

Oxidation Mechanisms for Toluene under Atmospheric Conditions

Cherelle Blazer

Academic Affiliation, Fall 2004: Graduate Student, Yale School of Forestry and Environmental Studies

SOARS Summer 2004

Science Research Mentors: John Orlando and Geoff Tyndall

Writing and Communication Mentor: Marika Holland

Peer Mentor: Roberto Cancel

ABSTRACT

Toluene is a hydrocarbon of anthropogenic origin that contributes to ozone-producing photochemistry in urban areas. Like all hydrocarbons, toluene oxidizes via the production of peroxy radicals which, in the presence of nitrogen oxides (NO_x), either generate ozone or lead to organic nitrate production. Organic nitrates are stable compounds that are ozone-limiting because their formation removes NO_x and organic radicals from the system. While it is generally believed that organic nitrate yields increase with increasing pressure, increasing number of carbons in the parent hydrocarbon, and decreasing temperature; this process has not been studied in any detail for toluene. The benzyl nitrate yield from toluene oxidation specifically has only been the subject of one other study which was restricted to room temperature. In this present work, the goal was to examine the yield of benzyl nitrate over a range of temperatures and pressures in a temperature-regulated stainless steel environmental chamber. The study was conducted by irradiating mixtures of toluene, NO_x, oxygen, nitrogen and chlorine in the chamber. Infrared spectra were recorded and analyzed to quantify the products formed as toluene was consumed. The results suggest that increased pressure increases benzyl nitrate yields. This finding is in agreement with results found by colleagues at Ford Motor Company. However, preliminary investigations do not reveal a strong correlation between benzyl nitrate yield and varying temperature.

This work was done under the auspice of the Significant Opportunities in atmospheric Research and Science (SOARS) program of the University Corporation for Atmospheric Research, with funding from the National Science Foundation, the U.S. Department of Energy, the National Oceanic and Atmospheric administration, and Goddard Space Flight Center, NASA.

INTRODUCTION

The oxidation of toluene in the atmosphere is important to study because it is emitted plentifully from anthropogenic sources, is very reactive in the air, contributes to ozone- and smog-producing photochemistry and results in the formation of secondary aerosols. Additionally it may serve as a model for how other hydrocarbons of similar size and structure may behave in the atmosphere.

The objective of this summer's research is to calculate a branching ratio of the yield of benzyl nitrate in the oxidation of toluene under atmospheric conditions, in particular as a function of temperature and pressure. These data will be useful in ascertaining the contribution of toluene to photochemical smog formation, and will also provide valuable information on the mechanism by which organic nitrates are formed in the reactions of peroxy radicals with NO.

Toluene is an aromatic hydrocarbon emitted to the atmosphere from anthropogenic sources such as the process of refining gasoline and other fuels from crude oil, making coke from coal, producing paints, paint thinners, fingernail polish, lacquers, adhesives, rubber, and tanning leather. Biogenic sources are minor, but include crude oil and the tolu tree.¹

The largest chemical use for toluene is in the manufacture of benzene and urethane. Though toluene is not as hazardous as some other hydrocarbons such as benzene which is a carcinogen, it is much more reactive in the atmosphere, is emitted plentifully, and contributes to photochemical smog through the formation of pollutants such as, tropospheric ozone, peroxy acetyl nitrate (PANs) and secondary aerosols.

This work was done under the auspice of the Significant Opportunities in atmospheric Research and Science (SOARS) program of the University Corporation for Atmospheric Research, with funding from the National Science Foundation, the U.S. Department of Energy, the National Oceanic and Atmospheric Administration, and Goddard Space Flight Center, NASA.

From a toxicological point of view, toluene is an important neurotoxin in urban industrialized areas, the workplace and in households. The Environmental Protection Agency (EPA) has not classified toluene as a carcinogen but has found it to potentially cause the following health effects when people are exposed to it for relatively short periods of time: minor nervous system disorders such as fatigue, nausea, weakness, confusion.

Long-term exposure can result in the following effects: more pronounced nervous disorders such as spasms, tremors, impairment of speech, hearing, vision, memory, coordination; liver and kidney damage, loss of consciousness, coma and, in extreme cases, death.

According to the EPA, production of toluene was 6.4 billion lbs in 1993. It is released in wastewaters or by spills on land during the storage, transport and disposal of fuels and oils.

From 1987 to 1993, the EPA's Toxic Chemical Release Inventory reports toluene releases to land and water totaled over 4 million lbs., primarily from petroleum refining industries. The largest releases over all occurred in Texas and California. The largest releases directly to water occurred in Connecticut and West Virginia.²

Toluene oxidation in the atmosphere is controlled primarily by its reaction with OH. The mechanism involved is complex and not quantitatively understood. The initial OH-toluene reaction occurs via two pathways, addition to the aromatic ring and abstraction from the methyl group. Since the focus of the present study is on the abstraction channel only, chlorine atoms (which react only via abstraction) are used to

initiate the photochemistry instead of OH. Thus, when oxidized by Cl-atoms, toluene

This work was done under the auspice of the Significant Opportunities in atmospheric Research and Science (SOARS) program of the University Corporation for Atmospheric Research, with funding from the National Science Foundation, the U.S. Department of Energy, the National Oceanic and Atmospheric Administration, and Goddard Space Flight Center, NASA.

