SOA Formation from Toluene Oxidation in the Presence of Inorganic Aerosols

Gang Cao

A dissertation submitted to the faculty of the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Environmental Sciences and Engineering, Gillings School of Global Public Health.

Chapel Hill
2008

Approved by:

Dr. Myoseon Jang

Dr. Harvey Jeffries

Dr. Chong Kim

Dr. David Leith

Dr. Deborah Luecken

Dr. Ken Sexton
ABSTRACT

GANG CAO: SOA Formation from Toluene Oxidation in the Presence of Inorganic Aerosols
(Under the direction of Dr. Myoseon Jang)

Recent studies have shown that particle acidity increases SOA yields from biogenic precursors (e.g. isoprene and terpenes). This dissertation is a first attempt to investigate systematically impacts of particle acidity on aromatic SOA formation via heterogeneous reactions. A large number of toluene SOA yield experiments have been conducted in a 2 m$^3$ indoor Teflon photoirradiation chamber under various experimental conditions (e.g. light conditions, NO$_x$ concentrations, humidity, inorganic seed compositions). In Chapter II and III, significant increase in toluene SOA yields by the presence of acidic sulfate have been observed under most of our experimental conditions, except at high NO$_x$ levels that are however not usual in the real atmosphere.

The observations of our yield studies stimulate the further investigation into the impacts of heterogeneous chemistry on partitioning of semivolatile organic compounds on aromatic SOA and also motivate the exploration of a SOA model including partitioning and heterogeneous chemistry for toluene SOA prediction. In Chapter IV, a newly developed approach using deuterated alkanes has been employed to semiempirically determine the model structure of oligomer species of the toluene SOA. The resulting SOA compositions containing oligomeric species are used to estimate absorptive partitioning coefficients ($^i K_{pi}^{cal}$) of toluene oxygenated products. The results show a considerable discrepancy between
and experimental partitioning coefficients ($K_{p}^{exp}$) of SOA products, suggesting that heterogeneous chemistry in aromatic SOA significantly impacts the gas particle partitioning of organic compounds.

In Chapter V, a predictive model for SOA formation through both partitioning and heterogeneous reactions is further explored for SOA produced from toluene oxidation. The SOA model performance is evaluated using a variety of SOA experiments in terms of the ozone formation, the NO to NO$_2$ conversion and the decay of toluene in the gas phase as well as the production of SOA mass. The model allows us to estimate the relative importance of partitioning and heterogeneous chemistry for SOA formation. Finally, Chapter VI summarizes the key findings of the dissertation research and provides the recommendations for future studies.
To my husband, my parents and my brother who love me so much
I wish to thank my advisor, Dr. Myoseon Jang, for her guidance and support through doing the research and writing the dissertation. The personal lessons and professional research skills I have learned from her will be invaluable in all of my future endeavors.

I also would like to give deep thanks to the remaining members of my doctoral committee: Dr. Harvey Jeffries, Dr. Chong Kim, Dr. David Leith, Dr. Deborah Lueckcn and Dr. Ken Sexton for their time, interest and helpful comments on this dissertation and also for their understanding and continuous support while I was doing the research off-campus. I must thank my department Chairs, Dr. Michael Aitken and Dr. Donald Fox for their special consideration and support with which I can continue my PhD study and complete my dissertation work away from UNC-Chapel Hill. Special thanks to Mr. Jack Whaley for his all-the-time prompt response to my request throughout my entire PhD study and for his kind help and useful suggestions to make my student life easier. I want to thank all of my past and present colleagues in Dr. Jang’s group: Dr. Nadine Czoschke, Dr. Amanda Northcross, Tianyi Chen, Jaeyoun Jang, Hyeonkook Kim for the wonderful mutual learning and teaching experience, the memorable happy time we spent and the precious friendship. I also would like to thank NSF for sponsoring this research and my department for financially supporting my research in the last semester of my PhD study. Finally, I am especially grateful to my husband, my parents and my brother for their unconditional love and constant encouragement and support throughout years.
TABLE OF CONTENTS

LIST OF TABLES .......................................................................................................................................................... xi

LIST OF FIGURES .................................................................................................................................................. xii

Chapter I Introduction .................................................................................................................................................. 1
1.1 Overview of secondary organic aerosol (SOA) formation ............................................................................. 1
1.2 Heterogeneous SOA formation in the presence of inorganic aerosols ..................................................... 2
1.3 Impacts of heterogeneous chemistry on toluene SOA yields ..................................................................... 3
1.4 Impacts of heterogeneous chemistry on partitioning of semivolatile organic compounds on toluene SOA ................................................................. 5
1.5 A predictive model including heterogeneous chemistry and partitioning for SOA formed from toluene oxidation ......................................................................................................................... 7

Reference ............................................................................................................................................................... 8

Chapter II Effects of Particle Acidity and UV Light on Secondary Organic Aerosol Formation from Oxidation of Aromatics .............................................................. 12
2.1 Introduction ..................................................................................................................................................... 14
2.2 Experimental methods ................................................................................................................................. 16
  2.2.1 Teflon film indoor chamber experiments .......................................................................................... 16
  2.2.2 Materials and instruments ................................................................................................................ 17
2.3 Results and discussion ................................................................................................................................. 19
  2.3.1 Particle acidity: seed aerosol composition and proton concentration ............................................... 19
  2.3.2 SOA Yields ........................................................................................................................................ 20
  2.3.3 Effect of molecular structures on the SOA formation .................................................................. 21
  2.3.4 Acid effects on SOA yield without irradiation ............................................................................. 23
  2.3.5 SOA formation with irradiation .................................................................................................... 25
2.4 Implications of this study............................................................................................... 29
Acknowledgements.............................................................................................................. 31
Reference ............................................................................................................................. 32

Chapter III Secondary Organic Aerosol Formation from Toluene Photooxidation
under the Various NO\textsubscript{x} Conditions and Particle Acidity ................................. 36

3.1 Introduction.................................................................................................................... 38
3.2 Experimental section...................................................................................................... 41
3.3 Results and discussion ................................................................................................... 43
  3.3.1 SOA yields ............................................................................................................. 43
    3.3.1.1 NO\textsubscript{x} effect on SOA formation.......................................................... 43
    3.3.1.2 Acidity and humidity effects on SOA formation.............................................. 49
  3.3.2 Time-dependent growth curve ............................................................................... 55
  3.3.3 Chamber experiments under conditions relevant to the atmosphere ................. 58
3.4 Summary........................................................................................................................ 59
Acknowledgements.............................................................................................................. 60
Reference............................................................................................................................. 61

Chapter IV Impacts of Heterogeneous Chemistry on Partitioning of Semivolatile
Organic Compounds on Aromatic SOA ........................................................................... 65

4.1 Introduction.................................................................................................................... 67
4.2 Experimental section...................................................................................................... 69
  4.2.1 Teflon film indoor chamber experiments .............................................................. 69
  4.2.2 Sampling ................................................................................................................ 71
  4.2.3 GC-ITMS Analysis of Denuder and Filter Samples .............................................. 71
  4.2.4 Materials and instruments ...................................................................................... 72
4.3 Results and discussion ................................................................................................... 73
  4.3.1 Composition of chamber SOA............................................................................... 73
LIST OF TABLES

Table 2.1 Experimental conditions and resulting SOA data for oxidation of toluene with OH radicals produced from ozonolysis of MB using the 2 m$^3$ Teflon Film Chamber .................................................................................................................. 18

Table 2.2 Experimental conditions and resulting SOA data for oxidation of 135-TMB with OH radicals produced from ozonolysis of MB using the 2 m$^3$ Teflon Film Chamber .................................................................................................................. 19

Table 3.1 Experimental conditions and resulting SOA data from photooxidation of toluene .............................................................................................................................................................................. 43

Table 3.2 Experimental conditions and resulting SOA data from photooxidation of toluene for the low NO region and the high NO region of high NO$_x$ experiments .......... 44

Table 3.3 Relative SOA yield increase under different NO$_x$ concentrations at a given particle acidity and humidity .................................................................................................................................................. 49

Table 3.4 Summary of particle acidity effect ($\Delta Y_{A-NA}$) and humidity effect ($\Delta Y_{HRH-LRH}$) on SOA formation under various experimental conditions ........................................................... 50

Table 3.5 SOA experiments conducted under the atmospheric relevant conditions at intermediate NO$_x$ level .............................................................................................................................................. 58

Table 4.1 Experimental conditions and the resulting SOA data .............................................................................................................................................................................................................. 70

Table 4.2 Experimental partitioning coefficients of two deuterated alkanes on aromatic SOA .......................................................................................................................................................... 78

Table 4.3 Estimated activity coefficients and vapor pressures of oxygenated toluene products and comparison of calculated and measured partitioning coefficients at T=295 K .......................................................................................................................... 81

Table 4.4 Mass percentage of the identified products in the SOA from toluene photooxidation .............................................................................................................................................................................. 82

Table 5.1 Experimental conditions and resulting SOA data from photooxidation of toluene .......................................................................................................................................................... 100

Table 5.2 Stoichiometric coefficient ($\alpha$) based on mass fraction for each lumped group obtained from MCM simulations of three experiments at different NO$_x$ levels. .... 104

Table 5.3 SOA experiments conducted under the atmospheric relevant conditions at middle NO$_x$ level and high NO$_x$ level .............................................................................................................. 108
LIST OF FIGURES

Figure 2.1 SOA yields in the presence of non-acidic and acidic seeds at two different %RH levels under dark and UV light conditions ...................................................... 21

Figure 2.2 $f(OM_{diff})$ as a function of a proton concentration at high %RH (42-52) describing the contribution of acid catalyzed heterogeneous reaction to the SOA mass ........ 23

Figure 2.3 SOA yields as a function of a proton concentration .............................................. 24

Figure 2.4 The absolute reduction of aromatic SOA yields ($\Delta Y_{dark-UV}$) due to the UV exposure at different humidity levels ................................................................. 26

Figure 2.5 The representative time profiles of SOA mass in the chamber with the UV light controlled by on-off/off-on mode showing UV light effects on the particle mass change ........................................................................................................ 28

Figure 3.1 SOA yields in the presence of neutral seed and acidic sulfate seed at two different %RH levels under three NO$_x$ conditions ....................................................... 45

Figure 3.2 The fates of RO$_2$ produced from toluene photooxidation under different NO$_x$ conditions ......................................................................................................... 46

Figure 3.3 The possible reaction channels for gas phase oxygenated products at high NO$_x$ level ..................................................................................................................... 48

Figure 3.4 A time profile of proton concentration [H$^+$] over the course of an SOA experiment at high NO$_x$ level in the presence of acidic sulfate seed .................. 54

Figure 3.5 Time-dependent growth curves and SOA yield curves over the course of an SOA experiment ................................................................................................. 56

Figure 4.1 Calculated partitioning coefficients of d$_{40}$-nonadecane on SOA comprising different oligomer structures in the presence of the non acidic seed ............ 75

Figure 4.2 Calculated partitioning coefficients of d$_{40}$-nonadecane on SOA comprising various oligomer structures in the presence of the acidic seed .............. 76

Figure 4.3 RF(Mass ratio/peak ratio) as a function of retention time for quantification of the identified products in the particle phase ...................................................... 80

Figure 5.1 Components of the SOA model including partitioning and heterogeneous reactions ..................................................................................................... 97

Figure 5.2 Comparison of model simulated and measured concentrations of toluene, NO, NO$_2$ and O$_3$ for experiments at middle NO$_x$ and high NO$_x$ levels .......... 102
Figure 5.3 Comparison of the predicted OM\textsubscript{T} and the measured OM\textsubscript{T} (Table 5.1) at three NO\textsubscript{X} levels in the non-acidic and acidic toluene systems ................................................................. 106

Figure 5.4 Predicted heterogeneous SOA mass fraction (OM\textsubscript{H}/OM\textsubscript{T}) at three NO\textsubscript{X} levels in the non-acidic and acidic toluene systems ................................................................. 107

Figure 5.5 Comparison of the predicted OM\textsubscript{T} and the measured OM\textsubscript{T} (Table 5.3) at middle NO\textsubscript{X} and high NO\textsubscript{X} levels under atmospheric relevant conditions in the non-acidic and acidic toluene systems ............................................................................ 109

Figure 5.6 Predicted heterogeneous SOA mass fraction (OM\textsubscript{H}/OM\textsubscript{T}) at middle NO\textsubscript{X} and high NO\textsubscript{X} levels in the non-acidic and acidic toluene systems ................................................................. 111

Figure A.1 Experimental setup of the GPT calibration system for calibrating NO\textsubscript{X} meter and O\textsubscript{3} meter ....................................................................................................... 121

Figure A.2 The calibration curve for the NO\textsubscript{X} meter (Jan 06, 2008). ............................................. 125

Figure A.3 Gas phase titration (GPT) chart for the calibration of the O\textsubscript{3} meter ....................... 126

Figure B.1 Particle wall loss rate as a function of particle size ......................................................... 128

Figure B.2 Fluorescence light spectrum compared with solar spectra for zenith angle of 51° ................................................................. 129

Figure B.3 All reactions included in the inorganic gas phase model .................................................. 131

Figure B.4 Computer screen print for files in the folder “stdinclude” used in Morpho ............... 133

Figure B.5 Comparison between measured and modeled values for NO, NO\textsubscript{2} and NO\textsubscript{X} for NO\textsubscript{2} actinometry experiments ................................................................. 133

Figure B.6 A flow chart for generation of photolysis files in Morpho ........................................... 134
Chapter I

Introduction

1.1 Overview of secondary organic aerosol (SOA) formation

Secondary organic aerosols (SOA) have potential impacts on the earth’s radiative balance, visibility and human health. The magnitude of these SOA effects depends on the concentration and composition of SOA in the atmosphere. Therefore, understanding mechanisms of SOA formation is essential for the correct estimation of their effects.

SOA refers to aerosols formed by gas phase multifunctional oxygenated products that are generated from volatile organic compounds (VOCs) reactions with atmospheric oxidants (e.g. ozone, hydroxy radical, and nitrate radical). For years, SOA formation has been explained using two physical processes: self-nucleation and gas-particle partitioning. Both processes depend on vapor pressure of compounds. Therefore, the potential of SOA formation from organic precursors has been estimated primarily by their vapor pressures. SOA products generated through these two pathways are believed to have the same structures as their gas phase products. Recent findings, however, challenge the conventional SOA formation theory. For example, some compounds (e.g. carbonyls) that weakly partition due to their high vapor pressure are found in large amounts in the particle phase (Jang et al., 2002); high molecular weight (MW) structures that are not seen in the gas phase are detected in both ambient aerosols and the laboratory generated aerosols (Dommen et al., 2006; Gao et al., 2004b; Tolocka, et al., 2004); some volatile VOCs (e.g. isoprene) that are expected to be
insignificant SOA precursors according to the gas-particle partitioning theory are found to be important SOA sources (Lane and Pandis, 2007; Lewandowski et al., 2007; Limbeck et al., 2003; Szmigielski et al., 2007). Such findings suggest that reactive gas phase organic products (e.g. carbonyls) condense on the particle phase and are further chemically transformed into high MW compounds, also called oligomers (characteristic products from heterogeneous reactions). Many recent studies have suggested that heterogeneous reactions in the particle phase are important pathways for SOA formation in addition to self-nucleation and gas-particle partitioning processes (Baltensperger et al., 2005; Gao et al., 2004b; Jang et al., 2002; Kalberer et al., 2004; Liggio et al., 2005a).

1.2 Heterogeneous SOA formation in the presence of inorganic aerosols

Potential mechanisms for particle phase heterogeneous chemistry of organic compounds such as carbonyls include hydration, polymerization, formation of hemiacetal/acetal/trioxane, aldol condensation and cationic rearrangement (Garland et al., 2006; Jang et al., 2004). The contribution of heterogeneous reactions to SOA formation is influenced by reactivity of gas phase products from oxidation of organics in these mechanisms. Jang et al. (2006) lumped major gas phase products of \(\alpha\)-pinene ozonolysis into three groups of reactivity (slow, medium and fast) for the estimation of heterogeneous SOA formation. For example, heterogeneous reactions of compounds with fast reactivity, such as oxoaldehydes—the aldehydes that contain at least two C=O groups, can occur without the need of an acidic catalyst but can be accelerated by an acidic catalyst. Heterogeneous reactions of compounds with slow and medium reactivity such as oxo-carboxylic acids are significant only when an acidic catalyst is present in the particle phase. Therefore, heterogeneous reactions of different types of gas phase oxygenated products respond
differently to particle acidity. From the aspect of acid-catalyzed heterogeneous reactions, the interactions between organic compounds and inorganic acid determine degree and rates of the reactions. The mass ratios of organic to inorganic compounds in aerosols directly influence the process of acid-catalyzed heterogeneous reactions. For example, if the mass ratios of organic to inorganic are low, the incidence of acid-catalyzed heterogeneous reactions could be high. Therefore, an accurate explanation of SOA formation requires consideration of the chemical interaction between organic and inorganic components in aerosols. In general, organic and inorganic constituents are often coexisting in the actual multicomponent ambient aerosols. For example, the mass ratios of organic to inorganic in ambient aerosols vary from 0.3 to 0.6 (Drewnick et al., 2004; Russell et al., 2004). Thus, laboratory studies of SOA formation in the presence of inorganic seed aerosol will be more relevant to the atmosphere.

1.3 Impacts of heterogeneous chemistry on toluene SOA yields

Aromatics are an important class of VOCs in the ambient air and also major precursors for SOA formation along with biogenic VOCs. Aromatic hydrocarbons constitute about 20-50% (in PPbC) of the total non methane VOCs in urban atmospheres of the United States and Europe (Calvert et al., 2002) and contribute a significant fraction of anthropogenic SOA loadings in urban area. In this dissertation, toluene is selected as an aromatic precursor for the study on SOA formation because it is the most abundant aromatic VOC in urban atmosphere comprising about 20-40% of the total aromatic compounds (Calvert et al., 2002) and produces high SOA yields compared to other aromatic VOCs (Dechapanya et al., 2003). Toluene reacts with OH radicals in gas phase and produces multifunctional carbonyls (Jang
and Kamens, 2001; Kleindienst et al., 2004; Smith et al., 1998, 1999; Yu et al., 1997) that are highly reactive for further particle phase reactions contributing significant SOA yields.

Most recent studies of particle acidity effects on SOA formation have mainly focused on the SOA from biogenic terpenes and isoprene (Czoschke et al., 2003; Czoschke and Jang, 2006; Edney et al., 2005; Gao et al., 2004a; 2004b; Iinuma et al., 2004; Northcross and Jang, 2007). Only a few studies (Kalberer et al., 2004; Liggio et al., 2005a; 2005b) suggested oligomer formation through heterogeneous reactions in the aromatic SOA in the absence of acidic aerosols or with no seed aerosols. Research efforts are urgently needed to fill the gap between the studies on particle acidity effects for biogenic SOA formation and the ones for aromatic SOA formation. This dissertation, for the first time, presents a systematic investigation on SOA formation from oxidation of toluene in the presence of inorganic seed.

In Chapter II, effects of particle acidity on SOA yields generated from oxidation of toluene are explored in the absence of NO\textsubscript{x}. For comparison purposes, SOA formation from oxidation of 1,3,5-trimethylbenzene (135-TMB) in the presence of inorganic seed is also studied. Chapter II also evaluates how UV-visible light influences the aromatic SOA formation at different particle acidity. Presto et al. (2005) reported the reduction of SOA yields by the presence of UV light for the SOA generated from the ozonolysis of α-pinene. Their study suggested that UV light decomposed the gas-phase organic products into low molecular weight species, resulting in less partitioning of gas-phase compounds to the particle and lower SOA production. In the aromatic systems, the similar phenomena of the SOA loss by the UV-visible exposure are expected due to the photolysis of carbonyl products in the gas phase. The degree of SOA yield reduction through UV irradiation is investigated for toluene and 135-TMB in Chapter II.
Previous studies on SOA formation from aromatic photooxidation (Hurley et al., 2001; Johnson et al., 2004; Ng et al., 2007; Song et al., 2005) have shown that NO\textsubscript{x} reduces the aromatic SOA formation suggesting that NO\textsubscript{x} influences the fate of gas phase organic peroxide radicals (RO\textsubscript{2}). Under high NO\textsubscript{x} conditions, RO\textsubscript{2} radicals react with NO\textsubscript{x} and produce relatively volatile organic nitrates; while under low NO\textsubscript{x} conditions, RO\textsubscript{2} radicals react with hydroperoxyl radicals (HO\textsubscript{2}) forming organic hydroperoxides (ROOH) that may further react with aldehyde species in the particle phase to produce the low volatile per oxyhemiacetals (Johnson et al., 2004). However, most of these previous studies were conducted under the neutral condition. The effects of particle acidity at varied NO\textsubscript{x} conditions are poorly understood. NO\textsubscript{x} concentrations are expected to influence particle acidity effects on SOA formation because different NO\textsubscript{x} concentration levels lead to different gas phase products with diverse physical and chemical properties. Hence, more comprehensive SOA studies at different NO\textsubscript{x} levels coupled with various particle acidity and humidity levels are needed. In Chapter III, SOA formation from photooxidation of toluene in the presence of inorganic neutral and acidic seed is comprehensively investigated at three NO\textsubscript{x} levels and two humidity levels.

