW: molar weight [g]

I₁/I₂: intermediate

k₂: reaction rate in units [m³/ug*s]

Appendix B: Simplified Reaction Models

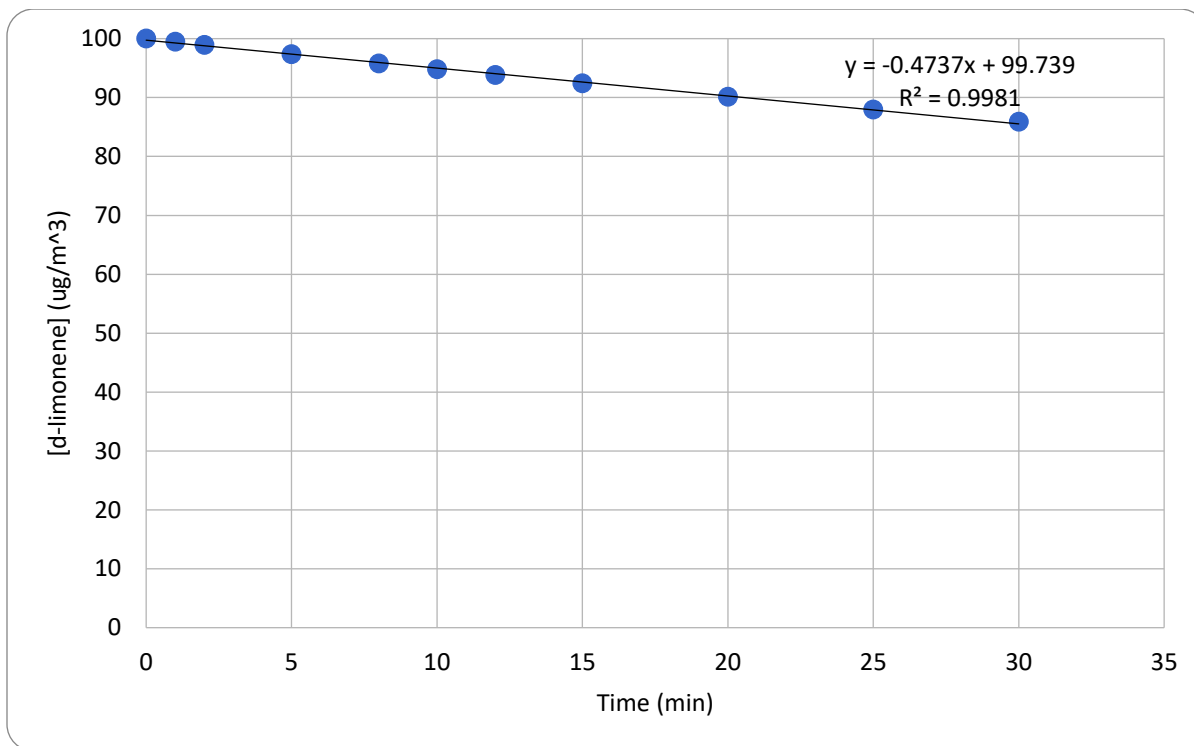


Figure B1. D-Limonene reaction