acts much like an alkane. A relatively simple alkylperoxy radical, $\text{C}_6\text{H}_5\text{CH}_2\text{O}_2$, is generated, which reacts with NO to form either an alkyl nitrate or an alkoxy radical. The nitrate is a termination point in the ozone producing photochemistry because it is stable, will not react further, and acts as a sink for reactive radicals:

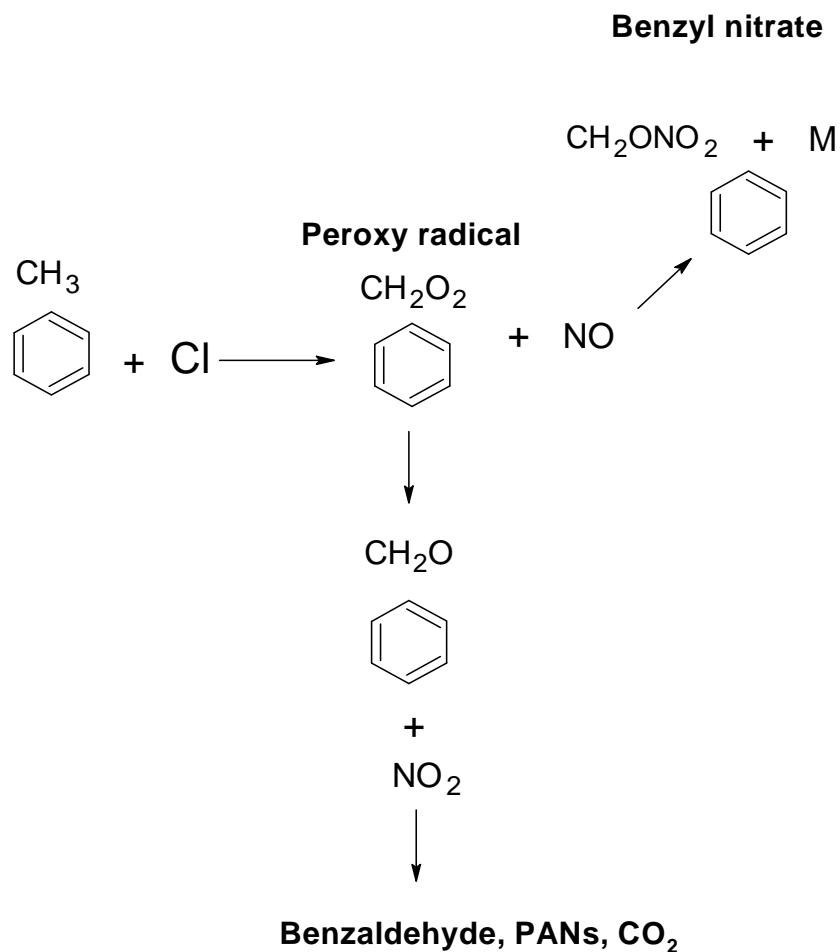
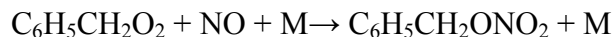
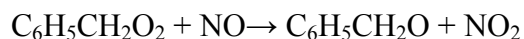


Figure 1 branching ratio of Benzyl nitrate

Rodger Atkinson's studies on alkyl nitrate formation:

This work was done under the auspice of the Significant Opportunities in atmospheric Research and Science (SOARS) program of the University Corporation for Atmospheric Research, with funding from the National Science Foundation, the U.S. Department of Energy, the National Oceanic and Atmospheric administration, and Goddard Space Flight Center, NASA.

Dr Rodger Atkinson used an equation based on a generalization of the fall off equations by Troe for simple addition reactions in the fall off regions, that calculates the organic nitrate yield from alkanes based on the belief that organic nitrate yield increases with pressure, # of carbons, and decrease in temperature.³ Though this is the basic belief of all organic nitrate production Benzyl nitrate yields from toluene specifically has not been examined. Scientist at the Ford motor company began investigating this problem oxidizing toluene in their lab to produce benzyl nitrate at room temperature only. They studied the pressure dependence of organic nitrate production by varying the pressure in their experiments from 68 Torr to 800 Torr. Their results were as expected from Dr Atkinson's equation. As pressure increased benzyl nitrate yields increased. The current study takes that research on step further by recreating their experiments on pressure dependence and incorporating temperature dependence as well.

METHODOLOGY

The Cl-atom initiated oxidation of toluene in air is being examined in a 47-L stainless steel chamber, using infrared spectroscopy to quantify products. Infrared spectra are taken between 800 and 3900 cm^{-1} at a resolution of 1cm^{-1} using a Bomen DA3.01 FTIR spectrometer. First, 150 Torr of O_2 is admitted to the chamber. Then gaseous samples of toluene are introduced from a gas handling system that is attached to the chamber. A known pressure is accumulated in a calibrated 1-L glass bulb and swept into the chamber using dry nitrogen. The same is done for NO , and Cl_2 and N_2 bath gas is added until a

total pressure of 700 Torr is achieved. In some cases, the sample is allowed to stand in

This work was done under the auspice of the Significant Opportunities in atmospheric Research and Science (SOARS) program of the University Corporation for Atmospheric Research, with funding from the National Science Foundation, the U.S. Department of Energy, the National Oceanic and Atmospheric administration, and Goddard Space Flight Center, NASA.

the dark for 10-15 min to ascertain any reactions occurring due to “night time” chemistry. In all cases, the gas mixtures are exposed to UV radiation for varying time intervals (2-5 min) and infrared spectra are taken between the irradiation periods to quantify the loss of toluene and to quantify the products that are generated⁴.