1.4 Impacts of heterogeneous chemistry on partitioning of semivolatile organic compounds on toluene SOA

Laboratory observations and model simulations for aromatic SOA formation indicate that a considerable fraction of aromatic SOA mass is oligomers (Hu et. al, 2007 and Kalberer et al., 2004), although the exact oligomer fraction is not certainly known due to the artifacts during the sample preparation, sample analysis and the lack of authentic standards. Such problems hinder the studies on how oligomers in the particle phase influence partitioning behavior of organic compounds on SOA by alteration of MW\textsubscript{om} and $\gamma_{\text{om}}^\infty$. In the
previous partitioning studies, the gas-particle partitioning of semivolatile organic compounds is estimated by an absorptive partitioning coefficient ($i K_p^{cal}$ in equation 1) (Pankow, 1994).

$$i K_p^{cal} = \frac{7.501RT f_{om}}{10^9 MW_{om} \gamma_{om}^{\infty} i P_L^0}$$  

(1)

where $i K_p^{cal}$ is the gas-particle partitioning coefficient (m$^3$/µg), T is the ambient temperature (K), R is the gas constant (8.314 JK$^{-1}$mol$^{-1}$), $f_{om}$ is the mass fraction of the absorptive liquid-like organic material (om), $MW_{om}$ is the average molecular weight (g/mol) of the organic matter, and $\gamma_{om}^{\infty}$ is the activity coefficient of $i$ at infinite dilution in a given liquid-like medium. The $i P_L^0$ is the subcooled liquid vapor pressure at the temperature of interest (torr).

For the previous studies on partitioning of oxygenated gas phase toluene products on aerosols, it was assumed that $\gamma_{om}^{\infty}$ was 1 and $MW_{om}$ was around 120 g/mol (Healy et al., 2008; Jang and Kamens, 2001; Johnson et al., 2006) based on simple gas phase products. However, such treatment should be reevaluated considering the new and important heterogeneous chemistry of organics in aerosols because the formation of oligomeric species in aerosols would considerably influence $MW_{om}$ and $\gamma_{om}^{\infty}$.

Chapter IV presents an approach using two deturated alkanes to determine semiempirically the SOA compositions including oligomers generated from photooxidation of toluene in the absence of NO$_x$. The resulting SOA compositions are used to study the partitioning of toluene oxygenated products on aerosols.
A predictive model including heterogeneous chemistry and partitioning for SOA formed from toluene oxidation

The current SOA predictive models by the gas particle partitioning theory solely are limited to describing the realistic SOA formation. The SOA models in the next generation should take into account the compounds that might be relatively volatile but reactive for heterogeneous reactions. Including heterogeneous reactions into SOA models can significantly reduce the deviation between the modeled and observed SOA mass so that the predictability of SOA model can be improved considerably. In Chapter V, the partitioning SOA model developed by Schell et al. (2001) and the heterogeneous SOA model developed by Jang et al. (2006) are explored for toluene SOA prediction. The partitioning SOA model is currently used for SOA prediction in the regional air quality model. Therefore, this study has initiated a preliminary step to incorporating contribution of heterogeneous reactions to toluene SOA formation into the regional air quality models for SOA prediction. The model evaluation, in terms of the ozone formation, the NO to NO$_2$ conversion, the decay of toluene in the gas phase, and the production of SOA mass, is addressed in this chapter.

Finally, Chapter VI summarizes the key findings of this dissertation work and provides recommendations for future studies on aromatic SOA formation.
Reference


Gao, S., Ng, N.L., Keywood, M., Varutbangkul, V., Bahreini, R., Nenes, A., He, J., Yoo,


Smith, D.F., Kleindienst, T.E., Mciver, C.D., 1999. Primary product distributions from the
reaction of OH from m-, p-xylene, 1,2,4- and 1,3,5-trimethylbenzene. Journal of Atmospheric Chemistry 34, 339-364.


Chapter II

Effects of Particle Acidity and UV Light on Secondary Organic Aerosol Formation from Oxidation of Aromatics in the Absence of NO\textsubscript{x}

Gang Cao, Myoseon Jang*
Department of Environmental Sciences and Engineering
University of North Carolina at Chapel Hill
CB#7431, Rosenau Hall, Chapel Hill, NC, 27599

Published in Atmospheric Environment, (2007), 41(35), 7603-7613.

*Corresponding Author: Myoseon Jang
Email: mjang@ufl.edu
**Abstract**

Recent laboratory observations have shown that particle acidity increases secondary organic aerosol (SOA) yields. However, these studies have mainly focused on biogenic precursors such as isoprene and terpenes. In this paper, the effects of particle acidity on aromatic SOA yields under both dark and UV-Visible light conditions were characterized through controlled chamber experiments. SOA was produced from oxidation of toluene and 1,3,5-trimethylbenzene (135-TMB) with OH radicals created by ozonolysis of 2-methyl-2-butene (MB). Particle acidity, described with proton concentrations, varied with inorganic seed aerosol composition and humidity (20%-52%). Overall, in the presence of acidic seeds, greater increases in SOA yields were observed for the toluene system than the 135-TMB system. UV irradiation reduced SOA yields for both toluene and 135-TMB systems to different extents.
2.1 Introduction

The gas phase reactions of volatile organic compounds (VOCs) associated with the photochemical cycles of atmospheric oxidants (e.g. ozone, OH radical, and NO$_x$) create semivolatile multifunctional oxy-products, which produce secondary organic aerosol (SOA) by either gas-particle partitioning on preexisting particulate matter or self-nucleation. For many years, SOA formation has been explained mainly by a gas-particle partitioning theory. However, recent studies (Czoschke et al., 2003; Czoschke and Jang, 2006; Edney et al., 2005; Gao et al., 2004a;2004b; Iinuma et al., 2004; Jang et al., 2002; Northcross and Jang, 2007) have suggested that SOA mass also increases by heterogeneous reactions, particularly in acidic aerosols (e.g. submicron sulfuric acid aerosol). Such findings suggest that further chemical transformation of organic compounds occurs in the particle phase via heterogeneous reactions, forming high molecular weight species. The particle phase heterogeneous reactions (e.g. hydration, polymerization, formation of hemiacetal/acetal/trioxane, aldol condensation, and cationic rearrangement) can be catalyzed by inorganic acids accelerating SOA formation (Jang et al., 2002; 2004; Garland et al., 2006) and can also produce organic sulfates through the reaction of sulfuric acid with organics (Liggio et al., 2005a).

Aromatics are an important class of VOCs in the ambient air and also major precursors for SOA formation along with biogenic VOCs. Aromatics react with OH radicals in the gas phase and produce multifunctional carbonyls (Jang and Kamens, 2001; Kleindienst et al., 2004; Smith et al., 1998, 1999; Yu et al., 1997) that are highly reactive for further particle phase reactions contributing significant SOA yields. Although in urban air, about 20-50% (on a carbon basis) by concentrations of the non-methane hydrocarbons is aromatic
compounds (Calvert et al., 2002; Fujita et al., 1997; Kurtenbach et al., 2000; Singh et al., 1985), no study until now characterized the influence of particle acidity on aromatic SOA formation. Most studies of the particle acidity effects on SOA formation have mainly focused on the SOA from biogenic terpenes and isoprene (Czoschke et al., 2003; Czoschke and Jang, 2006; Edney et al., 2005; Gao et al., 2004a; 2004b; Iinuma et al., 2004; Northcross and Jang, 2007). Only a few studies (Kalberer et al., 2004; Liggio et al., 2005a; 2005b) suggested oligomer formation through heterogeneous reactions in the aromatic SOA in the absence of acidic aerosols or with no seed aerosols. This paper is a first attempt to investigate the impact of particle acidity on aromatic SOA formation via heterogeneous reactions. Particle acidity varied with humidity and inorganic seed aerosol compositions comprising of sulfuric acid (HS), ammonium bisulfate (ABS), and ammonium sulfate (AS) aqueous solution.

In our study, NO\textsubscript{x} was excluded to simplify the inorganic thermodynamics into the sulfate-ammonia only system eliminating both interference from nitric acid and chemistries of organic nitrates in SOA formation. The controlled experimental condition of this study allows us to clearly evaluate the sulfuric acid effects on SOA yields thus reducing the uncertainties of analyzing the SOA yield data.

Another emphasis of this study is to evaluate how UV-visible light influences the aromatic SOA formation at the different particle acidity. Presto et al (2005) in their recent studies showed the reduction of SOA yields by the presence of UV light for the SOA from the ozonolysis of \(\alpha\)-pinene. Their study suggested that UV light decomposed the gas-phase organic products into low molecular weight species, resulting in less partitioning of gas-phase compounds to the particle and lower SOA production. In the aromatic systems, the
similar phenomena of the SOA loss by the UV-visible exposure are expected due to the photolysis of carbonyl products in the gas phase. In this study, the degree of SOA yield reduction through UV irradiation was investigated for the individual aromatic (toluene and 135-TMB).

2.2 Experimental methods

2.2.1 Teflon film indoor chamber experiments

Aromatic precursors were oxidized by OH radicals that were produced from the reaction of 2-methyl-2-butene (MB) with ozone in the gas phase. MB was selected due to its rapid reaction rate \(3.92 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) at a temperature \(T\) of 295 K with \(O_3\) (Carter, 2000), relatively high OH production (0.80 to 0.98) (Orzechowska and Paulson, 2002), and the negligible SOA formation. In order to confirm that ozonolysis of MB had a negligible SOA production, 0.30 ppm of MB reacted with 0.32 ppm of ozone in the presence of both non-acidic (128 nL/m\(^3\)) and acidic inorganic seed aerosol (165 nL/m\(^3\)) at a percent relative humidity (%RH) of 42 at 295 K. No detectable SOA formation appeared from ozonolysis of MB in both the non-acidic and the acidic systems.

All experiments were conducted in a 2 m\(^3\) indoor Teflon film chamber under either dark or UV-visible light conditions. The chamber was surrounded by sixteen fluorescent lamps (Solarc Systems Inc., FS40T12/UVB) that are controlled by switching “on” and “off”. Temperature increase due to our light sources is trivial (less than 2 K for the duration of the experiments). Prior to each experiment, the chamber was flushed with clean air from clean air generators. The inorganic composition of the seed aerosol was controlled by the different combinations of the inorganic aqueous solutions (0.01 mol/L) made of AS, ABS, and HS. The inorganic seed aerosols were injected into the chamber by atomizing the aqueous
inorganic solution. After injecting inorganic seed aerosol, O\textsubscript{3} was introduced into the indoor chamber followed by the injection of a mixture of MB and an aromatic compound (toluene or 135-TMB). The mixture of precursor organics was added to a T-shaped glass tube using a syringe, then volatilized under clean air streams passing through this T-shaped glass tube by heating with a heat gun. For all SOA experiments, the initial concentrations of MB and toluene/135-TMB in the chamber were 0.3 ppm and 3.12ppm (toluene)/2.4 ppm (135-TMB), respectively. For the light experiments, the chamber was exposed to the light source immediately after adding the organics. The experimental conditions and the resulting SOA data at different particle acidity associated with the composition of inorganic seed aerosol and humidity are summarized in Table 2.1 and Table 2.2.

2.2.2 Materials and instruments

All chemicals used for this study were purchased from Aldrich (Milwaukee, WI) and had purity levels greater than 99%. Clean air was generated using two clean air generators (Aadco Model 737, Rockville, MD; Whatman Model 75-52, Haverhill, MA). Inorganic seed aerosols were generated with a Constant Output Atomizer (TSI, Model 3076, Shoreview, MN) and ozone was generated photolytically using a Xonics ozone generator (Jelight Model 600, Irvine, CA). The ozone concentration was measured with a photometric ozone detector (Thermo Environmental Instruments, Model 49, Hopkinton, MA). The particle size distribution was monitored with a Scanning Mobility Particle Sizer (SMPS, TSI Model 3080, Shoreview, MN) together with a condensation nuclei counter (CNC, TSI, Model 3025A). Particle data were corrected for the aerosol loss to the chamber wall (McMurry and Grosjean, 1985) with a first order decay. The gas-phase concentrations of aromatics were measured with an HP 5890 GC-FID. The GC-FID was calibrated each time prior to SOA
experiments. The flow rate of GC carrier gas (Nitrogen) through a DB-5 (15m x 0.53mm) fused silica capillary column (J & W Scientific INC, Cat# 1255012) was 2.5 mL/min. The oven temperature was fixed at 150 °C for 7 min. Temperature (294-297 K) and %RH of the chamber were measured with an electronic thermo-hygrometer (Dwyer Instrument, INC, USA).

The uncertainties of our experiments were mainly from the particle volume concentration measured by the SMPS and the ∆ROG monitored by GC-FID. For all the experiments of this study, the estimated uncertainty for SMPS data was ±2% and that for the GC-FID measurement, within ±6%.

Table 2.1 Experimental conditions and resulting SOA data for oxidation of toluene with OH radicals produced from ozonolysis of MB using the 2 m$^3$ Teflon Film Chamber a,b.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>%RH</th>
<th>$F_{HS}$ c (µg/m$^3$)</th>
<th>[H$^+$] (ppm)</th>
<th>Init.</th>
<th>$V_{	ext{seed}}$ (10$^{11}$nm$^3$/cm$^3$)</th>
<th>$V_{	ext{mix}}$ (10$^{11}$nm$^3$/cm$^3$)</th>
<th>OM (µg/m$^3$)</th>
<th>Yield d</th>
</tr>
</thead>
<tbody>
<tr>
<td>dark</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>28.6</td>
<td>0.33</td>
<td>0.01</td>
<td>0.343</td>
<td>1.96</td>
<td>2.79</td>
<td>116</td>
<td>0.14±0.02</td>
</tr>
<tr>
<td>2</td>
<td>28.8</td>
<td>0.33</td>
<td>0.01</td>
<td>0.345</td>
<td>1.35</td>
<td>2.18</td>
<td>116</td>
<td>0.14±0.02</td>
</tr>
<tr>
<td>3</td>
<td>43.2</td>
<td>0.33</td>
<td>0.01</td>
<td>0.344</td>
<td>1.31</td>
<td>1.94</td>
<td>88</td>
<td>0.11±0.01</td>
</tr>
<tr>
<td>4</td>
<td>63.0</td>
<td>0.33</td>
<td>0.01</td>
<td>0.323</td>
<td>1.17</td>
<td>1.66</td>
<td>69</td>
<td>0.09±0.01</td>
</tr>
<tr>
<td>5</td>
<td>30.3</td>
<td>0.54</td>
<td>0.24</td>
<td>0.339</td>
<td>1.82</td>
<td>2.94</td>
<td>157</td>
<td>0.20±0.02</td>
</tr>
<tr>
<td>6</td>
<td>26.0</td>
<td>0.59</td>
<td>0.54</td>
<td>0.313</td>
<td>1.38</td>
<td>2.58</td>
<td>168</td>
<td>0.21±0.02</td>
</tr>
<tr>
<td>7</td>
<td>22.4</td>
<td>0.67</td>
<td>0.75</td>
<td>0.321</td>
<td>1.53</td>
<td>3.02</td>
<td>209</td>
<td>0.26±0.03</td>
</tr>
<tr>
<td>8</td>
<td>25.9</td>
<td>0.67</td>
<td>0.75</td>
<td>0.328</td>
<td>1.61</td>
<td>3.11</td>
<td>210</td>
<td>0.26±0.03</td>
</tr>
<tr>
<td>9</td>
<td>49.2</td>
<td>0.54</td>
<td>0.24</td>
<td>0.324</td>
<td>2.02</td>
<td>2.90</td>
<td>123</td>
<td>0.15±0.02</td>
</tr>
<tr>
<td>10</td>
<td>51.5</td>
<td>0.59</td>
<td>0.44</td>
<td>0.337</td>
<td>1.99</td>
<td>2.99</td>
<td>140</td>
<td>0.17±0.02</td>
</tr>
<tr>
<td>11</td>
<td>42.3</td>
<td>0.67</td>
<td>0.70</td>
<td>0.328</td>
<td>1.77</td>
<td>2.86</td>
<td>153</td>
<td>0.19±0.02</td>
</tr>
<tr>
<td>light</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>30.8</td>
<td>0.33</td>
<td>0.01</td>
<td>0.338</td>
<td>1.44</td>
<td>1.91</td>
<td>66</td>
<td>0.11±0.01</td>
</tr>
<tr>
<td>2</td>
<td>41.8</td>
<td>0.33</td>
<td>0.01</td>
<td>0.332</td>
<td>1.68</td>
<td>2.09</td>
<td>57</td>
<td>0.09±0.01</td>
</tr>
<tr>
<td>3</td>
<td>25.5</td>
<td>0.67</td>
<td>0.81</td>
<td>0.350</td>
<td>1.67</td>
<td>2.31</td>
<td>90</td>
<td>0.15±0.01</td>
</tr>
<tr>
<td>4</td>
<td>44.4</td>
<td>0.67</td>
<td>0.55</td>
<td>0.335</td>
<td>1.85</td>
<td>2.36</td>
<td>71</td>
<td>0.12±0.01</td>
</tr>
<tr>
<td>5</td>
<td>41.0</td>
<td>0.67</td>
<td>0.65</td>
<td>0.328</td>
<td>1.45</td>
<td>1.95</td>
<td>70</td>
<td>0.11±0.01</td>
</tr>
</tbody>
</table>

a Temperature in the range of 294-297 K
b ∆ROG was 802.85 ± 45.35 (µg/m$^3$) for dark experiments and 611.69 ± 22.94 (µg/m$^3$) for light experiments
c $F_{HS}$=0.33 (AS); $F_{HS}$=0.54 (ABS:HS=85:15); $F_{HS}$=0.59 (ABS:HS=70:30); $F_{HS}$=0.67 (ABS:HS=50:50)
d Yield was calculated by equation 1 with the density of organic matter of 1.4 g/mL. The uncertainties of the resulting SOA yields were calculated using the uncertainties of OM and ∆ROG through the propagation of uncertainty for divisions (Levie, 1997)
Table 2.2 Experimental conditions and resulting SOA data for oxidation of 135-TMB with OH radicals produced from ozonolysis of MB using the 2 m$^3$ Teflon Film Chamber $^{a,b}$.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>%RH</th>
<th>$F_{HS}^c$</th>
<th>$[H^+]$</th>
<th>Init. $[O_3]$</th>
<th>$V_{seed}$</th>
<th>$V_{mix}$</th>
<th>OM</th>
<th>Yield$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(μg/m$^3$)</td>
<td>(ppm)</td>
<td>(10$^{11}$ nm$^3$/cm$^3$)</td>
<td>(10$^{11}$ nm$^3$/cm$^3$)</td>
<td>(μg/m$^3$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dark</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>20.8</td>
<td>0.33</td>
<td>0.01</td>
<td>0.330</td>
<td>1.56</td>
<td>2.51</td>
<td>133</td>
<td>0.103±0.004</td>
</tr>
<tr>
<td>2</td>
<td>28.8</td>
<td>0.33</td>
<td>0.01</td>
<td>0.355</td>
<td>1.43</td>
<td>2.41</td>
<td>137</td>
<td>0.106±0.004</td>
</tr>
<tr>
<td>3</td>
<td>48.3</td>
<td>0.33</td>
<td>0.01</td>
<td>0.325</td>
<td>2.08</td>
<td>2.79</td>
<td>99</td>
<td>0.077±0.003</td>
</tr>
<tr>
<td>4</td>
<td>66.0</td>
<td>0.33</td>
<td>0.01</td>
<td>0.337</td>
<td>1.42</td>
<td>2.08</td>
<td>92</td>
<td>0.071±0.003</td>
</tr>
<tr>
<td>5</td>
<td>30.8</td>
<td>0.54</td>
<td>0.25</td>
<td>0.333</td>
<td>1.98</td>
<td>3.07</td>
<td>153</td>
<td>0.119±0.005</td>
</tr>
<tr>
<td>6</td>
<td>29.3</td>
<td>0.59</td>
<td>0.45</td>
<td>0.342</td>
<td>1.61</td>
<td>2.75</td>
<td>160</td>
<td>0.124±0.005</td>
</tr>
<tr>
<td>7</td>
<td>18.0</td>
<td>0.67</td>
<td>0.86</td>
<td>0.325</td>
<td>1.69</td>
<td>2.96</td>
<td>178</td>
<td>0.138±0.006</td>
</tr>
<tr>
<td>8</td>
<td>20.4</td>
<td>0.67</td>
<td>0.66</td>
<td>0.318</td>
<td>1.31</td>
<td>2.52</td>
<td>169</td>
<td>0.131±0.005</td>
</tr>
<tr>
<td>9</td>
<td>49.1</td>
<td>0.54</td>
<td>0.21</td>
<td>0.342</td>
<td>1.79</td>
<td>2.65</td>
<td>120</td>
<td>0.093±0.004</td>
</tr>
<tr>
<td>10</td>
<td>49.5</td>
<td>0.59</td>
<td>0.27</td>
<td>0.331</td>
<td>1.32</td>
<td>2.21</td>
<td>125</td>
<td>0.097±0.004</td>
</tr>
<tr>
<td>11</td>
<td>44.8</td>
<td>0.67</td>
<td>0.73</td>
<td>0.340</td>
<td>1.92</td>
<td>3.18</td>
<td>176</td>
<td>0.136±0.005</td>
</tr>
<tr>
<td>12</td>
<td>48.6</td>
<td>0.67</td>
<td>0.72</td>
<td>0.313</td>
<td>1.99</td>
<td>3.01</td>
<td>143</td>
<td>0.111±0.004</td>
</tr>
<tr>
<td>light</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>24.4</td>
<td>0.33</td>
<td>0.01</td>
<td>0.360</td>
<td>1.55</td>
<td>1.98</td>
<td>60</td>
<td>0.056±0.004</td>
</tr>
<tr>
<td>2</td>
<td>43.4</td>
<td>0.33</td>
<td>0.01</td>
<td>0.331</td>
<td>1.74</td>
<td>2.15</td>
<td>57</td>
<td>0.055±0.004</td>
</tr>
<tr>
<td>3</td>
<td>21.1</td>
<td>0.67</td>
<td>0.81</td>
<td>0.321</td>
<td>1.77</td>
<td>2.68</td>
<td>127</td>
<td>0.122±0.009</td>
</tr>
<tr>
<td>4</td>
<td>19.1</td>
<td>0.67</td>
<td>0.76</td>
<td>0.322</td>
<td>1.66</td>
<td>2.46</td>
<td>112</td>
<td>0.107±0.008</td>
</tr>
<tr>
<td>5</td>
<td>43.4</td>
<td>0.67</td>
<td>0.64</td>
<td>0.360</td>
<td>1.61</td>
<td>2.26</td>
<td>91</td>
<td>0.087±0.007</td>
</tr>
<tr>
<td>6</td>
<td>41.3</td>
<td>0.67</td>
<td>0.68</td>
<td>0.330</td>
<td>1.77</td>
<td>2.38</td>
<td>85</td>
<td>0.082±0.006</td>
</tr>
</tbody>
</table>