with ozone in excess over time

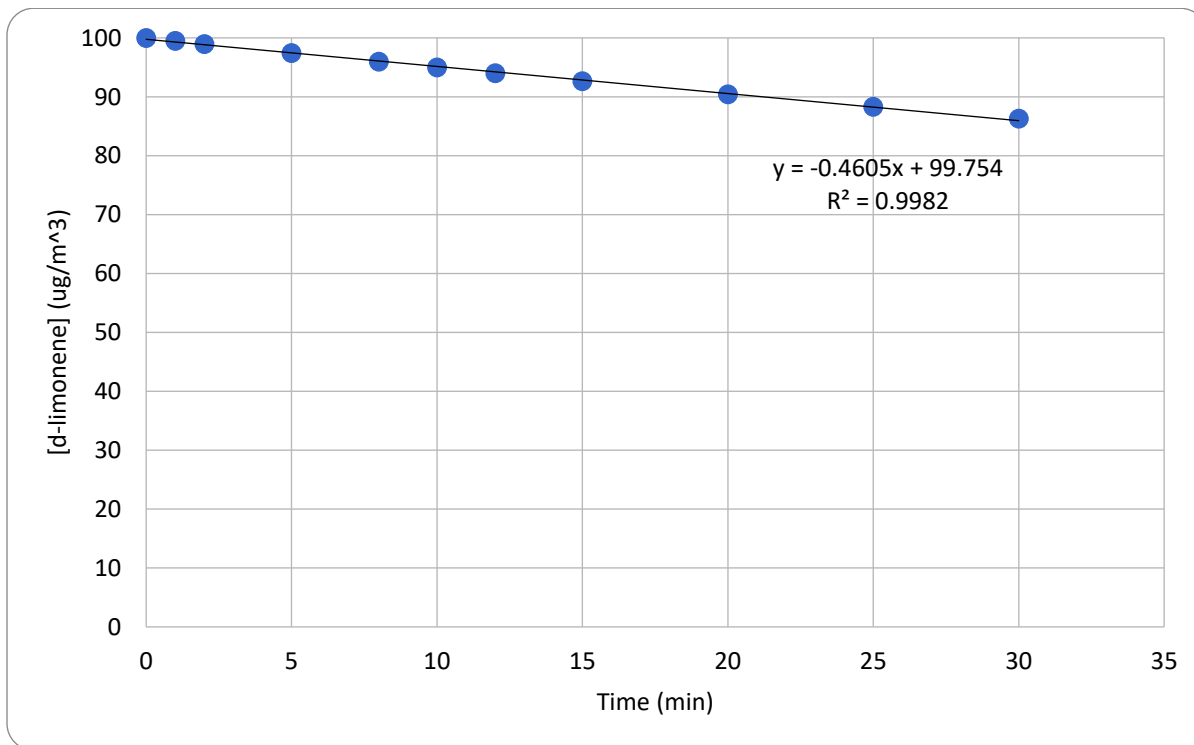


Figure B2. D-Limonene reaction with NO₂ in excess over time

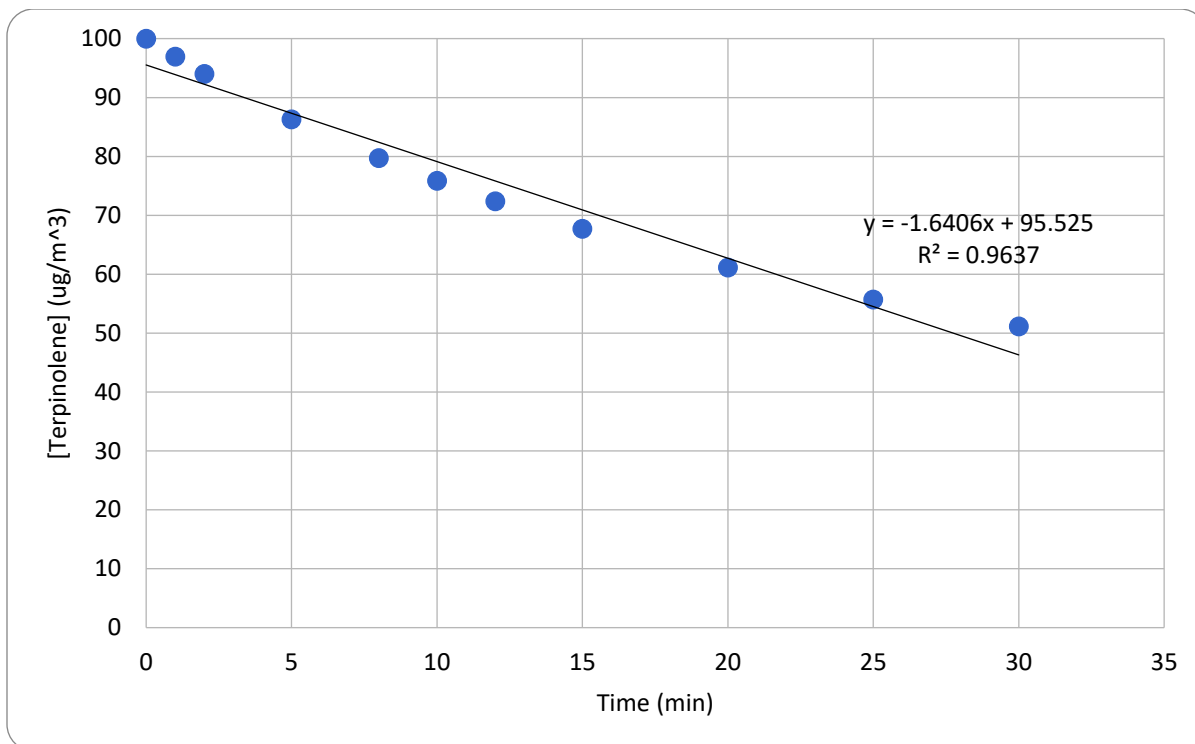