Photolysis is accomplished using a xenon arc lamp filtered by a Corning glass 7-54 filter (240-415nm). The toluene is quantified by spectral stripping of bands at 1500 cm^{-1} and 1050 cm^{-1} . Benzyl nitrate bands appear at 1280 cm^{-1} - 1290 cm^{-1} , and 1660 cm^{-1} .

The yields of benzyl nitrate and other photolysis products are obtained by comparison of the product spectra with those of pure standards.

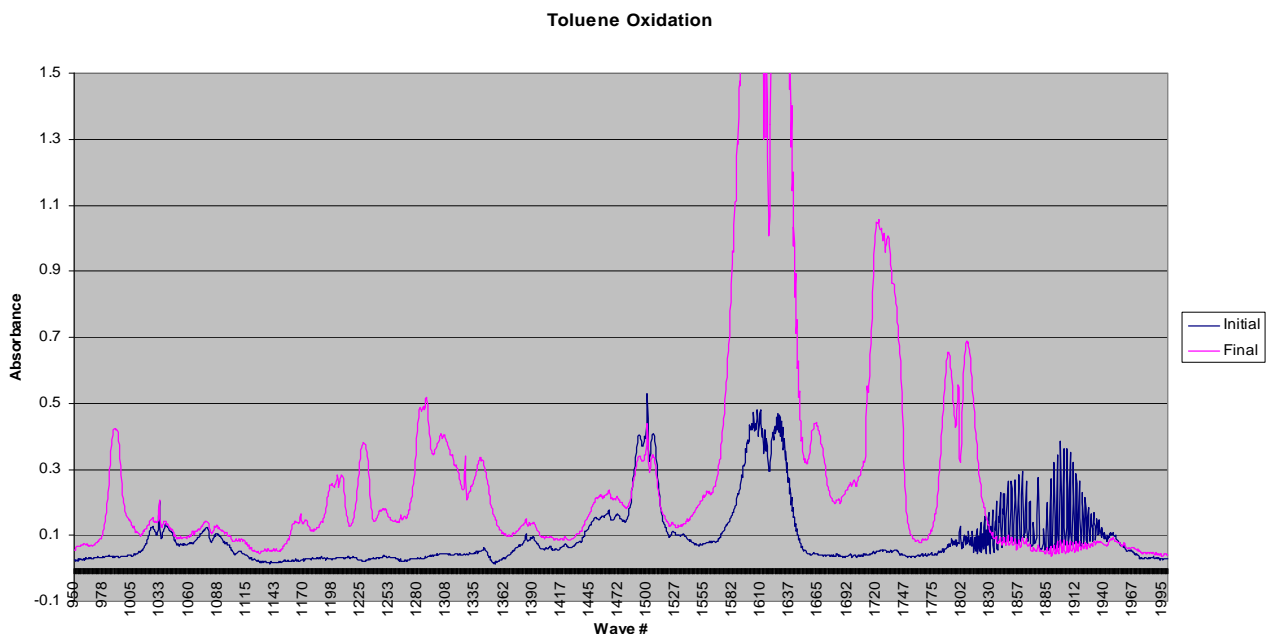


Figure 2 toluene oxidation spectra at 298K

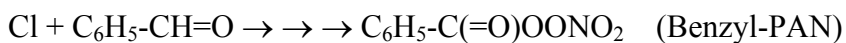
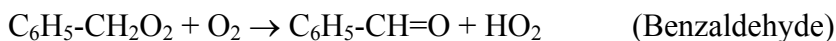
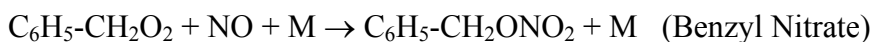
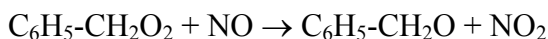
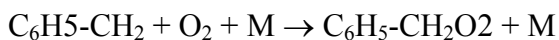
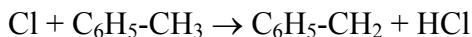
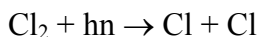
This work was done under the auspice of the Significant Opportunities in atmospheric Research and Science (SOARS) program of the University Corporation for Atmospheric Research, with funding from the National Science Foundation, the U.S. Department of Energy, the National Oceanic and Atmospheric administration, and Goddard Space Flight Center, NASA.

RESULTS

Figure 2 above is a typical spectra at room temperature, 298K. The blue line is an initial run where the mixture of gasses has not yet been irradiated. Where the X-axis is wave number and Y-axis is absorbance: peaks of NO (1830-1940) and toluene (1033 & 1500) are high, NO₂ (1610) is relatively low, and most of the products have not been made. The pink line is the same gas mixture after five irradiations. The NO and toluene are being reacted away and the products: benzyl PAN (1225 & 1000), benzyl nitrate (1170), CO₂ (2300), benzaldehyde (1198 & 1720), and NO₂.

The products formed as a result of toluene oxidation are described in detail below in chemical equation and **Figure 3**.