$a$ Temperature in the range of 294 -297 K  
$b$ $\Delta$ROG was 1290.05 ± 69.46 (μg/m$^3$) for the dark experiments and 1041.97 ± 50.09 (μg/m$^3$) for the light experiments  
$c$ $F_{HS} = 0.33$ (AS); $F_{HS} = 0.54$ (ABS:HS=85:15); $F_{HS} = 0.59$ (ABS:HS=70:30); $F_{HS} = 0.67$ (ABS:HS=50:50)  
$d$ Yield was calculated by equation 1 with the density of organic matter of 1.4 g/mL. The uncertainties of the resulting SOA yields were calculated using the uncertainties of OM and $\Delta$ROG through the propagation of uncertainty for divisions (Levie, 1997)

2.3 Results and discussion

2.3.1 Particle acidity: seed aerosol composition and proton concentration

$F_{HS}$ denotes the sulfuric acid mole fraction of the inorganic seed aerosol consisting of $\text{H}_2\text{SO}_4$ and $\text{NH}_3$ (Czoschke and Jang, 2006). $F_{HS}$ can be expressed as

$$F_{HS} = \frac{\text{molH}_2\text{SO}_4}{\text{molH}_2\text{SO}_4 + \text{molNH}_3} \quad (1)$$

$F_{HS}$ is a mathematical descriptor for inorganic seed aerosol compositions. For example, Non-acidic seed was made of 100% AS ($\text{(NH}_4\text{)}_2\text{SO}_4$) solution ($F_{HS} = 0.33$) and acidic seed was
composed of a combination of ABS (NH₄HSO₄) and HS (H₂SO₄) (e.g. \( F_{HS} = 0.54 \) with 85% ABS and 15% HS, \( F_{HS} = 0.59 \) with 70% ABS and 30% HS, and \( F_{HS} = 0.67 \) with 50% ABS and 50% HS solution).

Proton concentrations ([H⁺], \( \mu g/m^3 \)) are used to describe the actual particle acidity and calculated from the mass fraction of H⁺ estimated using an inorganic thermodynamic model (ISORROPIA) (Nenes, 2006) and the inorganic seed mass \( (M_{seed}) \) which is calculated from the density of the inorganic seed aerosol and the volume concentration of seed aerosol in the chamber air. The density of inorganic seed aerosol ranging from 1.28-1.62 g/mL was calculated with the method developed by Semmler et al. (2006) at a given composition of aqueous inorganic solution. The [H⁺] in the seed aerosol of this study ranges 0.01-0.86 \( \mu g/m^3 \) as shown in Table 2.1 and Table 2.2.

2.3.2 SOA Yields

The fractional aerosol yield (\( Y \)) was defined as (Odum et al., 1996)

\[
Y = \frac{OM}{\Delta ROG}
\]

where \( OM \) is the produced SOA mass concentration \( (\mu g/m^3) \) and \( \Delta ROG \) is the concentration of the consumed reactive precursor organic gas \( (\mu g/m^3) \). In this study, \( OM \) was calculated by equation 3.

\[
OM = d_{om}(V_{mix} - V_{seed})
\]

where \( d_{om} \) is the density of an organic aerosol, \( V_{mix} \) is the volume concentration of the aerosol mixtures, and \( V_{seed} \) is the volume concentration of inorganic seed aerosols. According to the recent studies (Dommen, et al., 2006; Gao, et al., 2004a; Kalberer, et al., 2000; Northcross and Jang, 2007), the OM density of 1.4 g/ml was used in this paper. Table 2.1 and Table 2.2 show \( OM, V_{mix}, \) and \( V_{seed} \) for each experiment. The gas-phase concentrations of aromatics
were measured using a GC-FID and the resulting ∆ROG was highly reproducible with the estimated uncertainty of less than ±6% for the dark experiments and the UV-Visible light experiments.

2.3.3 Effect of molecular structures on the SOA formation

Table 2.1, Table 2.2, and Figure 2.1 summarize the SOA data for the oxidation of both toluene and 135-TMB, varying the seed composition and humidity in the absence and the presence of UV light. Overall, the oxidation of toluene with OH radicals gives higher SOA yields than 135-TMB for all types of inorganic seeds under the same irradiation conditions. A similar tendency has been reported by other studies (Johnson et al., 2005; Takekawa et al., 2003; Dechapanya et al., 2003; Odum et al., 1997) for the SOA produced from the photochemical reactions of aromatics in the presence of NOx.

![Figure 2.1 SOA yields in the presence of non-acidic and acidic seeds at two different %RH levels under dark and UV light conditions. %RH is grouped into two levels: low %RH (22-30) and high %RH (42-52). Non-acidic seed: (NH₄)₂SO₄ (F₉₇ =0.33). Acidic seed: NH₄HSO₄: H₂SO₄ = 1:1 (F₉₇=0.67). This observed trend in SOA yields for two aromatic systems indicates significant contribution of heterogeneous reactions to SOA production. In the conventional gas-particle]
partitioning theory, SOA formation is mainly evaluated by volatility of secondary organic products. Volatility described by vapor pressure of a compound is often predicted by a molecular structure. 135-TMB has two more methyl substitutes attached to the aromatic ring than toluene. Thus, the oxygenated compounds from 135-TMB also contain two more methyl substitutes than those from toluene. On average, the additional two methyl groups in organic compounds decrease the vapor pressure by one order of magnitude. Therefore, the vapor pressures of oxygenated products of 135-TMB are lower than those for toluene, and higher SOA yields are expected for 135-TMB than for toluene. However, this is exactly the opposite of observations from our experiments and other studies (Odum et al., 1997; Johnson et al., 2005). This suggests that in addition to the gas-particle partitioning, heterogeneous reactions in the aerosol are an important process for the aromatic SOA formation. For example, the multifunctional carbonyls, which are produced from the gas phase reaction of aromatics with OH radicals through the ring opening pathway, are major oxygenated products and are highly reactive for heterogeneous reactions in aerosol. However, the molecular structures of these multifunctional carbonyl products impact heterogeneous SOA growth. In general, aldehydes have higher reactivity and favorable equilibrium constants for formation of hydrates and hemiacetals/hemiketal that are important intermediates for heterogeneous reactions (Carey and Sundberg, 2000). Therefore, aldehydes results in greater SOA yields than ketones. The oxidation of toluene produces more aldehydes leading to higher SOA yields while the oxidation of 135-TMB generates more ketones giving less SOA yields.
2.3.4 Acid effects on SOA yield without irradiation

Overall, acidic aerosols lead to higher SOA yield than non-acidic aerosols for both the toluene and 135-TMB systems. Under dark, the effects of particle acidity appear to be much stronger with toluene SOA than 135-TMB SOA. To evaluate acid effects on SOA formation, we estimate the difference in the aerosol mass ($OM_{\text{diff}}$) between the OM in the acidic aerosol ($OM_{\text{acid}}$) and OM in the non-acidic aerosol ($OM_{\text{nonacid}}$). $OM_{\text{diff}}$, expressed as equation 4, indicates additional organic aerosol mass increases by heterogeneous reactions in the presence of acidic aerosol.

$$OM_{\text{diff}} = OM_{\text{acid}} - OM_{\text{nonacid}}$$ (4)

Figure 2.2 $f(OM_{\text{diff}})$ as a function of a proton concentration at high %RH (42-52) describing the contribution of acid catalyzed heterogeneous reaction to the SOA mass.

The non-acidic seed aerosol made of AS is solid below the efflorescence point that is in the range of 30-35%RH (Colberg et al, 2004; Gao et al, 2006; Martin et al, 2003), while the acidic seed particles are aqueous regardless of %RH under our experimental conditions. In order to consider the same liquid phase for two seed aerosols, we applied the equation 4
only to the experimental data at %RH = 42-52 in this study. The $OM_{\text{diff}}$ fraction, $f(OM_{\text{diff}})$, is calculated by dividing $OM_{\text{diff}}$ by $OM_{\text{acid}}$. $f(OM_{\text{diff}})$ indicates relative significance of the mass contribution of heterogeneous acid-catalyzed reactions to the total acidic SOA. Figure 2.2 displays the strong linearity ($R^2 = 0.96-0.99$) between $f(OM_{\text{diff}})$ and $[H^+]$ at high %RH (42-52) for both toluene and 135-TMB. Overall, $f(OM_{\text{diff}})$ is much greater with toluene than those with 135-TMB. For example, $f(OM_{\text{diff}})$ is 0.41-0.53 for toluene and 0.20-0.40 for 135-TMB.

In Figure 2.3, SOA yields at different levels of humidity were plotted vs. $[H^+]$ estimated with ISORROPIA at a given humidity, inorganic seed composition, and $M_{\text{seed}}$. The SOA yields of the toluene system are more sensitive to humidity and $[H^+]$ (at the same level of %RH) than that of the 135-TMB system in the acidic aerosol. This result again indicates that heterogeneous acid-catalyzed reactions in the toluene system are more effective than those in the 135-TMB system.

![Figure 2.3 SOA yields as a function of a proton concentration. %RH is grouped into two levels: low %RH (22-30) and high %RH (42-52).](image-url)
Figure 2.3 also illustrates that SOA yields of both toluene and 135-TMB were greater at low %RH than at high %RH (42-52) in the similar range of [H⁺]. In order to determine whether the difference in SOA yield between low %RH (22-30) and high %RH (42-52) is statistically significant, the t-test for the linear regression analysis (Kleinbaum et al., 1988) between [H⁺] and SOA yields was performed at two levels of %RH within toluene or 135-TMB system. In detail, for each aromatic system, the two separate t-tests were conducted for evaluating parallelism and comparing the intercepts of the regression line ([H⁺] vs. SOA yields) at different %RH levels at the 95% confidence interval. These results show two regression lines at two different levels of %RH are significantly different, suggesting that [H⁺] is a useful parameter but [H⁺] alone is not sufficient to explain the acid effects on SOA. As suggested in the previous study (Jang et al., 2006), the description of a role of water in the particle phase reactions and the additional kinetic analysis through activity coefficient (e.g. excess acidity) of carbonyl species in the non-ideality solution such as strong and medium acidic media are necessary to thoroughly understand the interaction between inorganic acid and SOA.

2.3.5 SOA formation with irradiation

To investigate the effects of UV light on SOA yields, several sets of SOA experiments were conducted under similar experimental conditions of those without UV light. The outcome of UV irradiation is the suppression of the SOA formation for both aromatic systems. The observation of our study is consistent with the previous report by Presto et al (2005), who showed that SOA yields from ozonolysis of α-pinene were reduced by the presence of UV. Figure 2.4 summarizes the impact of the UV irradiation on SOA yields under different experimental conditions (aerosol acidity and humidity). SOA yield reduction
\( \Delta Y_{\text{dark-UV}} \) was obtained by subtracting the SOA yield under light from the SOA yield under dark at the same experimental conditions. The precision of our measurement was good enough to distinguish the difference of the toluene SOA yields beyond 0.03 and the difference of the 135-TMB SOA yields beyond 0.009. Therefore, as shown in Figure 2.4, \( \Delta Y_{\text{dark-UV}} \) for the toluene SOA with the non acidic seed was negligible. However, for all other SOA experiments, depending on the particle acidity, UV exposure leads to significant \( \Delta Y_{\text{dark-UV}} \) values by 0.07-0.11 for the toluene SOA and 0.02-0.05 for the 135-TMB SOA. The explanations for the decreases in SOA are not yet clear.

![Figure 2.4](image)

Figure 2.4 The absolute reduction of aromatic SOA yields (\( \Delta Y_{\text{dark-UV}} \)) due to the UV exposure at different humidity levels. %RH is grouped into two levels: low %RH (22-30) and high %RH (42-52). “NA” denotes the non-acidic condition and “A” denotes the acidic condition.

We hypothesize that UV irradiation may change the gas phase chemistry resulting in the SOA loss. UV light decomposes some organic products into smaller and less condensable or oligomerizable products in the gas phase and decreases the contribution of these species to the SOA formation. For example, gas phase carbonyls such as conjugated aldehydes, which are highly reactive for the heterogeneous reactions, undergo photolysis due to the accessibility of long-wave absorption bands in the near UV-visible region. UV-visible
light converts these carbonyls to other compounds that may be more volatile or less reactive for the heterogeneous reactions. In addition to the altered gas phase chemistry, it is possible that the oxidized products in the particle phase can be degraded into the smaller size molecules by UV irradiation, resulting in off-gassing of organics into the air. However, this pathway in the particle has been shown not significant by our experiments discussed below.

A similar experimental approach reported by Presto and coworkers (2005) was used in this study to examine the UV impact on aromatic SOA after the aerosol formation was completed. Basically, two sets of experiments were performed under two different humidity (42-52% and 22-30%) and two different inorganic compositions (non-acidic and acidic inorganic seed). In the first sets, the chamber initially remained in darkness over the duration of the SOA experiments (100-130 minutes). Then the UV-Vis lights were switched on and off every 27 minutes for another 108 minutes to change the lighting conditions of the chamber (Figure 2.5A and 2.5C). In the second sets of experiments, the chamber was first exposed to the UV-Vis light during the SOA experiments. Then the UV-Vis lights were switched off and on as shown in Figure 2.5B and 2.5D. The results showed that after the completion of SOA formation, the changes in either OM or the particle size distribution were negligible by alternating UV irradiation condition (the on-off mode) for both aromatic systems (Figure 2.5). Such observations indicate that the presence/absence of UV light through the on-off mode afterwards was not influential on SOA formation. According to the hypothesis suggested by Presto et al (2005), certain products created from heterogeneous reactions in SOA hardly return to the original compounds that are controlled by the gas-particle partitioning.
Figure 2.5 The representative time profiles of SOA mass in the chamber with the UV light controlled by on-off/off-on mode showing UV light effects on the particle mass change. (A) TOL/MB (%RH=42, F_HS=0.67); (B) TOL/MB (%RH=30, F_HS=0.33); (C) TMB/MB (%RH=26, F_HS=0.33) and (D) TMB/MB (%RH=21, F_HS=0.67). The open circle represents the SOA mass obtained under UV light exposure; the solid circle represents the SOA mass under dark conditions. Each data point is the average SOA mass of three SMPS sampling cycles (3 minutes/cycle).

The effects of particle acidity on the SOA yields remain for both aromatic systems in the presence of UV light, although the magnitude of acidity impacts is less compared to the dark experiments, for all aromatic SOA except 135-TMB system at low humidity. As discussed earlier, multifunctional carbonyls are believed to be highly reactive for the acid-catalyzed heterogeneous reactions in SOA. However, UV irradiation might decompose...
certain carbonyls into less reactive compounds for the acid-catalyzed heterogeneous reactions. Compared to the toluene SOA, the 135-TMB SOA was influenced by UV irradiation to a less extent. The difference in UV effects on SOA formation between two aromatic systems is likely due to the difference in the molecular structures of carbonyl products. The carbonyls produced from toluene are mostly aldehydes while the carbonyls from 135-TMB are ketones. Generally, the UV-absorption cross sections of aldehydes are larger than ketones (Finlayson-Pitts and Pitts, 2000; Martinez et al., 1992) in our light source (260-480 nm). The aldehydes from the toluene oxidation are more readily photo-dissociated than ketones from the 135-TMB. Therefore, UV irradiation effects are stronger on toluene SOA.

2.4 Implications of this study

In summary, our laboratory studies show particle acidity enhances the aromatic SOA production through heterogeneous reactions in the aerosol under both dark and UV light conditions. Under the weak acidic conditions of our experiments ($F_{HS}$=0.54, $[H^+]$ =0.21-0.24) at %RH=42-52, we observed 36% (dark) and 14% (UV light) SOA yield increases for toluene SOA compared to SOA yields in the non-acidic seed ($F_{HS}$=0.33, $[H^+]$ =0.01) with the toluene consumption ($\Delta$ROG) of 802.85 µg/m$^3$ (dark) and 611.69 µg/m$^3$ (UV light). Under the similar experimental conditions, 22% (dark) and 24 % (UV light) SOA yield increases were obtained for 135-TMB SOA at $\Delta$ROG = 1290.05 µg/m$^3$ (dark) and 1041.97 µg/m$^3$ (UV light). Czoschke and Jang (2006) reported that under the similar acidic conditions, about 20% yield increase for the SOA formed by the ozonolysis of $\alpha$-pinene under dark. Therefore, heterogeneous acid-catalyzed reactions appear to be effective for the aromatic SOA formation in the dark at least equally to biogenic SOA. This conclusion is limited to SOA
data in the dark conditions because no data is available for the acid effects on biogenic SOA under UV light.

Our studies under NO\textsubscript{x} free conditions can be applicable to the aromatic SOA formation in the ambient air which has relative low NO\textsubscript{x} concentrations. For example, in the weekday afternoon (especially 12pm-3pm) of the urban area such as Atlanta, Georgia (Wade, 2005), the NO\textsubscript{x} concentrations decrease below 10 ppb. Compared to the ambient conditions, the concentrations of inorganic seed (AS; ABS and HS combination) and precursor aromatics in our laboratory study were relatively high. However, the mass ratio of organic to inorganic in the particle phase is one of important parameters to be considered if one estimates the SOA growth by the heterogeneous acid-catalyzed reactions in the atmosphere. The mass ratios of organic to inorganic compounds directly correspond to the degree and the rates of the acid-catalyzed heterogeneous reactions of organic species in aerosol. For example, when the mass ratios of organic to inorganic are low, the incidence of acid-catalyzed heterogeneous reactions could be high. The mass ratios of organic to inorganic in the ambient aerosols vary from 0.3 to 0.6(Drewnick et al., 2004; Russell et al., 2004) and the mass ratios in our experiments under weak acidity conditions are about 0.6. The comparison of our experiments run under weakly acidic and neutral conditions imply that under ambient condition, the upper bounds of the average aromatic SOA increase due to particle acidity are about 15%-25% in the day time and 20%-40% during the night, provided that toluene and 135-TMB are good representatives of aromatic precursors.