Figure B3. Exocyclic Terpinolene reaction with ozone in excess over time

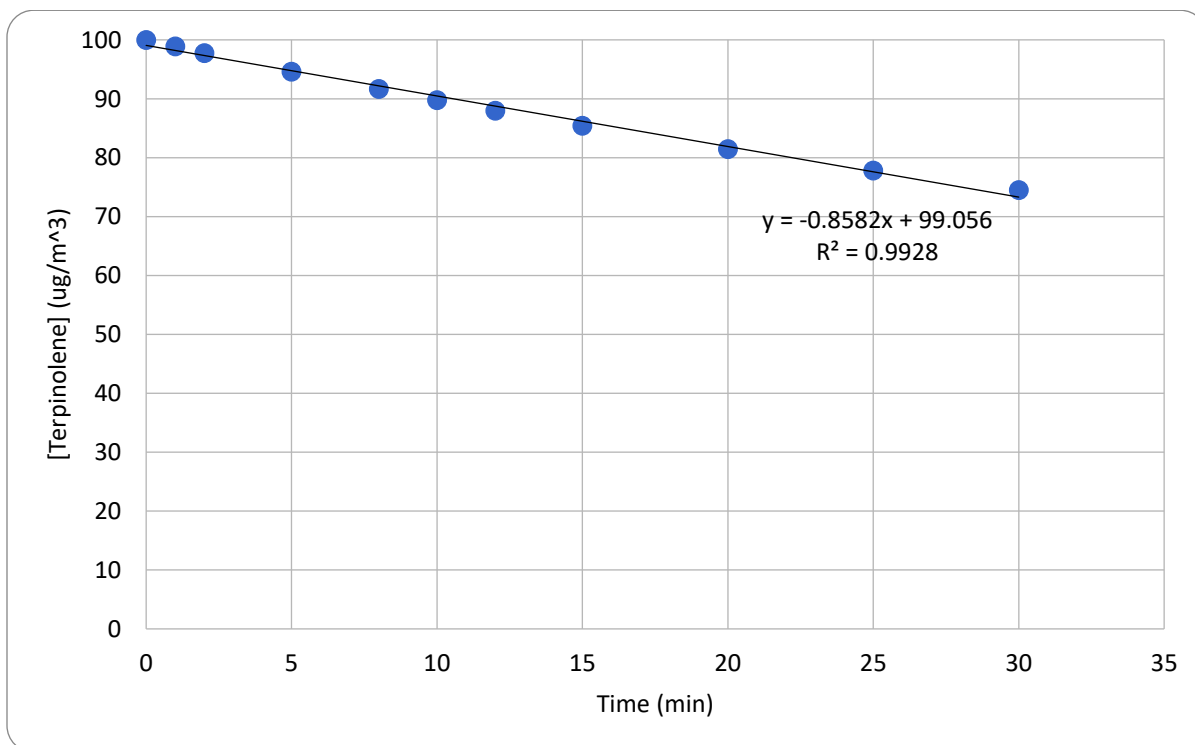


Figure B4. Endocyclic Terpinolene reaction with ozone in excess over time