Products:



This work was done under the auspice of the Significant Opportunities in atmospheric Research and Science (SOARS) program of the University Corporation for Atmospheric Research, with funding from the National Science Foundation, the U.S. Department of Energy, the National Oceanic and Atmospheric administration, and Goddard Space Flight Center, NASA.

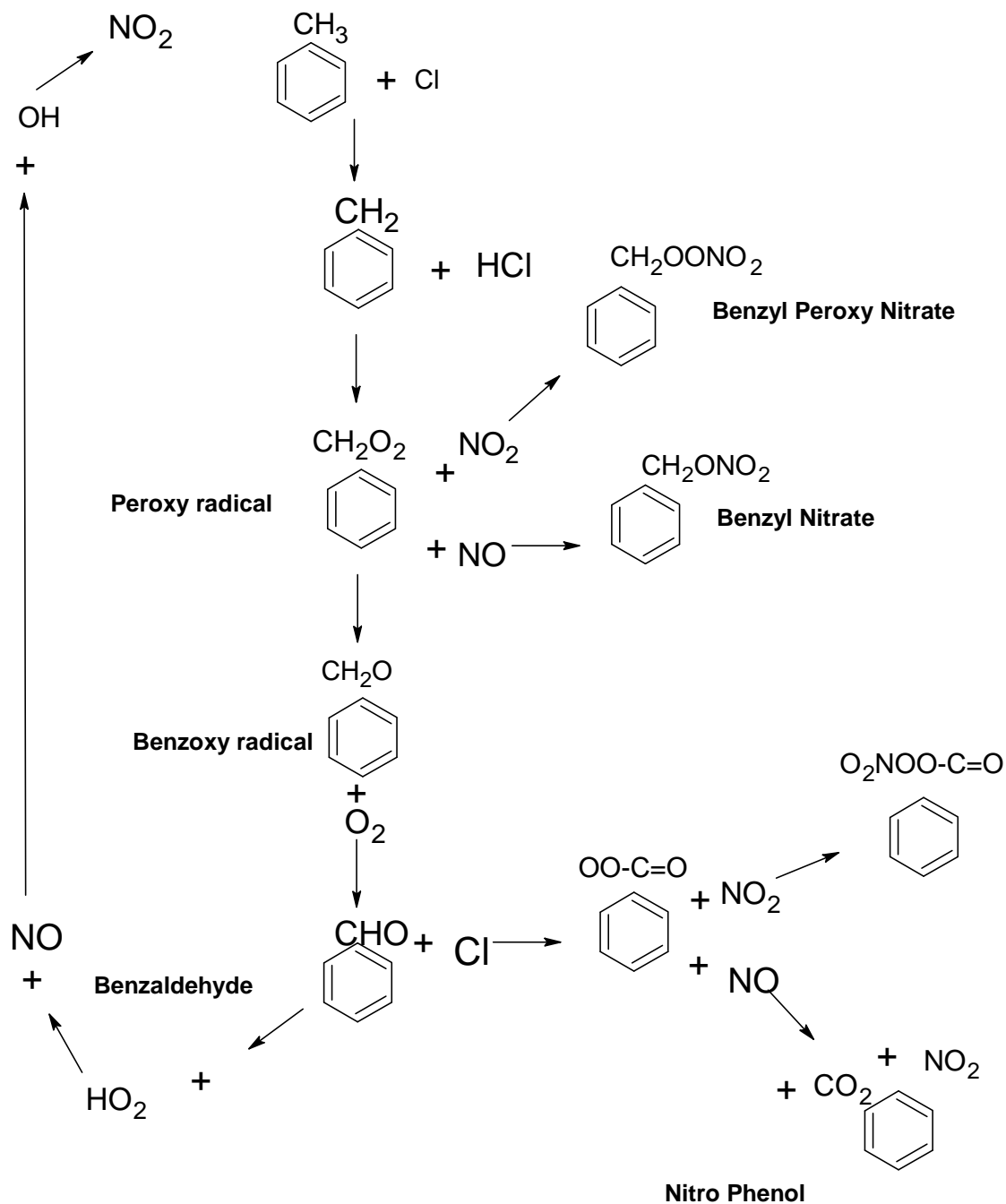


Figure3

The following graphs show the benzyl nitrate yield and product yield versus toluene consumption for all experiments performed at 300 Torr and 700 Torr.

This work was done under the auspice of the Significant Opportunities in atmospheric Research and Science (SOARS) program of the University Corporation for Atmospheric Research, with funding from the National Science Foundation, the U.S. Department of Energy, the National Oceanic and Atmospheric administration, and Goddard Space Flight Center, NASA.