This study, focused on inorganic acidity associated with solely H\textsubscript{2}SO\textsubscript{4}, was the first step to explore the impact of particle acidity on the aromatic SOA formation. These results can be used as a reference for comparison in future studies on SOA formation in the presence
of NO$_x$. The resulting experimental data set along with the future work on product analysis will be used to develop a model for SOA formation incorporating both gas-particle partitioning and heterogeneous reactions.

**Acknowledgements**

This work was supported by a Grant from National Science Foundation (ATM-0314128).
Reference


Coordinating Research Council, 3650 Mansell Road, Suite 140, Alpharetta, GA, 30022-8246.


Chapter III

Secondary Organic Aerosol Formation from Toluene Photooxidation under the Various NO\textsubscript{x} Conditions and Particle Acidity

Gang Cao\textsuperscript{1}, Myoseon Jang\textsuperscript{2}*  
1. Department of Environmental Sciences and Engineering
University of North Carolina at Chapel Hill
CB#7431, Rosenau Hall, Chapel Hill, NC, 27599  
2. Department of Environmental Engineering Sciences, University of Florida,
P.O. Box 116450, Gainesville, FL 32611

Published in Atmospheric Chemistry and Physics Discussion (2008) 8, 14467–14495. Atmospheric Chemistry and Physics, in revision.

*Corresponding Author: Myoseon Jang  
Email: mjang@ufl.edu
Abstract

Secondary organic aerosol (SOA) formation from photooxidation of toluene is studied using a 2 m³ indoor Teflon film chamber under three different NOₓ conditions: low (<3 ppb), intermediate (90-105 ppb) and high (280-315 ppb). SOA experiments are conducted in the presence of either neutral or acidic sulfate seed aerosols under two different humidity levels (%RH~15-22 or 38-49). NOₓ concentrations in the chamber air affect not only SOA yields but also SOA growth described by the organic mass (OM) produced as a function of the toluene concentration consumed over the course of a single SOA experiment. The particle acidity effect on toluene SOA formation varies with NOₓ concentrations. For the low and the intermediate NOₓ experiments, SOA yields with acidic sulfate seed considerably increase by: 36%-115% at low %RH and 25-44% at high %RH compared to those with neutral seed. No significant particle acidity effect is observed for the high NOₓ experiments. The humidity effect on SOA formation is also different at the three NOₓ levels. For the low NOₓ experiments, SOA yields are 29%-34% lower at high %RH than those at low %RH in the presence of either neutral or acidic sulfate seed. For the intermediate NOx experiments, SOA yields at high %RH increase by 39% in the presence of neutral seed but slightly decrease by 7% in the presence of acidic sulfate seed compared to those at low %RH. For the high NOₓ experiments with a high NO fraction, no significant humidity effect on SOA yields is found with both neutral and acidic sulfate seeds.
3.1 Introduction

As an important class of atmospheric particulate matter, secondary organic aerosol (SOA) refers to the aerosols formed by various atmospheric oxidation reactions of volatile organic compounds (VOCs) with atmospheric oxidants (e.g. ozone, hydroxyl radical, and nitrate radical). The last three decades of studies through a large number of chamber experiments suggest that the possible SOA formation pathways include self-nucleation, gas-particle partitioning and heterogeneous reactions.

In recent years, studies on contribution of heterogeneous reactions to SOA formation have drawn increasing attention. It is believed that particle phase heterogeneous reactions of atmospheric organics such as carbonyls are important mechanisms for SOA formation (Jang et al., 2002, 2006; Johnson et al., 2004). The products of heterogeneous reactions—oligomeric species have been observed on diverse SOA generated from either biogenic or aromatic precursors (Gao et al., 2004a; Hamilton et al., 2008; Heaton et al., 2007; Iinuma et al., 2004, 2007; Kalberer et al., 2004; Tolocka et al., 2004). The contribution of heterogeneous reactions to SOA formation is influenced by reactivity of gas phase products from oxidation of organics. Jang et al. (2006) lumped major gas phase products of α-pinene ozonolysis into three groups of reactivity (slow, medium and fast) for the estimation of heterogeneous SOA formation. For example, heterogeneous reactions of compounds with fast reactivity, such as oxoaldehydes—the aldehydes that contain at least two C=O groups, can occur without the need of an acidic catalyst but can be accelerated by an acidic catalyst. Heterogeneous reactions of compounds with slow and medium reactivity such as oxo-carboxylic acids will be significant only when an acidic catalyst is present in the particle phase. Therefore, heterogeneous reactions of different types of gas phase oxygenated products will respond
differently to particle acidity. In addition to acid-catalyzed chemistry, organic sulfate formation in aerosols appears to be an important pathway for heterogeneous SOA formation in the presence of acidic sulfate seed (Iinuma et al., 2007; Surratt et al., 2007). The relative importance of the proposed heterogeneous reactions to SOA production depends on the composition of gas phase products from a precursor VOC, NO$_x$ concentrations, particle acidity, temperature, and humidity.

The recent studies (Czoschke and Jang, 2006; Gao et al., 2004b; Iinuma et al., 2004; Kleindienst et al., 2006; Liggio et al., 2007; Northcross and Jang, 2007) on SOA formation from the atmospheric oxidation of biogenic terpene and isoprene have shown that particle acidity considerably influence biogenic SOA formation. Only a few studies have addressed the influence of acidic sulfates on the aromatic SOA formation and shown the contradictory results. For example, Ng et al. (2007) reported negligible SOA yield difference between acidic and neutral aerosols for aromatic SOA under two different NO$_x$ conditions at extremely low humidity (%RH~5%). However, Cao and Jang (2007) observed that SOA yields were significantly enhanced by the presence of acidic sulfate seed aerosols without NO$_x$ at two humidity levels (%RH~26 and 47), no matter whether the SOA experiments were conducted in the dark or under UV-Visible irradiation. Therefore, further research efforts are needed to clarify the effects of particle acidity on aromatic SOA formation. Such studies will be essential for the estimation of aromatic SOA loadings particularly in the acidic atmosphere.

Previous studies on SOA formation from aromatic photooxidation (Hurley et al., 2001; Johnson et al., 2004; Ng et al., 2007; Song et al., 2005) have shown that NO$_x$ reduces the aromatic SOA formation, suggesting that NO$_x$ influences the fate of gas phase organic
peroxide radicals (RO\textsubscript{2}). Under high NO\textsubscript{x} conditions, RO\textsubscript{2} radicals react with NO\textsubscript{x} and produce relatively volatile organic nitrates; while under low NO\textsubscript{x} conditions, RO\textsubscript{2} radicals react with hydroperoxyl radicals (HO\textsubscript{2}) forming organic hydroperoxides (ROOH) that may further react with aldehyde species in the particle phase to produce the low volatile peroxyhemiacetals (Johnson et al., 2004). However, most of these previous studies were conducted under the neutral condition. The effects of particle acidity at varied NO\textsubscript{x} conditions are poorly understood. NO\textsubscript{x} levels are expected to influence the particle acidity effect on SOA formation because different NO\textsubscript{x} levels lead to different gas phase products with diverse physical and chemical properties. Hence, more comprehensive SOA studies at different NO\textsubscript{x} levels coupled with various particle acidities and humidity levels are needed.

Aromatic hydrocarbons constitute about 20-50\% (in PPbC) of the total non methane VOCs in urban atmospheres of the United States and Europe (Calvert et al., 2002) and contribute a significant fraction of anthropogenic SOA loadings in urban area. In this paper, toluene is selected as an aromatic precursor for the study on SOA formation because toluene is the most abundant aromatic VOC in urban atmosphere comprising about 20-40\% of the total aromatic compounds (Calvert et al., 2002) and produces high SOA yields compared to other aromatic VOCs (Dechapanya et al., 2003). The main focus of the present study is to investigate the effect of NO\textsubscript{x}, particle acidity and humidity on the toluene SOA formation. The SOA yields and the aerosol growth patterns have been studied based on three levels of NO\textsubscript{x} concentrations (low: <3 ppb, intermediate: 90-105 ppb and high: 280-315 ppb). Each level of the NO\textsubscript{x} studies included four sub-level experiments under two different particle acidities (non acid vs. acid) and two different humidity levels (%RH: 15-22 or 38-49). The particle
acidity and humidity effects on SOA formation have been evaluated within the uniform NO$_x$ levels to exclude the possible confounding NO$_x$ influences.

3.2 Experimental section

All experiments were conducted in a 2 m$^3$ indoor Teflon film chamber under UV-visible light conditions. The detailed description for the chamber experiments has been provided elsewhere (Cao and Jang, 2007). The chamber is equipped with sixteen fluorescent lamps (Solarc Systems Inc., FS40T12/UVB) that have emission in the UV range between 300-400 nm with the maximum near 314 nm. Temperature increase due to the light sources is less than 2 K for the duration of the experiments. The particle size distribution was monitored with a Scanning Mobility Particle Sizer (SMPS, TSI Model 3080, Shoreview, MN) coupled with a condensation nuclei counter (CNC, TSI, Model 3025A). Particle data were corrected for the aerosol loss to the chamber wall (McMurry and Grosjean, 1985) with a first order decay. The gas-phase toluene concentrations were measured with an HP 5890 GC-FID. Temperature (295-299 K) and %RH of the chamber were measured with an electronic thermo-hygrometer (Dwyer Instrument, INC, USA). Prior to each experiment, the chamber was flushed with clean air from clean air generators (Aadco Model 737, Rockville, MD; Whatman Model 75-52, Haverhill, MA). The inorganic seed aerosols were injected into the chamber by atomizing 0.005 mol/L inorganic aqueous solution (various combinations of ammonium sulfate, ammonium bisulfate and sulfuric acid) with a Constant Output Atomizer (TSI, Model 3076, Shoreview, MN).

For the low NO$_x$ (<3 ppb) experiments, toluene was oxidized by OH radicals from the photolysis of H$_2$O$_2$. When the seed aerosols stabilized, a known volume of toluene was injected into the chamber. The gas phase of H$_2$O$_2$ was then introduced into the chamber by
gently purging the nitrogen at 1 L/min over a 50% H₂O₂ aqueous solution (Aldrich). The UV-Visible lights were turned on at the beginning of the H₂O₂ injection. The initial H₂O₂ concentrations in the chamber ranged from 3.48-3.71 ppm which were estimated by mass loss of the 50% H₂O₂ solution between before and after H₂O₂ injection and the mole fraction of H₂O₂ in vapor mixture (water + H₂O₂) (Manatt and Manatt, 2004).

For the intermediate (90-105 ppb) and the high NOₓ (280-315 ppb) experiments, a known amount of NO and NO₂ was added in the chamber from a certificate NO tank (99.5% nitric oxide, Linde Gas). After the NOₓ concentrations stabilized, a known volume of toluene was injected and the UV lights were turned on, which marked the starting point of the SOA experiment. During the experiments, ozone and NOₓ concentrations were monitored with a photometric ozone analyzer (model 400E, Teledyne Instruments, San Diego, CA) and a chemiluminescence NOₓ detector (model 200E, Teledyne Instruments, San Diego, CA).

The experimental conditions and the resulting SOA data are summarized in Table 3.1 and Table 3.2. The SOA yield (Y) defined as the ratio of the produced secondary organic mass (OM, µg/m³) to the consumed toluene concentration (ΔROG, µg/m³), was calculated with the OM density of 1.4 g/mL (Dommen et al., 2006; Gao et al., 2004a).

In Table 3.1, the particle acidity is described by proton concentrations ([H⁺], µg/m³) that are calculated from the mass fraction of H⁺ estimated using an inorganic thermodynamic model (ISORROPIA) (Nenes, 2006) and the inorganic seed mass (M_{seed}) at a given humidity and a seed composition. M_{seed} is calculated from the density and the volume concentration of seed aerosols in the chamber air. The density of inorganic seed aerosols ranging from 1.332-1.634 g/mL is calculated with the method developed by Semmler et al. (2006) at a given
composition of aqueous inorganic solution. The $[\text{H}^+]$ in the seed aerosols of this study ranged from 0.01 to 1.19 µg/m$^3$ (Table 3.1).

Table 3.1 Experimental conditions and resulting SOA data from photooxidation of toluene$^a$

<table>
<thead>
<tr>
<th>Exp #$^b$</th>
<th>%RH</th>
<th>$[\text{H}^+]$ (µg/m$^3$)</th>
<th>NO$^c$ (ppb)</th>
<th>NO$_2^c$ (ppb)</th>
<th>∆TOL (ppm)</th>
<th>$V_{\text{seed}}$ (nL/m$^3$)</th>
<th>$V_{\text{mix}}$ (nL/m$^3$)</th>
<th>OM (µg/m$^3$)</th>
<th>Yield$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNOx-NA-LRH</td>
<td>18.4</td>
<td>0.01</td>
<td>&lt;1.5</td>
<td>&lt;1.5</td>
<td>0.10</td>
<td>169</td>
<td>245</td>
<td>106.3</td>
<td>0.28±0.020</td>
</tr>
<tr>
<td>LNOx-NA-HRH</td>
<td>48.2</td>
<td>0.01</td>
<td>&lt;1.5</td>
<td>&lt;1.5</td>
<td>0.09</td>
<td>179</td>
<td>229</td>
<td>70.5</td>
<td>0.20±0.015</td>
</tr>
<tr>
<td>LNOx-A-LRH</td>
<td>17.0</td>
<td>0.80</td>
<td>&lt;1.5</td>
<td>&lt;1.5</td>
<td>0.13</td>
<td>153</td>
<td>285</td>
<td>183.2</td>
<td>0.38±0.028</td>
</tr>
<tr>
<td>LNOx-A-HRH</td>
<td>48.2</td>
<td>0.69</td>
<td>&lt;1.5</td>
<td>&lt;1.5</td>
<td>0.10</td>
<td>185</td>
<td>249</td>
<td>89.4</td>
<td>0.25±0.020</td>
</tr>
<tr>
<td>MNOx-NA-LRH</td>
<td>15.8</td>
<td>0.01</td>
<td>66.2</td>
<td>28.6</td>
<td>0.13</td>
<td>218</td>
<td>263</td>
<td>66.5</td>
<td>0.13±0.010</td>
</tr>
<tr>
<td>MNOx-NA-HRH</td>
<td>41.0</td>
<td>0.02</td>
<td>78.1</td>
<td>14.8</td>
<td>0.10</td>
<td>215</td>
<td>262</td>
<td>65.3</td>
<td>0.18±0.013</td>
</tr>
<tr>
<td>MNOx-A-LRH</td>
<td>21.1</td>
<td>1.05</td>
<td>69.2</td>
<td>30.0</td>
<td>0.12</td>
<td>203</td>
<td>292</td>
<td>124.4</td>
<td>0.28±0.020</td>
</tr>
<tr>
<td>MNOx-A-HRH</td>
<td>38.5</td>
<td>0.87</td>
<td>82.7</td>
<td>22.0</td>
<td>0.12</td>
<td>212</td>
<td>295</td>
<td>116.5</td>
<td>0.26±0.019</td>
</tr>
<tr>
<td>HNOx-NA-LRH</td>
<td>14.6</td>
<td>0.01</td>
<td>241.4</td>
<td>70.4</td>
<td>0.30</td>
<td>246</td>
<td>340</td>
<td>130.9</td>
<td>0.12±0.010</td>
</tr>
<tr>
<td>HNOx-NA-HRH</td>
<td>42.7</td>
<td>0.02</td>
<td>229.4</td>
<td>85.1</td>
<td>0.29</td>
<td>210</td>
<td>309</td>
<td>138.0</td>
<td>0.13±0.010</td>
</tr>
<tr>
<td>HNOx-A-LRH</td>
<td>19.9</td>
<td>1.19</td>
<td>226.1</td>
<td>62.0</td>
<td>0.28</td>
<td>227</td>
<td>328</td>
<td>141.4</td>
<td>0.13±0.010</td>
</tr>
<tr>
<td>HNOx-A-HRH</td>
<td>40.9</td>
<td>0.94</td>
<td>222.2</td>
<td>81.6</td>
<td>0.31</td>
<td>235</td>
<td>336</td>
<td>142.0</td>
<td>0.12±0.010</td>
</tr>
</tbody>
</table>

a. Temperature: 295 -299 K.
b. LNO$_x$: low NO$_x$ level (OH radical source: photolysis of H$_2$O$_2$); MNO$_x$: intermediate NO$_x$ level ([NO$_x$]~90-105 ppb); HNO$_x$: high NO$_x$ level ([NO$_x$]~280-315 ppb); NA: in the presence of non acidic seed; A: in the presence of acidic sulfate seed; LRH: low %RH; HRH: high %RH.
c. initial concentrations

d. SOA yield was calculated with the density of organic matter of 1.4 g/mL. The uncertainties of the resulting SOA yields were calculated using the uncertainties of OM and ∆ROG through the propagation of uncertainty for divisions (Levie, 1997).

3.3 Results and discussion

3.3.1 SOA yields

3.3.1.1 NO$_x$ effect on SOA formation

Table 3.1, Table 3.2 and Figure 3.1 summarize the toluene SOA yields under three NO$_x$ conditions and two humidity levels in the presence of non acidic/acidic sulfate seed.
aerosols. For each high NOx experiment, the SOA formation was investigated for the two separate NOx profiles: low NO and high NO, since the conversion of NO to NO2 over the course of the experiment turned the high NO conditions to the low NO conditions leading to the different SOA formation patterns (see Sect. 3.3.2). The SOA yields (Table 3.1) were 0.2-0.38 at low NOx; 0.13-0.28 at intermediate NOx; 0.12-0.13 at high NOx. Within the high NOx experiments, the SOA yields (Table 3.2) were 0.17-0.21 at low NO faction of high NOx conditions and 0.027-0.031 at high NO fraction of high NOx conditions. Overall, SOA formation was considerably influenced by NOx concentrations showing the highest SOA yield at low NOx and the lowest SOA yield at high NOx with high NO fraction of NOx. This observation is consistent with the studies of other research groups (Hurley et al., 2001; Johnson et al., 2004; Ng et al., 2007; Song et al.2005).

Table 3.2 Experimental conditions and resulting SOA data from photooxidation of toluene for the low NO region and the high NO region of high NOx experiments

<table>
<thead>
<tr>
<th>Exp #(^3)</th>
<th>%RH</th>
<th>[H(^+)] (µg/m(^3))</th>
<th>NO(^x) (ppb)</th>
<th>NO(^2) (ppb)</th>
<th>ATOI (ppm)</th>
<th>V(_{seed}) (nL/m(^3))</th>
<th>V(_{mix}) (nL/m(^3))</th>
<th>OM (µg/m(^3))</th>
<th>Yield(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNOx(LNO) -NA-LRH</td>
<td>14.6</td>
<td>N/A(^e)</td>
<td>90.5</td>
<td>180.2</td>
<td>0.17</td>
<td>256</td>
<td>340</td>
<td>117.6</td>
<td>0.18±0.013</td>
</tr>
<tr>
<td>HNOx(LNO) -NA-HRH</td>
<td>42.7</td>
<td>N/A(^e)</td>
<td>72.3</td>
<td>214.9</td>
<td>0.18</td>
<td>219</td>
<td>309</td>
<td>126.0</td>
<td>0.18±0.013</td>
</tr>
<tr>
<td>HNOx(LNO) -A-LRH</td>
<td>19.9</td>
<td>N/A(^e)</td>
<td>58.6</td>
<td>192.8</td>
<td>0.16</td>
<td>236</td>
<td>328</td>
<td>128.8</td>
<td>0.21±0.015</td>
</tr>
<tr>
<td>HNOx(LNO) -A-HRH</td>
<td>40.9</td>
<td>N/A(^e)</td>
<td>64.7</td>
<td>186.9</td>
<td>0.20</td>
<td>244</td>
<td>336</td>
<td>128.8</td>
<td>0.17±0.013</td>
</tr>
<tr>
<td>HNOx(HNO) -NA-LRH</td>
<td>14.6</td>
<td>0.01</td>
<td>241.4</td>
<td>70.4</td>
<td>0.13</td>
<td>246</td>
<td>256</td>
<td>13.3</td>
<td>0.027±0.003</td>
</tr>
<tr>
<td>HNOx(HNO) -NA-HRH</td>
<td>42.7</td>
<td>0.02</td>
<td>229.4</td>
<td>85.1</td>
<td>0.11</td>
<td>210</td>
<td>219</td>
<td>12.0</td>
<td>0.029±0.004</td>
</tr>
<tr>
<td>HNOx(HNO) -A-LRH</td>
<td>19.9</td>
<td>1.19</td>
<td>226.1</td>
<td>62.0</td>
<td>0.12</td>
<td>227</td>
<td>236</td>
<td>12.6</td>
<td>0.027±0.003</td>
</tr>
<tr>
<td>HNOx(HNO) -A-HRH</td>
<td>40.9</td>
<td>0.94</td>
<td>222.2</td>
<td>81.6</td>
<td>0.11</td>
<td>235</td>
<td>244</td>
<td>13.2</td>
<td>0.031±0.004</td>
</tr>
</tbody>
</table>

a. Temperature: 295 -299 K.
b. HNOx: high NOx level ([NOx]~280-315 ppb); HNO: high NO fraction; LNO: low NO fraction; NA: in the presence of non acidic seed; A: in the presence of acidic sulfate seed; LRH: low %RH; HRH: high %RH.
c. Initial concentrations.
d. SOA yield was calculated with the density of organic matter of 1.4 g/mL. The uncertainties of the resulting SOA yields were calculated using the uncertainties of OM and ∆ROG through the propagation of uncertainty for divisions (Levie, 1997).
e. N/A: not available.
Figure 3.1 SOA yields in the presence of neutral seed and acidic sulfate seed at two different \%RH levels under three NO$_x$ conditions. The data used are shown in Table 3.1.