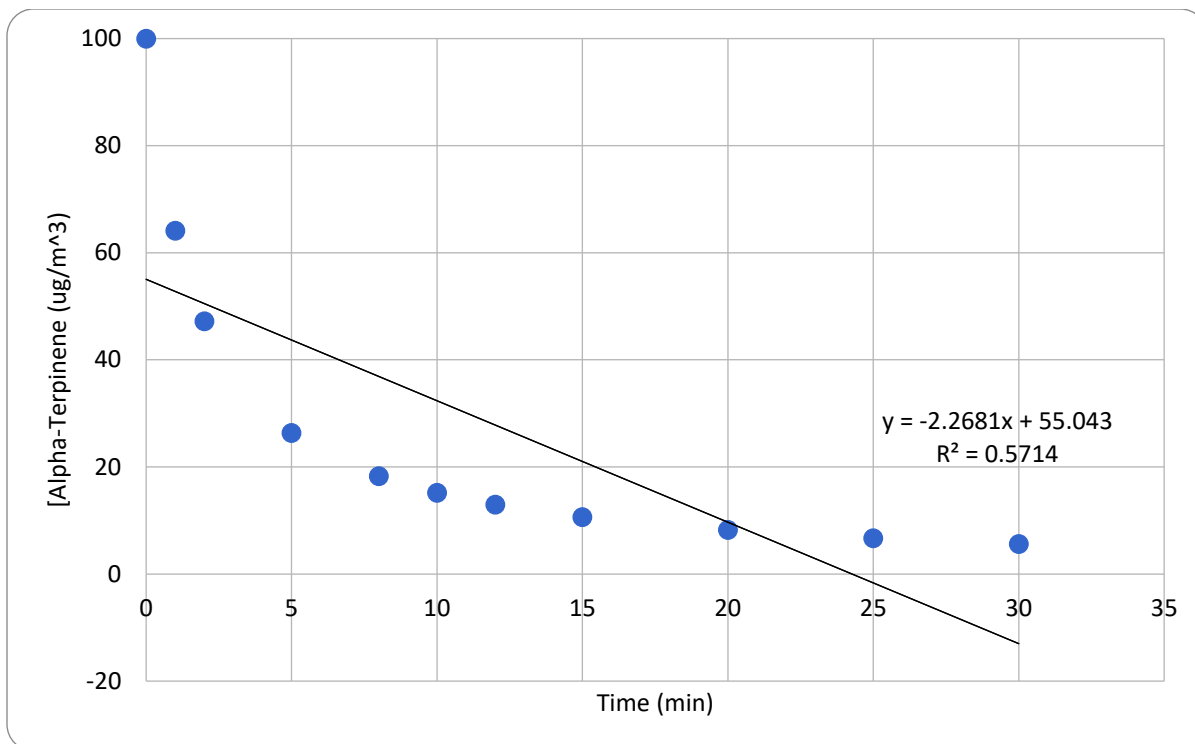


Figure B5. α -terpinene reaction with ozone in excess over time

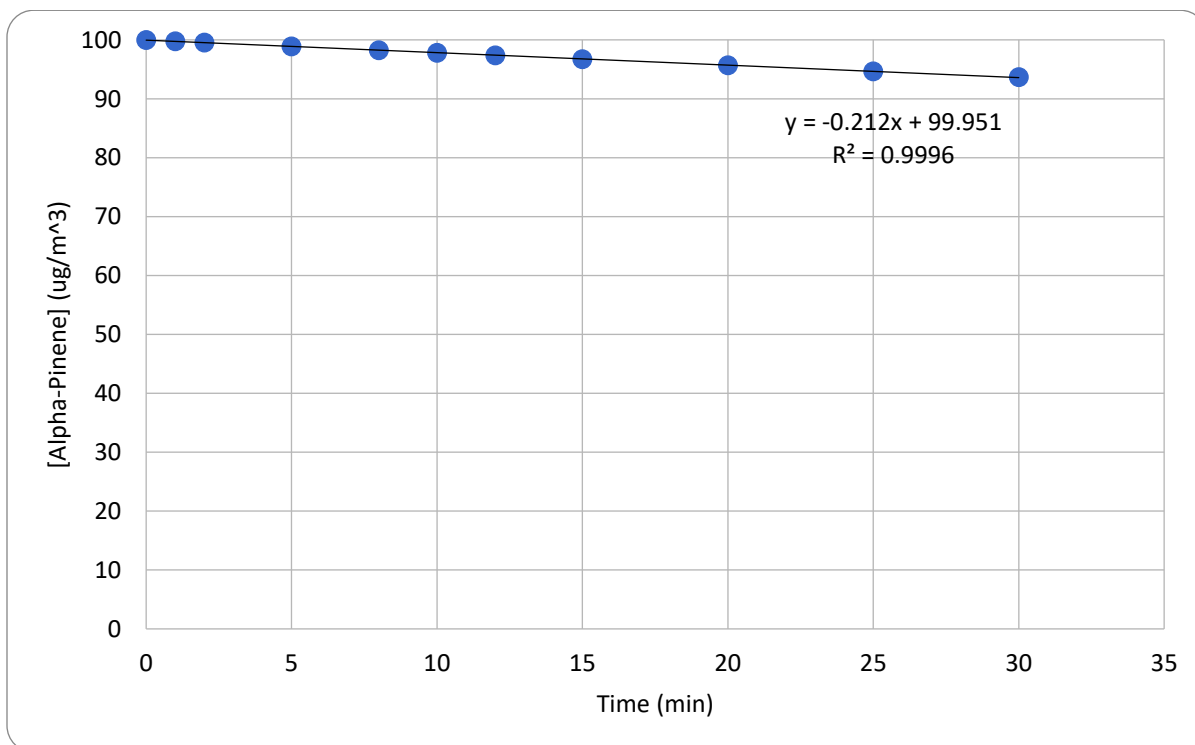


Figure B6. α -Pinene reaction with ozone in excess over time