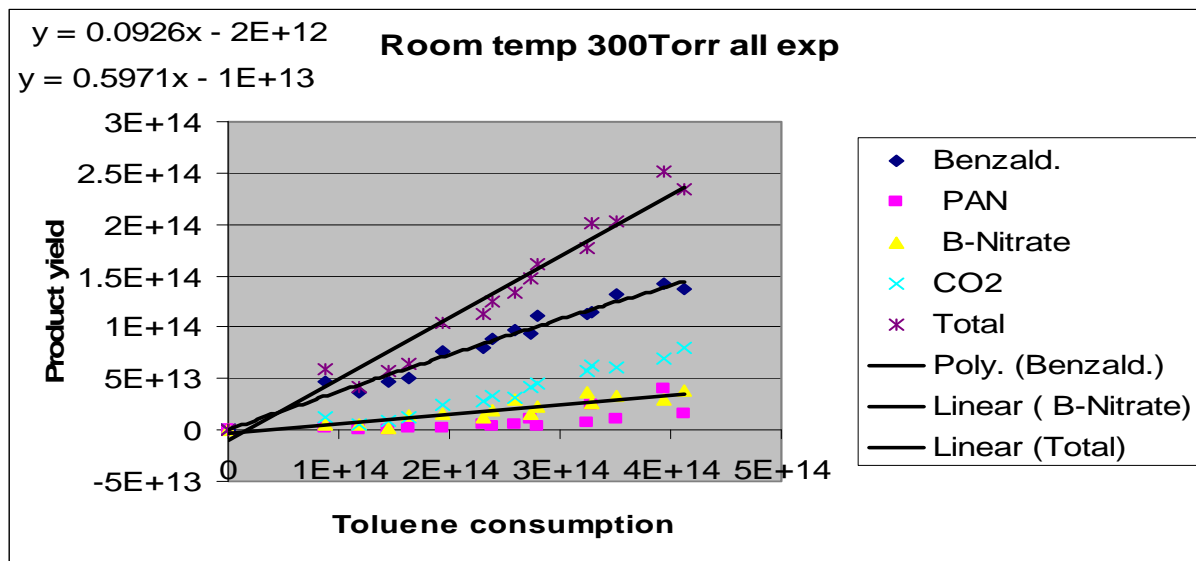


Figure 4

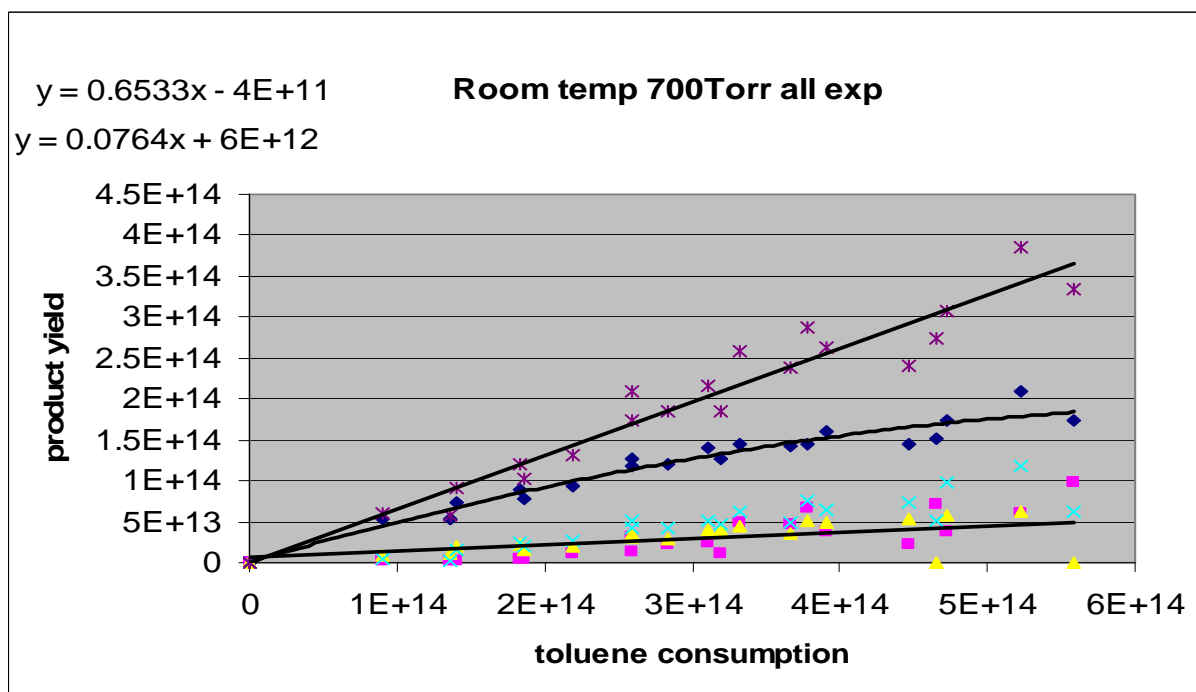


Figure 5

This work was done under the auspice of the Significant Opportunities in atmospheric Research and Science (SOARS) program of the University Corporation for Atmospheric Research, with funding from the National Science Foundation, the U.S. Department of Energy, the National Oceanic and Atmospheric administration, and Goddard Space Flight Center, NASA.

The slope of the Benzyl nitrate trend line quantifies the benzyl nitrate yields for the experiments at 300 and 700 Torr as 9% and 12% respectively. This result is to be expected based on Atkinson's findings and are in agreement with the results from Ford Motor Company seen in **Figure 6**.