Such tendency can be explained by the fact that different NO$_x$ levels lead to different reaction pathways of peroxy radicals (RO$_2$), which are produced from the gas phase reactions of toluene with OH radicals in the presence of oxygen. The possible subsequent reactions of RO$_2$ include the self-reaction of RO$_2$ (channel A in Figure 3.2); the reaction with HO$_2$ (channel B in Figure 3.2) to generate hydroperoxide (ROOH) and carbonyls; the reaction with NO to produce RO radicals and further carbonyls (channel C in Figure 3.2); and the formation of organic nitrates (channel D in Figure 3.2). According to the Master Chemical Mechanism (MCM) (Jenkin et al., 2003), the ratio of the rate constants of RO2 reacting with RO$_2$, HO$_2$ and NO is 1.0: 21.3: 1.1(producing RONO$_2$): 8.6 (producing RO + NO$_2$). The relative importance of these reactions depends on the concentrations of NO and HO$_2$ in the system. Channels A and B are the dominant pathways under the low NO$_x$ conditions, while channels C and D are significant under the intermediate and high NO$_x$ conditions. The higher
SOA yield with low NOx concentrations indicates that the ROOH readily produces SOA mass through heterogeneous reactions with carbonyls in the particle phase (Johnson et al., 2004). For the intermediate NOx conditions, channel C is likely the dominant pathway to convert NO to NO2 and generate carbonyls. The multifunctional carbonyls from toluene oxidation have been considered highly reactive compounds for heterogeneous reactions (either in the presence or the absence of acidic sulfate seed aerosols) and increase SOA mass.

Figure 3.2 The fates of RO2 produced from toluene photooxidation under different NOx conditions. Peroxides (ROOR) are produced from self-reactions of RO2 radicals (channel A); Hydroperoxide (ROOH) and carbonyls (RR'(C=O)) are produced from reactions of RO2 and OH2 radicals (channel B); Carbonyls, RR’(C=O), are produced from reaction of RO2 with NO (channel C); Organic nitrates (RONO2) are formed from reactions of RO2 with NO (channel D). Gray boxes show the major influential factors on reaction channels in the gas and particle phase: the acidity and humidity effects discussed in Sect. 3.3.1.2 and Table 3.4.

The presence of high initial concentrations of NOx with the high NO fraction of the total NOx is likely to facilitate the generation of compounds with no or very small contribution to SOA formation resulting in the low SOA yields. Figure 3.3 demonstrates the simplified possible reaction pathways which produce organic nitrates (e.g. peroxybenzoyl...
nitrate, benzyl nitrate and peroxy acyl nitrates) or nitro compounds (e.g. nitrotoluene) in the presence of high NOx concentrations. Peroxybenzoyl nitrate is formed from reactions between peroxybenzoyl radicals and NO2; Benzyl nitrate is produced from reactions of benzyl peroxy radicals with NO; Nitrotoluene is from OH-aromatic adducts reacting with NO2; and peroxy acyl nitrates (PAN-like products) are likely to be formed at high NO2 concentrations from the reactions of NO2 with RC(O)OO \cdot radicals which are produced from H-abstraction of aldehydes in the presence of oxygen. Laboratory studies (Hurley et al., 2001; Jang and Kamens, 2001) of aromatic oxidation at high NOx observed nitro compounds and organic nitrates that are expected to be stable for particle phase heterogeneous reactions and contribute to SOA formation mainly through the gas-particle partitioning. However, organic nitrates (e.g. benzyl nitrate and peroxy acyl nitrates) are volatile and thus the contribution of organic nitrates to SOA formation may be insignificant: e.g. the estimated vapor pressure for benzyl nitrate is 0.00155 atm using the group contribution methods by Schwarzenbach et al.(1993). Nitro compounds in the gas phase may partition to the preexisting aerosols increasing SOA. But under the high NOx conditions with high NO fraction, the nitro compounds comprise only a small fraction of the gas phase oxygenated products compared to the organic nitrates, therefore SOA formation is greatly suppressed in the beginning of the experiments. It is believed that these channels may be significant in the laboratory studies under the high NOx concentrations. The suppression of SOA formation with high NOx (high NO fraction) in the laboratory chamber may not be observed in the atmosphere.
Figure 3.3 The possible reaction channels for gas phase oxygenated products at high NO\textsubscript{x} level. The numbers in the brackets are the branch ratios of the reaction channels. AR represents the benzene ring. R represents ring-opening structures.
Table 3.3 summarizes the relative SOA yield increase under different NO\textsubscript{x} concentrations at a given particle acidity and %RH level. The relative SOA yield increase between the low and the intermediate NO\textsubscript{x} conditions was the smallest at high %RH in the presence of acidic seed, compared to those under other particle acidity and humidity levels. The detailed description for NO\textsubscript{x} effect on SOA incorporated with impacts of acidity and humidity will be discussed in the Sect. 3.3.1.2.

Table 3.3 Relative SOA yield increase under different NO\textsubscript{x} concentrations at a given particle acidity and humidity\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Exp. conditions</th>
<th>( \frac{(Y_{\text{LNOx}}-Y_{\text{MNOx}})}{Y_{\text{MNOx}}} ) (%)</th>
<th>( \frac{(Y_{\text{LNOx}}-Y_{\text{HNOx(LNO)}})}{Y_{\text{HNOx(LNO)}}} ) (%)</th>
<th>( \frac{(Y_{\text{LNOx}}-Y_{\text{HNOx(HNO)}})}{Y_{\text{HNOx(HNO)}}} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA-LRH</td>
<td>115</td>
<td>56</td>
<td>937</td>
</tr>
<tr>
<td>NA-HRH</td>
<td>11</td>
<td>11</td>
<td>590</td>
</tr>
<tr>
<td>A-LRH</td>
<td>36</td>
<td>81</td>
<td>1307</td>
</tr>
<tr>
<td>A-HRH</td>
<td>-4</td>
<td>47</td>
<td>706</td>
</tr>
</tbody>
</table>

\textsuperscript{a} NA: in the presence of non acidic seed; A: in the presence of acidic sulfate seed; LRH: low %RH level; HRH: high %RH level.
\textsuperscript{b} LNO\textsubscript{x}: low NO\textsubscript{x} level (OH radical source: photolysis of H\textsubscript{2}O\textsubscript{2}); MNO\textsubscript{x}: intermediate NO\textsubscript{x} level ([NO\textsubscript{x}]=90-105 ppb); HNO\textsubscript{x}: high NO\textsubscript{x} level ([NO\textsubscript{x}]=280-315 ppb); HNO: high NO fraction; LNO: low NO fraction.

3.3.1.2 Acidity and humidity effects on SOA formation

Relative SOA yield difference. Both acidity and humidity effects on the SOA yields were examined for each NO\textsubscript{x} level. Two types of the relative SOA yield difference are defined: the SOA yield difference (\( \Delta Y_{A-NA} \)) between neutral and acidic sulfate seed experiments at the same humidity level (equation 1) and the SOA difference (\( \Delta Y_{\text{HRH-LRH}} \)) between low humidity and high humidity experiments with the same type of the seed aerosols (equation 2).

\[
\Delta Y_{A-NA} \text{ (%) } = \frac{Y_{\text{acid}} - Y_{\text{nonacid}}}{Y_{\text{nonacid}}} \times 100\% \quad \text{(at the same %RH level)}
\]
\[ \Delta Y_{HRH-LRH} \, (\%) = \frac{Y_{HRH} - Y_{LRH}}{Y_{LRH}} \times 100\% \quad \text{(for the same type of seed aerosols)} \]  

(2)

The resulting \(\Delta Y_{A-NA}\) and \(\Delta Y_{HRH-LRH}\) are summarized in Table 3.4 along with experimental conditions used for this study.

Table 3.4 Summary of particle acidity effect (\(\Delta Y_{A-NA}\)) and humidity effect (\(\Delta Y_{HRH-LRH}\)) on SOA formation under various experimental conditions

<table>
<thead>
<tr>
<th>(\Delta Y_{A-NA}) at LRH</th>
<th>(\Delta Y_{A-NA}) at HRH</th>
<th>(\Delta Y_{A-NA}) at LRH</th>
<th>(\Delta Y_{A-NA}) at HRH</th>
<th>(\Delta Y_{A-NA}) at LRH</th>
<th>(\Delta Y_{A-NA}) at HRH</th>
<th>(\Delta Y_{HRH-LRH}) with NA</th>
<th>(\Delta Y_{HRH-LRH}) with A</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNO(_x)</td>
<td>LNO(_x)</td>
<td>MNO(_x)</td>
<td>MNO(_x)</td>
<td>HNO(_x)(HNO)</td>
<td>HNO(_x)(LNO)</td>
<td>LNO(_x)</td>
<td>LNO(_x)</td>
</tr>
<tr>
<td>36</td>
<td>25</td>
<td>115</td>
<td>44</td>
<td>0</td>
<td>17</td>
<td>-29</td>
<td>-29</td>
</tr>
<tr>
<td>Net %WV</td>
<td>Net %WV</td>
<td>Net %WV</td>
<td>Net %WV</td>
<td>Net %WV</td>
<td>Net %WV</td>
<td>Net %WV</td>
<td>Net %WV</td>
</tr>
<tr>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>WP</td>
<td>WP</td>
<td>WP</td>
<td>WP</td>
<td>WP</td>
<td>WP</td>
<td>WP</td>
<td>WP</td>
</tr>
<tr>
<td>↑↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Acid</td>
<td>Acid</td>
<td>Acid</td>
<td>Acid</td>
<td>Acid</td>
<td>Acid</td>
<td>Acid</td>
<td>Acid</td>
</tr>
<tr>
<td>↑↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
</tbody>
</table>

a. ↑ represents SOA yield increase due to the specific effect; ↓ represents SOA yield decrease by the specific effect. The number of arrows represents the magnitude of the effects: ↑↑↑ (strong), ↑↑ (medium), and ↑ (weak). “-” sign denotes insignificant effects. N/A: not applicable.

The three major factors which operate the acidity effect and humidity effect on \(\Delta Y_{A-NA}\) and \(\Delta Y_{HRH-LRH}\) are particle acidity, water vapor concentration (WV) and water content in the particle (WP) at a given temperature. The impacts of WV and WP on SOA formation depend on the types of gas phase products and thus vary under different NO\(_x\) conditions as shown in Figure 3.2. The WV effect may be significant only for the low NO\(_x\) conditions by affecting the HO\(_2\) chemistry in the gas phase (discussed in “low NO\(_x\) conditions” of this section). The effect of WP on SOA formation is considerable for aldehydes- the major products for the
intermediate NO\textsubscript{x} level (discussed in “intermediate NO\textsubscript{x} conditions” of this section). WP may also influence the gas-particle partitioning of hydrophilic products. More water content in the particle at high \%RH can facilitate partitioning of hydrophilic products resulting in more SOA production. The magnitude of such WP effect varies with the fraction of hydrophilic products of the total oxygenated products which depends upon NO\textsubscript{x} levels.

**Low NO\textsubscript{x} conditions.** Shown in Table 3.4, \(\Delta Y_{A-NA}\) values are 36\% at low \%RH and 25\% at high \%RH. At the same \%RH level, \(\Delta Y_{A-NA}\) refers to the additional SOA formation by the presence of acidic sulfate seed through heterogeneous acid-catalyzed reactions or organic sulfate formation. The particle acidity effect described by \(\Delta Y_{A-NA}\) is 11\% higher at low \%RH than at high \%RH because the proton concentrations in the acidic seed aerosols are higher at low \%RH \((\Delta[H^+] = 0.11 \mu g/m^3)\).

\(\Delta Y_{HRH-LRH}\) values are –29\% with non acidic seed and –34\% with acidic sulfate seed as shown in Table 3.4. \(\Delta Y_{HRH-LRH}\) is influenced by WV, particle acidity and WP, corresponding to the reactions in the gas and the particle phase and the partitioning process of oxygenated gas products. Firstly, the role of water is more important than that of particle acidity for a certain type of reactions such as the formation of peroxyhemiacetals (Figure 3.2) between a hydroperoxide and an aldehyde in the particle phase (Johnson et al., 2004), although various heterogeneous reactions in the particle phase are sensitive to particle acidity and water (WV and WP) in the system. Organic hydroperoxides are produced through the reactions of RO\textsubscript{2} with HO\textsubscript{2} radicals. Kanno et al. (2005) found that the HO\textsubscript{2} self-reactions were considerably enhanced by the presence of water vapor. Therefore, at high \%RH, the available amounts of HO\textsubscript{2} radicals for the formation of hydroperoxide decrease, leading to less SOA formation. Secondly, heterogeneous reactions of carbonyls (e.g. heterogeneous acid-catalyzed
reactions or organic sulfate formation) are responsible for the higher SOA yields in the presence of acidic sulfate seed aerosols compared to those in neutral seed aerosols. SOA yield reduction ($\Delta Y_{HRH-LRH}$) is larger for the SOA with acidic sulfate seed than with neutral seed. This is probably due to the acidity decrease by water dilution of proton concentration in the acidic particle. Thirdly, the partitioning processes may be influenced by WP particularly for hydrophilic products.

**Intermediate NO$_x$ conditions.** The WP effect on $\Delta Y_{HRH-LRH}$ is significant in the presence of neutral seed aerosols with the SOA yield 39% higher at high %RH than at low %RH. This is likely due to the reactions of gas phase toluene oxidation products such as aldehydes with particle phase water on the seed aerosols - the mechanisms for SOA formation proposed by Koehler et al. (2004). Such carbonyls are dominantly produced by Channel C in Figure 3.2 under the intermediate NO$_x$ conditions. In addition, Hastings et al. (2005) suggested that the surface water layer of solid aerosols can trigger polymerization of glyoxal dihydrate monomer to form an organic layer. In the presence of acidic sulfate seed, SOA yields are not apparently changed by %RH ($\Delta Y_{HRH-LRH} = -7\%$) due to the combination of two opposite effects: increase of SOA yields (↑↑) via heterogeneous reactions of carbonyls triggered by water and decreases of SOA yields (↓) by the reduced particle acidity associated with dilution of proton concentration at higher humidity (Table 3.4). The results for $\Delta Y_{HRH-LRH}$ suggest that these two effects are equally important under our experimental conditions.

The apparent particle acidity effect ($\Delta Y_{A-NA}$) on SOA formation at intermediate NO$_x$ levels is much stronger compared to those under low and high NO$_x$ levels. $\Delta Y_{A-NA}$ is 115% at low %RH and 44% at high %RH (Table 3.4). The high $\Delta Y_{A-NA}$ value (115%) at the low %RH is due to not only the particle acidity but also the WP. The non acidic seed aerosols made of
ammonium sulfate are solid below the efflorescence point (30-35% RH) (Martin et al., 2003), while the acidic sulfate seed particles are aqueous regardless of % RH. Therefore, the difference in WP between neutral and acidic sulfate seeds is significant in the SOA experiments at low %RH. Compared to non acidic aerosols, more WP is available in acidic sulfate seed aerosols, increasing SOA formation *via* heterogeneous reactions of the gas phase oxygenated products with WP.

**High NOx conditions.** For the SOA experiments at high NO fraction of the high NOx conditions, both $\Delta Y_{A-NA}$ and $\Delta Y_{HRH-LRH}$ are within the uncertainty range for all particle acidities and humidity levels. This observation is in agreement with the previous studies by Cocker et al. (2001) and Edney et al. (2000) showing no humidity effect on the aromatic SOA formation at high NOx levels. The main pathway for SOA formation under the high NOx conditions is likely the gas-particle partitioning of organic nitrates and nitro compounds (see Sect. 3.3.1.1) that are relatively volatile with the estimated vapor pressure ranging from $10^{-3}$ to $10^{-6}$ atm (Schwarzenbach et al., 1993) and inert for heterogeneous reactions. Therefore, insignificant particle acidity effect on SOA yields is observed in the high NO fraction of the high NOx conditions.

NOx conditions change from high NO to low NO fraction as the SOA formation progresses. For the low NO fraction of high NOx experiments, no SOA yield difference ($\Delta Y_{HRH-LRH}=0$) is observed with the neutral seed indicating that the WP effect is not significant in this condition. The inorganic seed aerosol is coated with organic matter as the NO fraction converts from high to low conditions. Although heterogeneous reactions of gas phase oxygenated products with WP could be enhanced by the water on the inorganic seed
aerosols (Koehler et al., 2004), WP effect may be reduced when this organic mass is present in the particle phase.

Unlike the observations under the neutral conditions, humidity effect in the presence of acidic aerosols is noticeable for the low NO fraction of the high NO\textsubscript{x} conditions, leading to lower SOA yields at the high %RH ($\Delta Y_{HRH-LRH} = -19\%$). The gas phase chemistry for SOA formation in the low NO fraction of the high NO\textsubscript{x} conditions is similar to that under the intermediate NO\textsubscript{x} conditions. Channel C in Figure 3.2 becomes dominant and produces carbonyls as the major oxidation products. Therefore, the SOA yield reduction by high %RH is likely due to the decrease in heterogeneous reactions of carbonyls by the reduction of particle acidity.

![Figure 3.4](image.png)

Figure 3.4 A time profile of proton concentration [H$^+$] over the course of an SOA experiment at high NO\textsubscript{x} level in the presence of acidic sulfate seed.

The particle acidity effect in the low NO fraction is only found at the low %RH ($\Delta Y_{A-NA} = 17\%$) and is not as strong as that observed in the intermediate NO\textsubscript{x} conditions. The NO concentrations of the intermediate NO\textsubscript{x} in the beginning of toluene oxidation are similar to
those in the low NO fraction, which occurs at about 90 minutes after the high NOx experiments begin, but particle acitudes are different between these two systems. The aerosol acidity decreases as the acidic seed aerosol is coated with SOA through organic sulfate formation in the aerosol. In our study, the change of aerosol acidity was monitored over the course of the experiments using the colorimetric method integrated with a UV-Visible spectrometer (Jang et al., 2008) (Figure 3.4). Although both the intermediate NOx and the high NOx experiments were initiated at the similar particle acidity, the particle acidity was lower in the low NO region of the high NOx experiments (e.g. after 90 minutes, Figure 3.4) than it was at the intermediate NOx experiments, due to the fact that the acidity decayed over the course of the experiments.

3.3.2 Time-dependent growth curve

A time-dependent growth curve, expressed by a plot of the produced OM vs. the concentrations of the organic precursor consumed over the course of an experiment, has been recently used in a few studies (Chan et al., 2007; Ng et al., 2007) to understand SOA formation mechanisms. Figure 3.5 illustrates the time-dependent growth curves for our experiments at three different NOx levels. For the low (Figure 3.5A) and the intermediate NOx experiments (Figure 3.5B), the time-dependent growth curves appear to be linear over the course of the experiments. This tendency is also observed in other chamber studies for the aromatic SOA formation under no NOx conditions (Song et al., 2007) and the low NOx conditions (Ng et al., 2007).

However, the shape of the dynamic SOA yield curve (the figure on the top of each Figure 3.5A, 3.5B, 3.5C), presented by plots of yield vs. OM for a single experiment, clearly shows that SOA formation varies with particle acidity particularly in the beginning of the
experiments. In the presence of acidic sulfate seed, SOA yields are the highest in the beginning followed by a plateau; while in the presence of neutral seed, SOA yields increase for a short period and reach a plateau. These observations infer that different mechanisms would contribute to SOA formation to different degrees between neutral and acidic sulfate seed aerosols. With the acidic sulfate seed available, heterogeneous acid-catalyzed reactions and organic sulfate formation would be major pathways for SOA formation and occur rapidly in the beginning when the inorganic acid is abundant. The reduction in acidic SOA yields after the maximum SOA yield possibly results from the decrease in the amount of acid available to catalyze the reactions in the SOA through the conversion of acidic sulfates to organic sulfates over time. In addition, as heterogeneous reactions proceed in aerosols, the gas-particle partitioning of oxygenated products that are inert to heterogeneous reactions may become less favorable due to increases in both the average molecular weight of OM and the activity coefficients of SOA products (Jang et. al., 2006).

Figure 3.5 Time-dependent growth curves and SOA yield curves over the course of an SOA experiment in Table 3.1 at low NO\textsubscript{x} (A), intermediate NO\textsubscript{x} (B) and high NO\textsubscript{x} (C).
The high NO\textsubscript{x} experiments began with high NO concentrations (~ 222-242 ppb) and changed to low NO concentrations (~ 59-91 ppb) due to the conversion of NO to NO\textsubscript{2} over the course of the experiment. Correspondingly, two different SOA formation patterns are observed in the high NO\textsubscript{x} experiments as illustrated in Figure 3.5C. The criterion between high and low NO conditions was set at the point where the instantaneous NO concentration fell into the range of the initial NO concentration of the intermediate NO\textsubscript{x} experiments. The fact that the two SOA growth patterns were distinguished by the NO criterion indicates that SOA formation is related to the NO concentrations.

The SOA slowly formed in the high NO fraction indicating that the oxygenated products of toluene irradiation in the presence of abundant NO are either relatively volatile or inert for heterogeneous reactions (also see Sect. 3.3.1.1). However, when the system turned into the low NO fraction with high concentrations of NO\textsubscript{2}, the aerosol growth pattern changed dramatically, showing a rapid increase of SOA formation. This is likely because reactions of RO\textsubscript{2} with HO\textsubscript{2} become the main channels to form less volatile compounds or more reactive compounds for heterogeneous reactions when NO concentration is low. Some nitro-containing compounds, which are possibly produced at high NO\textsubscript{2} concentrations, can contribute SOA formation through gas-particle partitioning. However, the study of Koch et al. (2007) shows that the production of nitro-containing compounds from aromatic-OH adducts is insignificant even at high NO\textsubscript{x} conditions. Hurley et al. (2001) who simulated the toluene SOA formation at high NO\textsubscript{x} levels using a chemical kinetic model have seen the similar SOA growth curves as observed in this study, which indicates another possible mechanism for toluene SOA formation: not only first-generation but also second-generation oxygenated products can contribute the toluene SOA formation. However, this mechanism may not very
significant in our system with high initial toluene concentrations where first-generation products are dominant.

**Table 3.5 SOA experiments conducted under the atmospheric relevant conditions at intermediate NO\(_x\) level\(^a\) ([NO\(_x\)] \sim 100-115 \text{ ppb}).**

<table>
<thead>
<tr>
<th>Exp #(^b)</th>
<th>%RH</th>
<th>([H^+]) ((\mu g/m^3))</th>
<th>NO(^+) ((\text{ppb}))</th>
<th>NO(_2) ((\text{ppb}))</th>
<th>(\Delta\text{TOI}) ((\text{ppm}))</th>
<th>(V_{\text{seed}}) ((\text{nL/m}^3))</th>
<th>(V_{\text{mix}}) ((\text{nL/m}^3))</th>
<th>OM ((\mu g/m^3))</th>
<th>Yield(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNO(_x)-NA-HRH</td>
<td>42.7</td>
<td>0.001</td>
<td>83.8</td>
<td>29.9</td>
<td>0.012</td>
<td>9.78</td>
<td>20.1</td>
<td>14.5</td>
<td>0.32±0.026</td>
</tr>
<tr>
<td>MNO(_x)-A-HRH</td>
<td>41.9</td>
<td>0.03</td>
<td>85.3</td>
<td>15.4</td>
<td>0.012</td>
<td>9.38</td>
<td>21.0</td>
<td>16.3</td>
<td>0.36±0.028</td>
</tr>
<tr>
<td>MNO(_x)-NA-HRH</td>
<td>42.5</td>
<td>0.001</td>
<td>88.9</td>
<td>31.5</td>
<td>0.010</td>
<td>11.8</td>
<td>20.1</td>
<td>11.6</td>
<td>0.31±0.024</td>
</tr>
<tr>
<td>MNO(_x)-A-HRH</td>
<td>43.7</td>
<td>0.03</td>
<td>92.5</td>
<td>20.7</td>
<td>0.013</td>
<td>10.4</td>
<td>23.7</td>
<td>18.6</td>
<td>0.38±0.028</td>
</tr>
<tr>
<td>MNO(_x)-NA-LRH(^e)</td>
<td>17.7</td>
<td>0.001</td>
<td>80.6</td>
<td>27.5</td>
<td>0.016</td>
<td>9.92</td>
<td>24.7</td>
<td>20.7</td>
<td>0.34±0.026</td>
</tr>
<tr>
<td>MNO(_x)-A-LRH(^e)</td>
<td>18.9</td>
<td>0.05</td>
<td>78.3</td>
<td>22.6</td>
<td>0.014</td>
<td>9.46</td>
<td>26.0</td>
<td>23.2</td>
<td>0.44±0.034</td>
</tr>
</tbody>
</table>

\(^a\) Temperature ≈299 K.

\(^b\) LT: Low initial toluene concentration; MNO\(_x\): intermediate NO\(_x\) level; NA: in the presence of non acidic seed; A: in the presence of acidic sulfate seed; HRH: high %RH level.

\(^c\) Initial concentrations

\(^d\) Yield was calculated with the density of organic matter of 1.4 g/mL. The uncertainties of the resulting SOA yields were calculated using the uncertainties of OM and \(\Delta\text{ROG}\) through the propagation of uncertainty for divisions (Levie, 1997).

\(^e\) The experiment was performed at low %RH level to demonstrate the effects of particle acidity with low initial toluene concentrations.

### 3.3.3 Chamber experiments under conditions relevant to the atmosphere

To gain insights into the atmospheric implication of the chamber experiments, SOA experiments (shown in Table 3.5) were conducted with low initial toluene concentrations (~40 ppb) in the presence of small amounts of inorganic seed aerosols (~10 μg/m\(^3\)). The acidic seed solution for the seed aerosols was made of 70% ammonium bisulfate and 30% sulfuric acid. As shown in Table 3.5, such weak particle acidity still increases SOA yields by 12.5 % compared to neutral SOA under our NO\(_x\) conditions (initial NO is about 100-115 ppb). The time-dependent growth curves for these experiments showed the similar pattern as those in Figure 3.5B. This result can be applied to SOA formation under the similar ambient NO\(_x\)
conditions. For example, on a weekday morning near freeways in California (Fujita et al., 2003), the average 1-hour NO\textsubscript{x} concentrations were about 100-200 ppb.

3.4 Summary

The present study demonstrates that SOA formation from photooxidation of toluene is influenced by NO\textsubscript{x} concentrations, particle acidity and humidity using controlled chamber experiments. NO\textsubscript{x} concentrations affect the types of gas phase products from toluene photooxidation and thus influence the contribution of possible mechanisms to SOA formation as well as the effects of particle acidity and humidity. At low NO\textsubscript{x} conditions, reactions of the major gas phase oxygenated products—ROOH with carbonyls are dominant pathways for SOA formation. Such reactions occur rapidly even in the absence of acidic sulfate seed, thus the particle acidity effect is not as significant as that at intermediate NO\textsubscript{x} conditions. At low NO\textsubscript{x}, high %RH decreases SOA yields, because water vapor decreases the availability of HO\textsubscript{2} for the production of ROOH, which reduces the contribution of heterogeneous reactions of ROOH and carbonyls to SOA formation. At intermediate NO\textsubscript{x} conditions, heterogeneous acid-catalyzed reactions and organic sulfate formation play an important role for SOA formation. Therefore, particle acidity effect on SOA formation is strongest at intermediate NO\textsubscript{x} compared to those at low and high NO\textsubscript{x}. Unlike the humidity effect at low NO\textsubscript{x}, high %RH increases SOA yields at intermediate NO\textsubscript{x}. This is probably due to heterogeneous reactions of gas phase oxygenated products with particle phase water enhancing SOA formation. At high NO\textsubscript{x}, the high initial NO and NO\textsubscript{2} concentrations facilitate formation of volatile organic nitrates and nitro compounds that are not reactive for heterogeneous reactions and undergo the gas particle partitioning processes for SOA.
formation. Hence, insignificant effects of particle acidity and humidity are observed at high NO$_x$. 

The fact that the physical process and chemistry of oxygenated products in the gas and the particle phase for SOA formation depend on NO$_x$ concentrations, particle acidity and humidity, emphasizes the need for comprehensive chamber studies under diverse environmental conditions. Such studies will be very useful to mimic the SOA formation under the ambient conditions of a certain area. Our SOA yield studies and time-dependent growth curves provide the insight into the possible gas phase product distributions and corresponding dominant pathways for SOA formation under different conditions. Further studies on characterization of the gas and the particle products are required to identify effects of NO$_x$ concentrations, particle acidity and humidity on SOA formation.

**Acknowledgements**

This work was supported by a Grant from National Science Foundation (ATM0703941).


Technology 38, 6582-6589.


Nenes, A. http://nenes.eas.gatech.edu/ISORROPIA/, last access: July 22, 2008.


Chapter IV

Impacts of Heterogeneous Chemistry on Partitioning of Semivolatile Organic Compounds on Aromatic SOA

Gang Cao¹, Myoseon Jang²*
1. Department of Environmental Sciences and Engineering
   University of North Carolina at Chapel Hill
   CB#7431, Rosenau Hall, Chapel Hill, NC, 27599
2. Department of Environmental Engineering Sciences, University of Florida,
   P.O. Box 116450, Gainesville, FL  32611

Submitted to Atmospheric Environment

*Corresponding Author: Myoseon Jang
Email: mjang@ufl.edu
Abstract

Secondary organic aerosol (SOA) was generated from oxidation of toluene by OH radicals from photolysis of H₂O₂ in a 2 m³ indoor Teflon film chamber. For individual SOA experiments, the gas and the particle phase products were tentatively identified using a gas chromatograph-ion trap mass spectrometer (GC-ITMS) and were applied to determine the experimental partitioning coefficients \( (iK^\text{exp}_p) \) of toluene oxidation products between the gas and the aerosol phase. The predictive absorptive partitioning coefficients \( (iK^\text{cal}_p) \) were also estimated by the thermodynamic model linked to calculation of the activity coefficients of organic products using UNIFAC at a given model composition. For the thermodynamic approach associated with UNIFAC calculation, we hypothesize that toluene SOA mainly comprises oligomeric species when the NO₃ concentration is very low. The model structure of oligomeric species of the toluene SOA was semi-empirically determined by fitting the theoretical partitioning coefficients to the experimental partitioning coefficients of deuterated alkanes (d₄₀-nonadecane and d₄₂-eicosane) which are inert for the aerosol phase reactions. Our results showed a considerable discrepancy between \( iK^\text{exp}_p \) and \( iK^\text{cal}_p \) of SOA products, suggesting that heterogeneous chemistry in aromatic SOA significantly impacts the gas particle partitioning of organic compounds.
4.1 Introduction

Gas phase reactions of volatile organic compounds (VOC) with atmospheric oxidants (e.g. ozone, OH radical, and NOx) generate semivolatile oxygenated products that either are self-nucleated or partition onto the preexisting particles to form secondary organic aerosols (SOA). In general, the gas-particle partitioning of semivolatile organic compounds is estimated by an absorptive partitioning coefficient ($iK_p^{cal}$ in equation 1) (Pankow, 1994).

$$iK_p^{cal} = \frac{7.501RTf_{om}^{i} \gamma_{om}^{\infty}}{10^9 MW_{om}^{i} \rho_L^{i}}$$

(1)

where $iK_p^{cal}$ is the gas-particle partitioning coefficient ($m^3/\mu g$), $T$ is the ambient temperature (K), $R$ is the gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$), $f_{om}$ is the mass fraction of the absorptive liquid-like organic material (om), $MW_{om}$ is the average molecular weight (g/mol) of the organic matter, and $\gamma_{om}^{\infty}$ is the activity coefficient of $i$ at infinite dilution in a given liquid-like medium. The $\rho_L^{i}$ is the subcooled liquid vapor pressure at the temperature of interest (torr).

Because $\rho_L^{i}$, $\gamma_{om}^{\infty}$ and $MW_{om}$ are difficult to measure experimentally, these values have been calculated using thermodynamic models associated with various group contribution methods. For example, Mackay et al. (1982) estimated $\rho_L^{i}$ using group contribution linked to the molecular structure of compound $i$ at a given temperature. $\gamma_{om}^{\infty}$ can be calculated by the UNIFAC (universal functional group activity coefficient) (Fredenslund and Sorensen, 1994; Gmehling et al., 1982; Jang et al, 1997) if the composition of om is available. $MW_{om}$ as the molecular weight of om in SOA is calculated based on the model SOA structures.
Recent studies have suggested that heterogeneous reactions (Baltensperger et al., 2005; Gao et al., 2004b; Jang et al., 2002; Kalberer et al., 2004; Liggio et al., 2005) in the particle phase are important pathways for SOA formation producing high molecular weight (MW) oligomers (Kalberer et al., 2004; Gao et al., 2004a). For example, Kalberer et al. (2004) observed that up to 50% of the aromatic SOA mass is oligomers. Hu et al. (2007) predicted from their model simulation that oligomers comprised about 70% of toluene SOA. The possible mechanisms of oligomer formation include hydration, polymerization, formation of hemiacetal/acetal/trioxane, aldol condensation, and cationic rearrangement (Garland et al., 2006; Jang et al., 2004). Although numerous advanced instruments have been used to analyze aerosols, either characterization of oligomers in aerosols or determination of aerosol compositions is still very limited. Such problems hinder the studies on how oligomers in the particle phase influence partitioning behavior of organic compounds on SOA by alteration of MW$_{om}$ and $\gamma$_{$\infty$}. In the previous partitioning studies, it was assumed that $\gamma$_{$\infty$} was 1 and MW$_{om}$ was around 120 g/mol (Healy et al., 2008; Jang and Kamens, 2001; Johnson et al., 2006) based on simple gas phase products. However, such treatment should be reevaluated, considering the new and important heterogeneous chemistry of organics in aerosols because the formation of oligomeric species in aerosol would considerably influence MW$_{om}$ and $\gamma$_{$\infty$}.

In this paper, we investigated an approach to study partitioning of semivolatile oxygenated products on SOA generated from photooxidation of toluene. We assumed that the toluene SOA formed in the absence of NO$_x$ consisted of oligomers solely. The main objectives of the present study are: 1) to semiempirically determine the structure of oligomers of aromatic SOA by fitting $K_{p}^{cal}$ to the experimentally observed partitioning
coefficients ($^i K_p^{\exp}$) of two deuterated alkanes ($d_{40}$-nonadecane and $d_{42}$-eicosane); 2) to estimate the $^i \gamma_{om}^\infty$ of semivolatile aromatic oxygenated products and $MW_{om}$ based on the resulting SOA model structure; 3) to calculate the $^i K_p^{cal}$ of aromatic oxidation products (equation 1) onto SOA based on the model oligomeric structure; 4) to evaluate the contribution of heterogeneous chemistry of oxygenated products to SOA formation by comparing $^i K_p^{cal}$ and $^i K_p^{\exp}$. Our results are beneficial to describe the SOA comprising oligomeric matter. The approach using deuterated alkanes applied in this study can be also extended to various SOA produced from either different precursors or different oxidations, particularly when the information of experimental SOA composition is limited.

4.2 Experimental section

4.2.1 Teflon film indoor chamber experiments

Toluene was oxidized by OH radicals from photolysis of $H_2O_2$. All experiments were conducted in a 2 m$^3$ indoor Teflon film chamber under UV-visible light conditions. A description of this chamber has been provided elsewhere (Cao and Jang, 2007). In this study, all chamber experiments were performed in the presence of inorganic seed aerosols (non acidic and acidic seed). The composition of the inorganic seed aerosol was controlled by the different combinations of the inorganic aqueous solutions (0.01 mol/L) made of ammonium sulfate ((NH$_4$)$_2$SO$_4$), ammonium bisulfate (NH$_4$HSO$_4$), and sulfuric acid (H$_2$SO$_4$). The inorganic seed aerosols were injected into the chamber by atomizing the inorganic aqueous solution. When the seed aerosols stabilized, a certain amount of toluene was injected into the chamber. The gas phase of $H_2O_2$ was then introduced into the chamber by gently purging the nitrogen at 1 L/min over a 50% $H_2O_2$ aqueous solution (Aldrich). The UV-Visible lights were turned on at the beginning of the $H_2O_2$ injection. The $H_2O_2$ concentrations (8.19-8.93
ppm) in the chamber were estimated by mass loss of the 50% \( \text{H}_2\text{O}_2 \) solution before and after \( \text{H}_2\text{O}_2 \) injection and the mole fraction of \( \text{H}_2\text{O}_2 \) in vapor mixture (water + \( \text{H}_2\text{O}_2 \)) (Manatt and Manatt, 2004). The experiments reached the completion point once the SOA growth stabilized. Table 4.1 presents a summary of the experimental conditions and the resulting SOA data. For the partitioning studies of deuterated alkanes, four SOA experiments were selected. Upon the completion of SOA experiments, UV-Visible lights were turned off. \( \text{D}_{40} \)-nonadecane (10.8 mg/mL) and \( \text{d}_{42} \)-eicosane (9.6 mg/mL) diluted with tetrachloromethane were volatilized into the chamber by passing the clean air through the T-glass tube heated by the heat gun.

Table 4.1 Experimental conditions and the resulting SOA data

<table>
<thead>
<tr>
<th>Exp. date</th>
<th>RH%</th>
<th>( [\text{H}^+] ) (( \mu \text{g/m}^3 ))</th>
<th>( \Delta \text{TOL} ) (ppm)</th>
<th>OM(( \mu \text{g/m}^3 ))</th>
<th>Yield(^b)</th>
<th>( f_{\text{on}} )</th>
<th>Sampling system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11/14/06</td>
<td>20.6</td>
<td>0.01</td>
<td>0.54</td>
<td>511.0±27.6</td>
<td>0.25±0.019</td>
<td>0.75</td>
<td>Filter-denuder</td>
</tr>
<tr>
<td>12/7/06</td>
<td>17.8</td>
<td>0.01</td>
<td>0.41</td>
<td>401.8±21.8</td>
<td>0.26±0.020</td>
<td>0.73</td>
<td>Filter-denuder</td>
</tr>
<tr>
<td>2/15/07</td>
<td>15.3</td>
<td>0.01</td>
<td>0.58</td>
<td>618.8±33.4</td>
<td>0.28±0.021</td>
<td>0.78</td>
<td>Denuder-filter-denuder</td>
</tr>
<tr>
<td>2/23/07</td>
<td>22.7</td>
<td>0.01</td>
<td>0.60</td>
<td>637.0±34.5</td>
<td>0.28±0.021</td>
<td>0.78</td>
<td>Denuder-filter-denuder</td>
</tr>
<tr>
<td>Acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11/13/06</td>
<td>18.2</td>
<td>0.90</td>
<td>0.36</td>
<td>471.8±25.5</td>
<td>0.34±0.025</td>
<td>0.73</td>
<td>Filter-denuder</td>
</tr>
<tr>
<td>12/7/06</td>
<td>14.0</td>
<td>0.93</td>
<td>0.42</td>
<td>561.4±30.4</td>
<td>0.35±0.026</td>
<td>0.78</td>
<td>Filter-denuder</td>
</tr>
<tr>
<td>2/16/07</td>
<td>15.4</td>
<td>0.85</td>
<td>0.40</td>
<td>553±29.9</td>
<td>0.36±0.027</td>
<td>0.76</td>
<td>Denuder-filter-denuder</td>
</tr>
<tr>
<td>2/20/07</td>
<td>14.8</td>
<td>0.90</td>
<td>0.42</td>
<td>579.6±31.4</td>
<td>0.36±0.027</td>
<td>0.78</td>
<td>Denuder-filter-denuder</td>
</tr>
</tbody>
</table>

a. Temp=295-296 K

b. Yield was calculated from equation \( \text{Y} = \frac{\text{OM}}{\Delta \text{ROG}} \) with the density of organic matter of 1.4 g/mL.
4.2.2 Sampling

For the SOA characterization, the gas and the particle phase samples were simultaneously collected through a filter-denuder sampling train that consisted of a 47 mm glass microfiber filter (EMFAB TX40HI20-ww, Gelman Sciences PallFlex) and a five-channel annular denuder (University Research Glassware, Carrboro, NC) coated with XAD-4 absorbent. The collected particle mass on the filter was estimated from the filter mass measurement (Mettler Toledo MX5) before and after sampling. Five µL of internal standard solution, including dimethyl terephalate, anthracene, and pyrene, was then spiked to each denuder and filter. The filter was extracted by dichloromethane in the micro soxhlet (Kontes, Fisher Scientific) for 4 hours. The denuder was extracted three times with dichloromethane. The extracted solutions from the denuder and the filter were concentrated using nitrogen stream for the further derivatization of products.