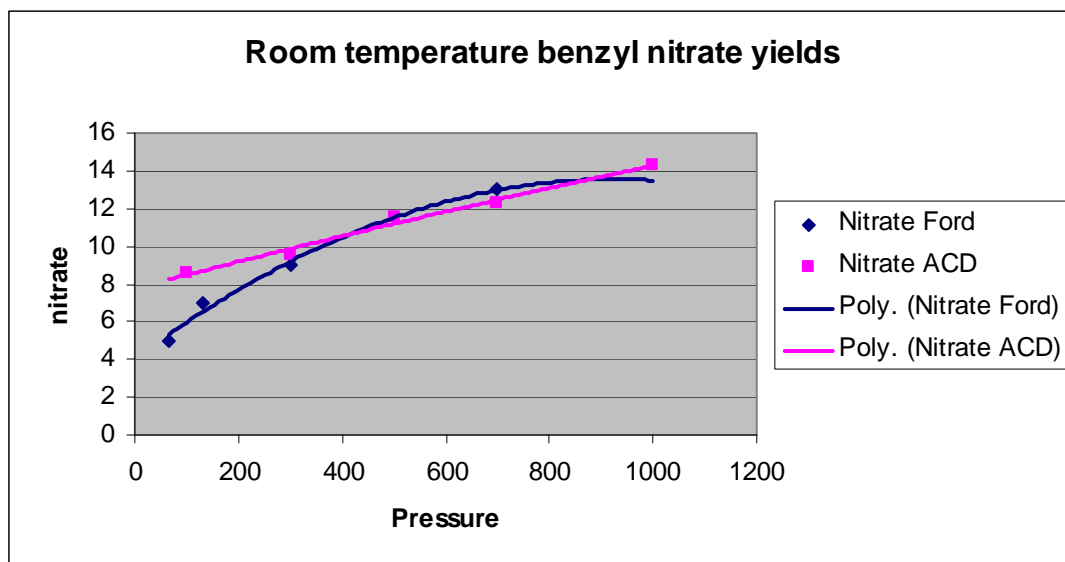


Figure 6

As described by Figure 6 above, multiple experiments were conducted at room temperature, 298K, for each pressure. The range of pressures spans from 100-1000 Torr where 700 Torr equals one atmosphere. As expected the benzyl nitrate yield increased as the pressure was increased in the environmental chamber.

The focus of this study is to rest the temperature dependence in addition to the pressure dependence of benzyl nitrate yields from toluene oxidation. To accomplish this goal, preliminary experiments were performed at 260K and two pressures: 300 and 700 Torr.

This work was done under the auspice of the Significant Opportunities in atmospheric Research and Science (SOARS) program of the University Corporation for Atmospheric Research, with funding from the National Science Foundation, the U.S. Department of Energy, the National Oceanic and Atmospheric administration, and Goddard Space Flight Center, NASA.

The results of these low temperature experiments are illustrated below in **Figures 7 & 8**.