For the partitioning studies of deuterated alkanes on the toluene SOA, the gas and the particle samples were collected using a denuder-filter-denuder sampling train. Five µL of internal standard solution was spiked to the denuders and the filter. The gas and particle samples were then extracted in the same way mentioned above and directly analyzed using a GC-ITMS.

4.2.3 GC-ITMS Analysis of Denuder and Filter Samples

Three different derivatization methods (Jaoui et al., 2004) were used for this study. O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) was used to derivatize carbonyl groups of products. N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) only or multi-derivatization combined with a PFBHA method was used to derivatize hydroxyl groups and carboxylic acid. To analyze products by the various derivatization
methods, the extracted sample solutions (about 1 mL) were divided into several portions. For the PFBHA derivatization, 0.5 mL water (HPLC-grade) and 0.5 mL acetonitrile were added to the sample vial, followed by 50 µL PFBHA (7.85 mg/mL in water). The vial was then placed in the oven at 40 °C for 18 hours. After the vial was removed from the oven, three drops of concentrated hydrochloric acid were added in the vial and the vial was then shaken for 2 minutes. The analytes were extracted three times with 1 mL of the solvent mixture (hexane: dichloromethane= 2:3). The extracts were collected in a clean vial and dried with anhydrous sodium sulfate. The final extract was decanted to another clean vial, concentrated using nitrogen gas streams and then split into two equal portions: one for GC-ITMS analyses and the other for further BSTFA derivatization.

For the BSTFA derivatization, the extracted sample was evaporated by nitrogen streams to the dryness. One hundred µL of pyridine and 10 µL of BSTFA with 10% trimethylchlorosilane (TMCS) were added into the vial. The vial was placed in 60 °C water bath for 2 hours. Then, the sample was analyzed using a GC-ITMS (Varian GC 3380 with a Saturn 2000 ion trap MS). The separation of compounds was conducted on a Factor Four capillary column (VF-5MS, 30m× 0.25mm). The ITMS was operated in the EI and the CI modes over a mass range of 40-650 amu. Compounds were tentatively identified based on their retention time and the fragmentation of mass spectra.

4.2.4 Materials and instruments

All solvents (Optima grade) were from Fisher Scientific. The derivatization reagents, PFBHA and BSTFA with 10% TMCS, were purchased from Sigma-Aldrich (Milwaukee, WI). The deuterated alkanes (d_{40}-nonadecane and d_{42}-eicosane) were from Cambridge Isotope Laboratories, Inc (Andover, MA). Clean air was generated using two clean air
generators (Aadco Model 737, Rockville, MD; Whatman Model 75-52, Haverhill, MA). Inorganic seed aerosols were generated with a Constant Output Atomizer (TSI, Model 3076, Shoreview, MN). The particle size distribution was monitored with a Scanning Mobility Particle Sizer (SMPS) (TSI Model 3080) coupled with a condensation nuclei counter (TSI, Model 3025A). Particle data were corrected for the aerosol loss to the chamber wall with a first order decay (McMurry and Grosjean, 1985). The gas phase toluene concentrations were measured with an HP 5890 GC-FID. The flow rate of the GC carrier gas (Nitrogen) through a DB-5 (15m x 0.53mm) fused silica capillary column (J & W Scientific INC, Cat# 1255012) was 2.5 mL/min. The oven temperature was fixed at 150 °C for 7 minutes. Temperature (295-296 K) and %RH of the chamber were measured with an electronic thermo-hygrometer (Dwyer Instrument, Inc, USA).

4.3 Results and discussion

4.3.1 Composition of chamber SOA

Our previous studies showed that SOA yields were higher in the NO\textsubscript{x} free air than those in the presence of NO\textsubscript{x} (Cao and Jang, 2008). Such difference is probably due to heterogeneous reactions of oxygenate products forming non-volatile oligomeric species in SOA (Kalberer et al., 2004; Hu et al., 2007). In this study, we hypothesize that toluene SOA generated in the absence of NO\textsubscript{x} comprises oligomeric species solely. The information about SOA composition is essential to determine $\gamma_{\text{om}}^\infty$ and $\text{MW}_{\text{om}}$ as well as the resulting $K_p^\text{cal}$ of aromatic oxygenated products on its SOA.

To estimate $\gamma_{\text{om}}^\infty$ using UNIFAC (Jang et al., 1997) at a given model oligomeric structure, we included several functional groups such as phenyl, $-$CH=CH$-$, CH\textsubscript{3}C(=O)$-$, and $-$HC(−)$-$O$. These functional groups have been also reported by other studies, showing
that oligomers in SOA have similar structural properties as humic substances that include both aromatic and aliphatic characteristics (Havers et al., 1998; Kiss et al., 2003). The phenyl group shows the aromatic characteristic in oligomers. The $-\text{CH}═\text{CH}$ and $\text{CH}_3\text{C(=O)}$ groups in aromatic SOA represent the structural features of ring opening products, which are also reactive for heterogeneous reactions. The $-\text{HC(=O)}$ group in SOA is one of the major characteristics of oligomers produced from reactive carbonyls such as glyoxal and methyl glyoxal. OH and COOH groups were excluded from the model structure because $iK_p^{\text{cal}}$ of the semivolatile alkanes using the $i\gamma_{om}^\infty$ values associated with UNIFAC calculation at the given composition including OH or COOH group extremely deviated from $iK_p^{\text{exp}}$. The recent study by Varutbangkul et al. (2006) also reported reduction in polarity of SOA as oligomerization progresses.

In this study, water content in the organic matter of toluene SOA was determined from the previous observation by Jang and Kamens (1998). The calculated water molar fraction ($f_{\text{water}}$) of toluene SOA was about 0.05 under the assumption that hygroscopic properties of aromatic SOA and $\alpha$-pinene SOA were similar. However, Cocker et al. (2001) reported that the hygroscopic growth factors of aromatic SOA were smaller than those of $\alpha$-pinene SOA at RH=50% or below, indicating that the actual water content might be less than our calculated values. Hence, two different $f_{\text{water}}$, 0.05 and 0.01, were tested for the UNIFAC calculation in this study. The variation in UNIFAC calculated $i\gamma_{om}^\infty$ values associated with the two different $f_{\text{water}}$ of SOA was insignificant for all tested model composition. For example, the average difference in calculated $i\gamma_{om}^\infty$ values of organic compounds between $f_{\text{water}}=0.01$
and $f_{\text{water}}=0.05$ was 2% at our model SOA compositions (A, B, C, D in Figure 4.1 and Figure 4.2). In this study we fixed $f_{\text{water}}$ at 0.01.

![Graph showing calculated partitioning coefficients ($K_{\text{cal}}^i$) of $d_{40}$-nonadecane on SOA comprising different oligomer structures in the presence of the non acidic seed. All oligomer structures included one phenyl group, one CH$_3$C(=O)- group and varied numbers of $-$CH=CH$-$ group and $-$HC(−)$-$O$-$ group. $K_{\text{cal}}^i$ values obtained from the compositions A and B matched the $K_{\text{exp}}^i$ values of $d_{40}$-nonadecane.]

The absorptive partitioning of two semivolatile alkanes ($d_{40}$-nonadecane and $d_{42}$-eicosane) onto the toluene SOA was studied to determine the number of each functional group contained in the proposed oligomer structure. Semivolatile alkanes are inert for heterogeneous reactions and sensitive to the change in polarity of SOA constituents because they are extremely hydrophobic. The $K_{\text{cal}}^i$ values were calculated using equation 1 with various $\gamma_{\infty}$ at different model oligomeric structures consisting of different functional groups and compared to the $K_{\text{exp}}^i$ of $d_{40}$-nonadecane. The proposed model SOA structures were determined at the points where the deviations between $K_{\text{cal}}^i$ and $K_{\text{exp}}^i$ were less than the
experimental uncertainties of \( iK_p^{\text{exp}} \) (15%). \( iK_p^{\text{exp}} \) was obtained by measuring the gas phase concentration \( (iC_g) \) and the particle phase concentration \( (iC_p) \) of organic compound \( i \), as well as \( TSP \) (the concentration of the total suspended particulate matter) as shown in equation 2 (Pankow and Bidleman, 1991; Yamasaki, 1982).

\[
iK_p^{\text{exp}} = \frac{iC_p}{iC_g TSP}
\]  

Figure 4.2 Calculated partitioning coefficients \( iK_p^{\text{cal}} \) of \( d_{40}\)-nonadecane on SOA comprising various oligomer structures in the presence of the acidic seed. All oligomer structures included one phenyl group and varied numbers of \(-\text{CH}=\text{CH}-\) group and \(-\text{HC}(\ldots)-\text{O}-\) group. \( iK_p^{\text{cal}} \) values obtained from the compositions C and D matched the \( iK_p^{\text{exp}} \) values of \( d_{40}\)-nonadecane.

The \( iK_p^{\text{cal}} \) values corresponding to various oligomeric structures are simulated in Figure 4.1 for the neutral aerosol and Figure 4.2 for the acidic aerosol. For the neutral aerosol, points A & B (Figure 4.1) represent the compositions which have minimum
deviation between $iK_p^{\exp}$ of d$_{40}$-nonadecane and the simulated $iK_p^{\cal}$ values: 0% deviation at point A and -3.97% for point B. Points C & D (Figure 4.2) are the simulated compositions for the acidic aerosol (Table 4.2) with the minimum deviation of -3.10% for point C and -4.79% for point D. The resulting model structure for the acidic aerosol shows no CH$_3$C(=O)-group in the oligomers. The oligomeric structures resulting from the gas-particle partitioning of d$_{40}$-nonadecane were used to predict the $iK_p^{\cal}$ of d$_{42}$-eicosane. The $iK_p^{\cal}$ values of d$_{42}$-eicosane were remarkably close to $iK_p^{\exp}$, indicating that the resulting model structures are feasible to represent the SOA composition. For example, the deviations between $iK_p^{\cal}$ and $iK_p^{\exp}$ are -8.04% (A), -11.92% (B), 9.17% (C) and 11.52% (D). We chose B and D which have even number of the –HC(−)–O– group in oligomers as the model SOA structures for the neutral and acidic conditions, according to the heterogeneous chemistry of bicarbonyls, such as glyoxal and methyl glyoxal, proposed in recent studies (Kalberer et al., 2004; Liggio et al., 2005).

The molecular weights of structures B and D are 366 Da and 446 Da respectively, which are within the range (200-500 Da) of the observed molecular weights of oligomers in toluene SOA (Sato et al., 2007). The O:C ratios of B and D are 0.227 and 0.455, respectively. The resulting O:C ratios of toluene SOA are lower compared to the O:C ratios (0.3-0.8) observed for the oligomers in the aged biogenic aerosols (Hallquist et al., 2008; Reinhardt et al., 2007). The higher O:C ratio of acidic SOA (D) than that of neutral SOA (B) indicates that heterogeneous acid-catalyzed reactions have the similar effects as atmospheric aging of organic particles.
### Table 4.2 Experimental partitioning coefficients of two deuterated alkanes on aromatic SOA

<table>
<thead>
<tr>
<th>Compound</th>
<th>Seed</th>
<th>TSP (µg/m³)</th>
<th>$i K_p^{exp}$ (m³/µg)</th>
<th>Average $i K_p^{exp}$ (m³/µg)</th>
<th>Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d₄₀-nonadecane</td>
<td>neutral</td>
<td>739</td>
<td>$3.09 \times 10^{-5}$</td>
<td>$2.99 \times 10^{-5}$</td>
<td>4</td>
</tr>
<tr>
<td>d₄₀-nonadecane</td>
<td>neutral</td>
<td>787</td>
<td>$2.89 \times 10^{-5}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d₄₀-nonadecane</td>
<td>acidic</td>
<td>685</td>
<td>$6.19 \times 10^{-6}$</td>
<td>$5.76 \times 10^{-6}$</td>
<td>11</td>
</tr>
<tr>
<td>d₄₀-nonadecane</td>
<td>acidic</td>
<td>706</td>
<td>$5.32 \times 10^{-6}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d₄₂-eicosane</td>
<td>neutral</td>
<td>739</td>
<td>$9.73 \times 10^{-5}$</td>
<td>$1.04 \times 10^{-4}$</td>
<td>9</td>
</tr>
<tr>
<td>d₄₂-eicosane</td>
<td>neutral</td>
<td>787</td>
<td>$1.11 \times 10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d₄₂-eicosane</td>
<td>acidic</td>
<td>685</td>
<td>$1.84 \times 10^{-5}$</td>
<td>$1.98 \times 10^{-5}$</td>
<td>10</td>
</tr>
<tr>
<td>d₄₂-eicosane</td>
<td>acidic</td>
<td>706</td>
<td>$2.12 \times 10^{-5}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. Deviation refers to the standard deviation between two $i K_p^{exp}$ values of the alkane (d₄₀-nonadecane or d₄₂-eicosane) obtained from two sets of experiments under the same experimental conditions.

### 4.3.2 Impacts of heterogeneous chemistry: $i K_p^{exp}$ vs. $i K_p^{cal}$ of toluene oxygenated products

$i K_p^{exp}$ values of the toluene oxygenated products were determined with equation 2 associated with the quantification of analytes using GC-ITMS. Because most authentic standards for the toluene oxygenated products were not commercially available, major products were semi-quantitatively quantified using a chromatographic retention time method (Jang and Kamens, 1999). The external calibration curve of response factor (RF) vs. retention time (RT) was constructed using the quantitative information of four known compounds (benzaldehyde, glyoxal, methylglyoxal, and acetol) and the internal standard (dimethyl terephalate, anthracene, and pyrene), as shown in Figure 4.3. The RF was
calculated by dividing the mass ratio of the model compound to the internal standard by the corresponding peak ratio of the 181 amu peak area of derivatives to the peak area of the internal standard in the EI mass spectrum. Based on the external calibration curve and the retention time of the analytes, the concentrations of the major SOA products were determined. A concern may arise over the use of glyoxal and methylglyoxal as the external standard since they contain more than one carbonyl group and could be both mono- and di-derivatized, causing the difficulty of quantification. Under our derivatization conditions of this study, the derivatization of glyoxal mainly produced di-derivatives. Therefore, the RF of glyoxal was calculated using the peak ratio of di-derivatized glyoxal. For methylglyoxal, our derivatization results showed that more than 70% of the total derivatized methylglyoxal peaks were mono-derivatized. Therefore, the RF values of methylglyoxal were tested for two cases: the peak ratios of the mono-derivatized methylglyoxal only and the peak ratios of both mono- and di-derivatized methylglyoxal. The resulting RF values were used to obtain the two external calibration curves (with the same RF values of the other three external standards). The differences of the product concentrations due to the two different RF values of methylglyoxal were insignificant (less than 5%). Figure 4.3 shows the calibration curve including the RF value of methylglyoxal obtained from the quantitative information of the mono-derivatized methylglyoxal.
Figure 4.3 RF(Mass ratio/peak ratio) as a function of retention time for quantification of the identified products in the particle phase.

The $i K_p^{\text{cal}}$ of each organic product was calculated using equation 1 with the $i Y_{om}^{\infty}$ calculated from UNIFAC. Table 4.3 presents the comparison results between $i K_p^{\text{exp}}$ and $i K_p^{\text{cal}}$ of the identified products of toluene oxidation under the neutral and the acidic conditions. Overall, all $i K_p^{\text{exp}}$ values (except 2- hydroxybenzoic acid in acidic aerosols) were greatly higher than the $i K_p^{\text{cal}}$ values, indicating that the partitioning theory solely can underestimate the actual amount of compounds existing in the particle phase. The deviation between the $i K_p^{\text{exp}}$ and the $i K_p^{\text{cal}}$ indicated contribution of heterogeneous chemistry of the compound to SOA formation. For example, multifunctional carbonyls such as 1,4-dioxo-2-butene show large deviation between $i K_p^{\text{exp}}$ and the $i K_p^{\text{cal}}$ (e.g. $i K_p^{\text{exp}} / i K_p^{\text{cal}}$ was in the order of $10^5$ and $10^6$), indicating that such compounds are dramatically reactive for heterogeneous reactions.
Table 4.3 Estimated activity coefficients and vapor pressures of oxygenated toluene products and comparison of calculated and measured partitioning coefficients at T=295 K

<table>
<thead>
<tr>
<th>Compound (seed type)</th>
<th>Estimated $P_L^0$ (mmHg)</th>
<th>Pred. $i'_{p,om}$</th>
<th>$i K_p^{cal}$ (m$^3$/µg)</th>
<th>$i K_p^{cal}$ ratio$^a$</th>
<th>$i K_p^{exp}$ (m$^3$/µg)</th>
<th>$i K_p^{exp}$ ratio$^b$</th>
<th>$i K_p^{cal}$/$i K_p^{exp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-oxo-2-pentenal (NA)</td>
<td>2.07</td>
<td>1.3472</td>
<td>$1.81 \times 10^{-8}$</td>
<td>0.56</td>
<td>$3.38 (\pm 0.14) \times 10^{-4}$</td>
<td>0.37</td>
<td>$1.87 \times 10^4$</td>
</tr>
<tr>
<td>4-oxo-2-pentenal (A)</td>
<td>2.07</td>
<td>2.2397</td>
<td>$1.01 \times 10^{-8}$</td>
<td>1.25 ($\pm 0.18$) $\times 10^{-4}$</td>
<td>1.24</td>
<td>$10^4$</td>
<td></td>
</tr>
<tr>
<td>4-oxo-2-pentenoic acid (NA)</td>
<td>$1.12 \times 10^{-2}$</td>
<td>2.0814</td>
<td>$2.16 \times 10^{-6}$</td>
<td>0.84</td>
<td>$8.70 (\pm 0.70) \times 10^{-4}$</td>
<td>403</td>
<td></td>
</tr>
<tr>
<td>4-oxo-2-pentenoic acid (A)</td>
<td>$1.12 \times 10^{-2}$</td>
<td>2.2979</td>
<td>$1.82 \times 10^{-6}$</td>
<td>1.30 ($\pm 0.05$) $\times 10^{-3}$</td>
<td>713</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,4-dioxo-2-butene (NA)</td>
<td>4.20</td>
<td>1.7053</td>
<td>$7.03 \times 10^{-9}$</td>
<td>1.43 ($\pm 0.09$) $\times 10^{-3}$</td>
<td>2.03</td>
<td>$10^3$</td>
<td></td>
</tr>
<tr>
<td>1,4-dioxo-2-butene (A)</td>
<td>4.20</td>
<td>2.5366</td>
<td>$4.40 \times 10^{-9}$</td>
<td>0.63</td>
<td>$8.70 (\pm 0.65) \times 10^{-3}$</td>
<td>1.98</td>
<td>$10^3$</td>
</tr>
<tr>
<td>hydroxybenzaldehyde (NA)</td>
<td>$2.89 \times 10^{-1}$</td>
<td>0.8681</td>
<td>$2.01 \times 10^{-7}$</td>
<td>5.06 ($\pm 0.38$) $\times 10^{-4}$</td>
<td>1.66</td>
<td>$10^4$</td>
<td></td>
</tr>
<tr>
<td>hydroxybenzaldehyde (A)</td>
<td>$2.89 \times 10^{-1}$</td>
<td>0.9939</td>
<td>$1.63 \times 10^{-7}$</td>
<td>8.41 ($\pm 0.55$) $\times 10^{-4}$</td>
<td>5151</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-methyl-6-oxo-2,4-hexadienoic acid (NA)</td>
<td>$5.50 \times 10^{-4}$</td>
<td>1.2333</td>
<td>$7.42 \times 10^{-5}$</td>
<td>6.85 ($\pm 0.32$) $\times 10^{-4}$</td>
<td>9.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-methyl-6-oxo-2,4-hexadienoic acid (A)</td>
<td>$5.50 \times 10^{-4}$</td>
<td>1.7505</td>
<td>$4.87 \times 10^{-5}$</td>
<td>3.03 ($\pm 0.16$) $\times 10^{-4}$</td>
<td>6.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cresol (NA)</td>
<td>5.66</td>
<td>0.2022</td>
<td>$4.40 \times 10^{-8}$</td>
<td>0.66</td>
<td>$4.29 (\pm 0.31) \times 10^{-4}$</td>
<td>0.58</td>
<td>9751</td>
</tr>
<tr>
<td>cresol (A)</td>
<td>5.66</td>
<td>0.2832</td>
<td>$2.93 \times 10^{-8}$</td>
<td>2.49 ($\pm 0.16$) $\times 10^{-4}$</td>
<td>1.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-furaldehyde (NA)</td>
<td>3.16</td>
<td>0.7867</td>
<td>$2.03 \times 10^{-8}$</td>
<td>2.62 ($\pm 0.05$) $\times 10^{-4}$</td>
<td>5.30</td>
<td>$10^4$</td>
<td></td>
</tr>
<tr>
<td>2-furaldehyde (A)</td>
<td>3.16</td>
<td>1.1082</td>
<td>$1.34 \times 10^{-8}$</td>
<td>1.39 ($\pm 0.11$) $\times 10^{-3}$</td>
<td>1.04</td>
<td>$10^3$</td>
<td></td>
</tr>
<tr>
<td>benzaldehyde (NA)</td>
<td>1.49</td>
<td>0.8137</td>
<td>$4.15 \times 10^{-8}$</td>
<td>2.66 ($\pm 0.13$) $\times 10^{-5}$</td>
<td>4.56</td>
<td>641</td>
<td></td>
</tr>
<tr>
<td>benzaldehyde (A)</td>
<td>1.49</td>
<td>0.9611</td>
<td>$3.27 \times 10^{-8}$</td>
<td>1.21 ($\pm 0.07$) $\times 10^{-4}$</td>
<td>3695</td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydroxybenzoic acid (NA)</td>
<td>$3.77 \times 10^{-4}$</td>
<td>0.4740</td>
<td>$2.82 \times 10^{-4}$</td>
<td>2.64 ($\pm 0.12$) $\times 10^{-4}$</td>
<td>2.28</td>
<td>94.9</td>
<td></td>
</tr>
<tr>
<td>hydroxybenzoic acid (A)</td>
<td>$3.77 \times 10^{-4}$</td>
<td>0.4073</td>
<td>$3.05 \times 10^{-4}$</td>
<td>6.02 ($\pm 0.57$) $\times 10^{-4}$</td>
<td>1.97</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ i \frac{K_p^{cal}}{K_p^{exp}} = \frac{i K_p^{cal} (A)}{i K_p^{cal} (NA)} \]

\[ i \frac{K_p^{exp}}{K_p^{cal}} = \frac{i K_p^{exp} (A)}{i K_p^{exp} (NA)} \]
Our study also shows that the $i K_p^\text{exp} / i K_p^\text{cal}$ values of carboxylic acids that are less reactive for heterogeneous chemistry are relatively small. For example, the $i K_p^\text{exp} / i K_p^\text{cal}$ of 5-methyl-6-oxo-2,4-hexadienoic acid is in the order of 10 and that of 2-hydroxybenzoic acid is less than 2.