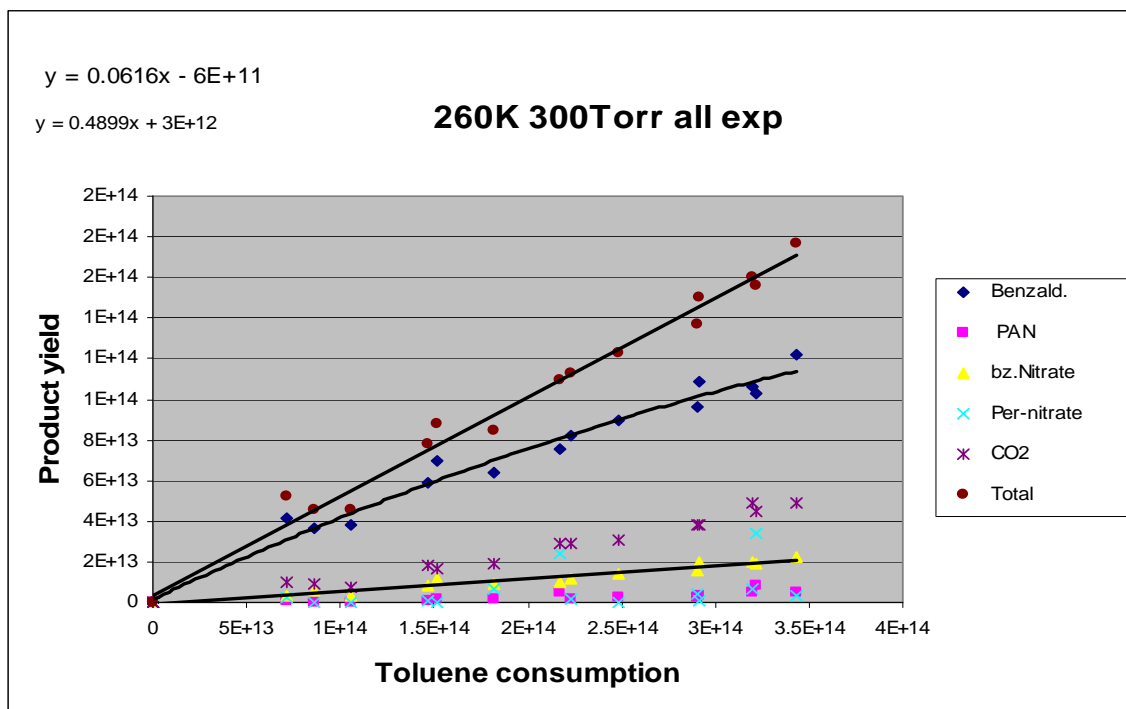


Figure 7

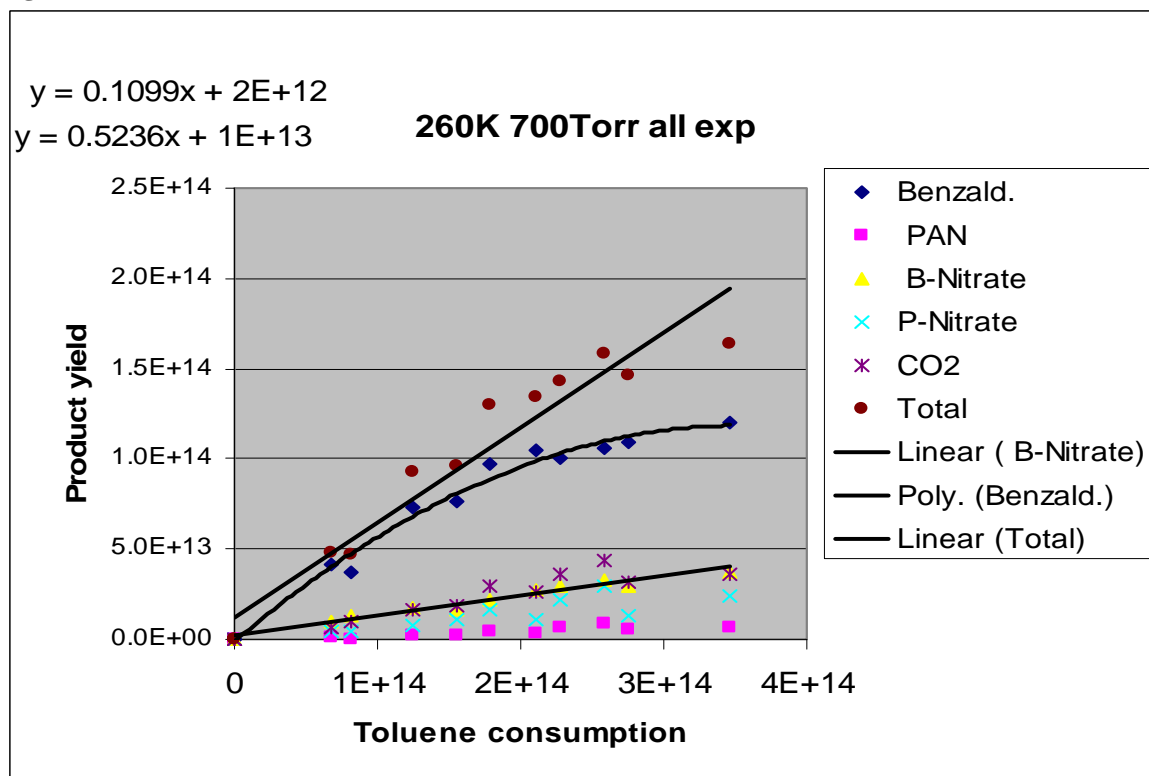


Figure 8

This work was done under the auspice of the Significant Opportunities in atmospheric Research and Science (SOARS) program of the University Corporation for Atmospheric Research, with funding from the National Science Foundation, the U.S. Department of Energy, the National Oceanic and Atmospheric administration, and Goddard Space Flight Center, NASA.

Contrary to what we would expect to find based on Atkinson's premise of organic nitrate yield increasing with decreasing temperature, at 260K the benzyl nitrate production decreased from 9% to 6% at 300 Torr and 12% to 10% at 700Torr.

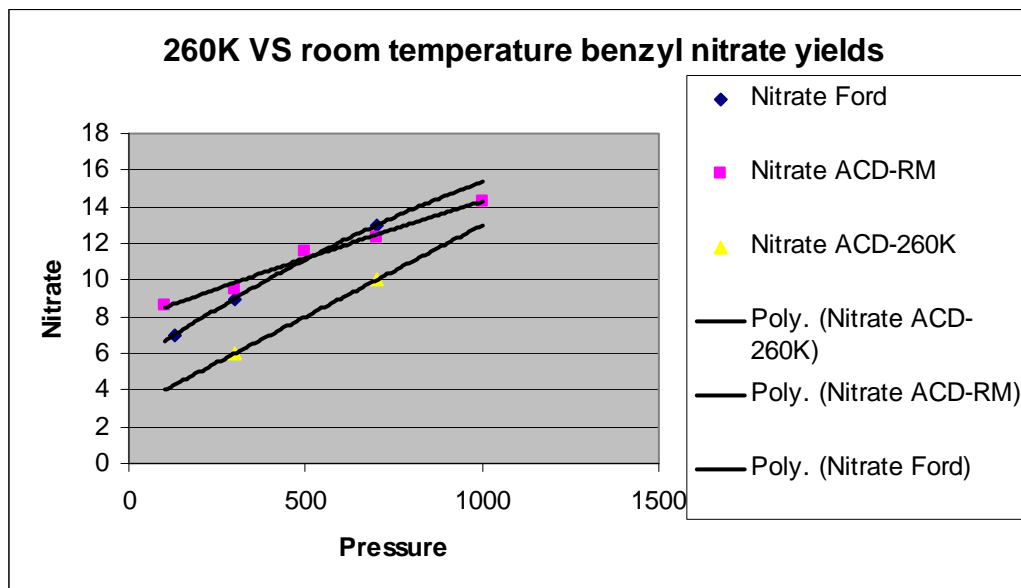


Figure 9

There are two possible reasons for these findings:

Explanation 1.) A trend line fitted to the total product data points reveals that at 300 and 700Torr only 48 and 52% of the reaction is going toward creating the products measured. If roughly 10% of the reaction is going toward making benzyl nitrate and 50% is creating measured products, then 40% of the chemistry is unaccounted for. Discussed earlier the research focuses on the branching ration illustrated in **Figure 1**. The toluene oxidation reactions illustrated in **Figure 3** shows a few other reactions that may be competing with the benzyl nitrate yield. In particular, nitro phenol and benzyl peroxy nitrate are more stable at low temperatures and complicating the results.

This work was done under the auspice of the Significant Opportunities in atmospheric Research and Science (SOARS) program of the University Corporation for Atmospheric Research, with funding from the National Science Foundation, the U.S. Department of Energy, the National Oceanic and Atmospheric administration, and Goddard Space Flight Center, NASA.

Explanation 2.) The Atkinson equation for organic nitrate yield is incorrect. According to the equation Atkinson formulated to predict organic nitrate yields, the results of these experiments and the Ford results should be much higher.

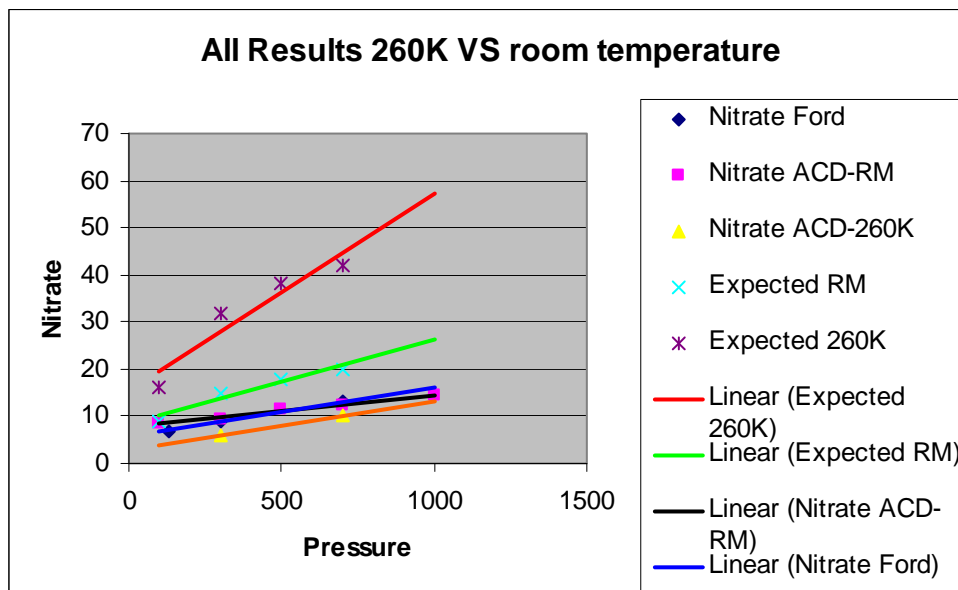


Figure10

These findings will be further investigated this Spring.

CONCLUTION

This research is most interested in the products of toluene photochemical reactions. The mechanism involved in benzyl nitrate yield and resulting branching ratio are very complex, and only partially understood at this point. In particular in the yield of benzyl nitrate as a function of pressure and temperature is important because it is a termination point in ozone and smog producing photochemistry and no published studies have been conducted at low temperature. Knowing the branching ration between benzyl

This work was done under the auspice of the Significant Opportunities in atmospheric Research and Science (SOARS) program of the University Corporation for Atmospheric Research, with funding from the National Science Foundation, the U.S. Department of Energy, the National Oceanic and Atmospheric administration, and Goddard Space Flight Center, NASA.

nitrate reactions and the reactions that go on to produce benzaldehyde, benzyl PAN, and eventually O_3 ; is crucial to fully understanding the contribution of hydrocarbons to harmful pollution production. The more organic nitrates formed, the less opportunity there is for more harmful and reactive products to be formed⁵.

Next steps toward realizing these goals are: 1) to quantify the competing nitro phenol reaction; 2) calculate the reaction rate between Cl and toluene at low temperatures; 3) run more experiments at a wide range of temperatures.

¹ Agency for Toxic Substances and Disease Registry, <http://www.atsdr.cdc.gov/tfacts56.html>, June 16, 2004.

² United States Environmental Protection Agency, http://www.epa.gov/safewater/contaminants/dw_contamfs/toluene.html, Ground Water and Drinking Water, June 16, 2004

³ William P.L. Carter and Roger Atkinson, 1989: Journal of Atmospheric Chemistry: Alkyl Nitrate Formation from the Atmospheric Photooxidation of Alkanes; a Revised Estimation Method, 8; 165-173

⁴ Orlando, J. J.; Tyndall, G. S.; Betterton, E. A., 2004: Atmospheric chemistry of HN_3 : UV absorption spectrum, OH reaction rate coefficient, and reactions of the N_3 radical, *Environ. Sci. Technol.*, submitted.

⁵ Atmospheric Chemistry and Global Change, editors G. P. Brasseur, J. J. Orlando, and G. S. Tyndall, Oxford Press, New York, 1998.