A majority of toluene oxygenated products was reactive for heterogeneous reactions except 5-methyl-6-oxo-2,4-hexadienoic acid and 2-hydroxybenzoic acid as shown in Table 4.3. Table 4.4 summarizes the analytical mass composition determined using GC-ITMS for toluene SOA in the presence of neutral and acidic seed aerosols. For the neutral aerosol, the identified mass accounted for only 11.3% of the total organic mass of toluene SOA and for the acidic aerosol, 6.7%. Most of these identified products are the compounds reactive for heterogeneous reactions as shown in Table 4.3. Such observations prove our hypothesis is reasonable in that the model SOA composition comprises oligomers solely.

Table 4.4 Mass percentage of the identified products in the SOA from toluene photooxidation

<table>
<thead>
<tr>
<th>Oxygenated products</th>
<th>Percentage of aerosol constituents</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non acid</td>
</tr>
<tr>
<td>2,3-dioxobutanal</td>
<td>3.74</td>
</tr>
<tr>
<td>Glyoxal</td>
<td>1.74</td>
</tr>
<tr>
<td>Methylglyoxal</td>
<td>1.77</td>
</tr>
<tr>
<td>1,4 dioxo-2-butene</td>
<td>0.67</td>
</tr>
<tr>
<td>4-oxo-2-pentenal</td>
<td>0.41</td>
</tr>
<tr>
<td>5-hydroxy-4,6-dioxo-2-heptenal</td>
<td>0.69</td>
</tr>
<tr>
<td>4-oxo-2-pentenoic acid</td>
<td>0.44</td>
</tr>
<tr>
<td>Cresol</td>
<td>0.41</td>
</tr>
<tr>
<td>Hydroxybenzaldehyde</td>
<td>0.45</td>
</tr>
<tr>
<td>4,5-dioxo-2-pentenoic acid</td>
<td>0.42</td>
</tr>
<tr>
<td>5-methyl-6-oxo-24 hexadienoic acid</td>
<td>0.39</td>
</tr>
<tr>
<td>2-furaldehyde</td>
<td>0.07</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>0.006</td>
</tr>
<tr>
<td>Hydroxybenzoic acid</td>
<td>0.086</td>
</tr>
<tr>
<td>Unknown</td>
<td>88.7</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>
4.3.3 Effects of particle acidity on the $iK_{p}^{cal}$ and the $iK_{p}^{exp}$ of oxygenated toluene products

In the presence of preexisting inorganic seeds, the gas phase oxygenated products can be driven into the particle by two pathways: one is the gas particle partitioning (physical process) and the other is heterogeneous reactions (chemical processes). In order to evaluate the effects of particle acidity on the gas particle partitioning, the $iK_{p}^{cal}$ (acid)/$iK_{p}^{cal}$ (non acid) was estimated. The resulting $iK_{p}^{cal}$ (acid)/$iK_{p}^{cal}$ (non acid) demonstrate how the aerosol composition associated with MW$_{om}$ and $\gamma_{om}$ under the different particle acidity affects the gas-particle partitioning.

The difference in $iK_{p}^{exp}$ values under the different particle acidity reflects not only the influence of water content in the inorganic seed but also the effects of particle acidity on both gas-particle partitioning process and heterogeneous reactions. All experiments in this study were conducted at RH=14-23%. Under such low RH conditions, the neutral seed aerosol made of ammonium sulfate is solid below the efflorescence relative humidity that is in the range of 30–35%RH (Colberg et al., 2004; Gao et al., 2006; Martin et al., 2003). Unlike the neutral seed, the acidic seed particles are aqueous regardless of %RH. Water content and particle acidity in the inorganic phase of aerosols possibly influence the transfer of oxygenated gas phase products from the gas to the particle in the following ways: (1) The presence of water in the inorganic phase of acidic aerosols possibly enhances the partitioning of hydrophilic compounds to the particle phase. (2) Water in the inorganic acid seed may also act as a reactant in heterogeneous reactions of gas phase oxygenated products such as aldehydes (Koehler et al., 2004) to facilitate the transfer of the oxygenated products from the gas phase to the particle phase. (3) Inorganic acid can catalyze heterogeneous reactions,
which increases transferring from the gas to the particle phase for the products reactive in heterogeneous acid-catalyzed reactions. (4) Alteration of \( \text{MW}_{\text{on}} \) and \( \text{i}_{\text{on}} \) due to the production of oligomers from heterogeneous reactions in the presence of inorganic acid affects partitioning process of organic compounds. The magnitude of this effect can be estimated by \( \text{i}_{\text{cal}} \frac{\text{K}_{\text{cal}}(\text{acid})}{\text{K}_{\text{cal}}(\text{non acid})} \) as mentioned earlier. The net results of the competing effects (1)-(3) can be assessed by comparing the \( \text{i}_{\text{exp}} \frac{\text{K}_{\text{exp}}(\text{acid})}{\text{K}_{\text{exp}}(\text{non acid})} \) to the \( \text{i}_{\text{cal}} \frac{\text{K}_{\text{cal}}(\text{acid})}{\text{K}_{\text{cal}}(\text{non acid})} \). Overall, \([ \text{i}_{\text{exp}} \frac{\text{K}_{\text{exp}}(\text{acid})}{\text{K}_{\text{exp}}(\text{non acid})} / \text{i}_{\text{cal}} \frac{\text{K}_{\text{cal}}(\text{acid})}{\text{K}_{\text{cal}}(\text{non acid})} \] ranges from 0.66-9.7, which are either within experimental uncertainties or larger than one, indicating that the presence of inorganic acid and water in aerosol enhanced the contributions of oxygenated products to SOA formation through heterogeneous reactions.

**4.3.4 Uncertainties**

The major uncertainty in this study exists in the gas/particle sampling associated with a filter-denuder train used to collect the semivolatile organic products. The adsorption of gas phase semivolatile products on the filter in the filter-denuder system may occur and could lead to overestimation of \( \text{i}_{\text{exp}} \frac{\text{K}_{\text{exp}}(\text{acid})}{\text{K}_{\text{exp}}(\text{non acid})} \) in this study. In this paper, a comparison study of \( \text{i}_{\text{exp}} \frac{\text{K}_{\text{exp}}(\text{acid})}{\text{K}_{\text{exp}}(\text{non acid})} \) values between the two sampling systems (denuder-filter-denuder vs. filter-denuder) has been performed for semivolatile alkanes. The result shows that the difference in \( \text{i}_{\text{exp}} \frac{\text{K}_{\text{exp}}(\text{acid})}{\text{K}_{\text{exp}}(\text{non acid})} \) values due to the two different sampling systems for the alkanes is in the order of magnitude 10. However, a majority of toluene oxygenated products are more volatile than the alkanes used. Hence, the possible artifacts on \( \text{i}_{\text{exp}} \frac{\text{K}_{\text{exp}}(\text{acid})}{\text{K}_{\text{exp}}(\text{non acid})} \) by the gas adsorption on a filter associated with
the filter-denuder sampling train should be smaller than the order of magnitude of 10 measured for semivolatile alkanes. Compared to the large deviations between $i\text{ }^K_p^{\text{exp}}$ and $i\text{ }^K_p^{\text{cal}}$ of toluene oxygenated products, such uncertainties cannot significantly influence our interpretation and conclusion about the impacts of heterogeneous reactions on toluene SOA formation.

4.4 Summary and implication

In this study, the SOA compositions consisting of different numbers of various function groups in oligomers have been semiempirically determined by comparing $i\text{ }^K_p^{\text{exp}}$ of semivolatile alkanes to $i\text{ }^K_p^{\text{cal}}$ obtained from equation 1 with their UNIFAC calculated $i\gamma_{om}^{\infty}$ values. The proposed SOA composition of this study includes mainly oligomers. Such approach appears to be realistic according to our GC-ITMS SOA product analysis. The resulting SOA composition can be applied to the organic aerosols in the ambient atmosphere, when SOA forms with very low NO$_x$ concentration. For example, in the weekday afternoon (12pm-3pm) of the urban area such as Atlanta, Georgia (Wade, 2005), the NO$_x$ concentrations decrease below 10 ppb.

The calculated $i\gamma_{om}^{\infty}$ values of toluene oxygenated products based on the hypothesized SOA composition were in the range of 1-2.0814 (under the neutral conditions) and 1-2.5366 (under the acidic conditions). To our knowledge, this study calculated $i\gamma_{om}^{\infty}$ of toluene oxygenated products based on SOA composition comprised of oligomers for the first time. Studies on the partitioning behavior of semivolatile compounds usually assumed activity coefficient as 1, which were not accurate for some toluene oxygenated products based on the findings of this study. The approach proposed here is useful for studies that require the prior
knowledge of SOA compositions which cannot be experimentally determined using conventional analytical methods.

Our study also found that the $iK_p^{exp}$ values of a majority of toluene oxygenated products (except some organic acids such as 5-methyl-6-oxo-2,4-hexadienoic acid and 2-hydroxybenzoic acid) are much larger (in the magnitude of $10^2$-$10^6$) than the $iK_p^{cal}$ under both the neutral and the acidic conditions, due to aerosol phase heterogeneous chemistry. The results imply that the current SOA predictive models by the gas particle partitioning theory solely are limited to describing the realistic SOA formation. The SOA models in the next generation should take into account the compounds that might be relatively volatile but reactive for heterogeneous reactions.

The presence of acidic sulfate apparently increases the contribution of most toluene oxygenated products to SOA formation through heterogeneous reactions. The acidic sulfate effects on the $iK_p^{exp}$ values are confounded by two factors: the water content in the inorganic seed and the particle acidity. In the recent study by Cao and Jang (2008), the confounding effects of water and particle acidity have been addressed.

**Acknowledgements**

This work was supported by a Grant from National Science Foundation (ATM0703941).
Reference


Cao, G., Jang, M., 2008. Secondary organic aerosol formation from toluene photooxidation under the various NOx conditions and particle acidity. Atmospheric Chemistry and Physics Discussion 8, 14467–14495.


molecular weight of humic-like substances isolated from fine atmospheric aerosol. Atmospheric Environment 37(27), 3783-3794.


Chapter V

An SOA Model for Toluene Oxidation in the Presence of Inorganic Aerosols

Gang Cao¹, Myoseon Jang²*
1. Department of Environmental Sciences and Engineering
University of North Carolina at Chapel Hill
CB#7431, Rosenau Hall, Chapel Hill, NC, 27599
2. Department of Environmental Engineering Sciences, University of Florida,
P.O. Box 116450, Gainesville, FL 32611

In preparation for submission to Environmental Science and Technology

*Corresponding Author: Myoseon Jang
Email: mjang@ufl.edu
Abstract

A predictive model for secondary organic aerosol (SOA) formation through both partitioning and heterogeneous reactions is explored for the SOA produced from oxidation of toluene in the presence of inorganic seed aerosols. The explicit gas-phase chemistry of toluene, gas-particle partitioning, and heterogeneous chemistry are implemented in the SOA predictive model. The explicit gas phase products are lumped based on their vapor pressure and reactivity for heterogeneous reactions. In our SOA model, the predictive SOA mass is decoupled into partitioning ($OM_P$) and heterogeneous aerosol production ($OM_H$). $OM_P$ is estimated from the SOA partitioning model developed by Schell et al. (2001) that is currently used in the regional air quality model. $OM_H$ is predicted from the heterogeneous SOA model developed by Jang et al. (2006). The SOA model is evaluated using a number of the experimental SOA data that is generated in a 2 m$^3$ indoor Teflon film chamber under various experimental conditions (e.g., humidity, inorganic seed compositions, NO$_x$ concentrations). The SOA model reasonably predicts not only the ozone formation, the conversion of NO to NO$_2$ and the decay of toluene in the gas phase but also the production of SOA mass. The model simulations show that the $OM_H$ fraction of the total toluene SOA mass depends on NO$_x$ concentrations. For example, the $OM_H$ fraction is about 73-83% at low NO$_x$ levels and 17%-47% at middle and high NO$_x$ levels for the SOA experiments with high initial toluene concentrations. However, for the SOA experiments with low initial toluene concentrations, the $OM_H$ mass accounts for 54%-83% of total SOA mass at middle and high NO$_x$ levels. Such significant increase in the $OM_H$ mass fractions implies that heterogeneous reactions of the second generation products of toluene oxidation can considerably contribute total SOA mass under the atmospheric relevant conditions.
5.1 Introduction

Secondary organic aerosol (SOA) formed from gas phase products of volatile organic compounds (VOC) oxidation constitutes a significant organic fraction of fine particulate matter in ambient air (Philip et al., 2008). The potential impacts of fine particulate matter on climate change (Rosenfeld, 2006; Pilinis et al., 1995), visibility (Eldering et al., 1996) and human health (Pope and Dockery, 2006) stimulate the strong research interest in SOA formation from biogenic and anthropogenic precursors. The formation mechanisms and yields of SOA from a single organic precursor have been often studied using laboratory chamber experiments due to the complexity in real atmospheric aerosols. The experimental data then is used to determine major parameters of SOA formation. The current SOA model that is incorporated in the regional air quality model is mainly based on the thermodynamic equilibrium gas-particle partitioning and tends to underestimate the observed SOA formation in the atmosphere. Recent laboratory studies have evinced that heterogeneous reactions are important pathways for SOA generation, in addition to the gas-particle partitioning (Baltensperger et al., 2005; Gao et al., 2004b; Jang et al., 2002; Kalberer et al., 2004; Liggio et al., 2005a). Moreover, many laboratory SOA studies (Cao and Jang, 2007, 2008; Czoschke et al., 2003; Czoschke and Jang, 2006; Edney et al., 2005; Gao et al., 2004a, 2004b; Inuma et al., 2004; Northcross and Jang, 2007) show that heterogeneous reactions in aerosols can be accelerated by the presence of inorganic acidic species, leading to greater SOA production. The chemical interaction between inorganic and organic components in aerosols needs to be considered in the SOA model, because inorganic and organic constituents are often coexisting in the actual multicomponent ambient aerosols. Thus, inclusion of heterogeneous reactions in the presence of inorganic seed into the SOA model will significantly improve our
ability to predict SOA mass and reduce the deviation between the observed and the predicted SOA mass by the gas-particle partitioning solely.

Jang et al. (2005) in their recent study first incorporated heterogeneous reactions of organic compounds into the SOA model. In their model, a mathematical relationship between rate constants and molecular structures of various carbonyl compounds has been semiempirically derived for heterogeneous reactions and has been later applied to develop a predictive SOA model for the SOA produced from α-pinene ozonolysis in the presence of inorganic seed (Jang et al., 2006). The SOA model that includes both the gas-particle partitioning and heterogeneous reactions shows the great improvement in predictability of SOA mass compared to the one based on partitioning solely.

Another advantage of Jang’s recent SOA model is that the model decouples the SOA mass into the mass from gas-particle partitioning (OM$_P$) and the mass from heterogeneous reactions (OM$_H$). The SOA model output can not only help us to evaluate the relative importance of two main pathways for SOA formation from various organic precursors under different environmental conditions, but also provide us the valuable information on SOA composition such as the fraction of high molecular weight oligmers in aerosols. Although great research effort has been made to analyze oligomer fraction using advanced analytical instruments, the exact fraction of oligomers in aerosols is not clearly understood due to the artifacts during the sample preparation and analyses as well as the lack of authentic standards. The fraction of simulated OM$_H$ can improve our understanding of how heterogeneous reactions of gas products for SOA formation are influenced by the surrounding atmospheric environment.
In this study, Jang’s SOA model is extended to toluene SOA formation in the presence of inorganic seed. Experimental toluene SOA data at different NO\textsubscript{x} levels generated in a 2 m\textsuperscript{3} indoor chamber is used for the SOA model development and evaluation. The SOA model begins with the explicit gas-phase chemistry of toluene oxidation along with OM\textsubscript{H} prediction. The resulting OM\textsubscript{H} mass is incorporated in the SOA partitioning model developed by Schell et al. (2001) for OM\textsubscript{P} prediction. The SOA model including OM\textsubscript{P} and OM\textsubscript{H} enables us to integrate heterogeneous chemistry in the SOA model used in the regional air quality model.

5.2 Experimental Section

All experiments are conducted in a 2 m\textsuperscript{3} indoor Teflon film chamber under UV-visible light conditions. The detailed description for the chamber experiments has been provided elsewhere (Cao and Jang, 2008). The chamber is equipped with sixteen fluorescent lamps (Solarc Systems Inc., FS40T12/UVB) that have emission in the UV range between 300-400 nm with the maximum near 314 nm. Temperature increase due to the light sources is less than 2 K for the duration of the experiments. The particle size distribution is monitored with a Scanning Mobility Particle Sizer (SMPS, TSI Model 3080, Shoreview, MN) coupled with a condensation nuclei counter (CNC, TSI, Model 3025A). Particle data is corrected for the aerosol loss to the chamber wall (McMurry and Grosjean, 1985) with a first order decay. The gas-phase toluene concentrations are measured with an HP 5890 GC-FID. Temperature (295-299 K) and %RH of the chamber are measured with an electronic thermo-hygrometer (Dwyer Instrument, INC, USA). Prior to each experiment, the chamber is flushed with clean air from clean air generators (Aadco Model 737, Rockville, MD; Whatman Model 75-52, Haverhill, MA). The inorganic seed aerosols are injected into the chamber by atomizing the
inorganic aqueous solution (various combinations of ammonium sulfate, ammonium bisulfate and sulfuric acid) with a Constant Output Atomizer (TSI, Model 3076, Shoreview, MN).

For the low NO\textsubscript{x} (< 3 ppb) experiments, toluene is oxidized by OH radicals from the photolysis of H\textsubscript{2}O\textsubscript{2}. When the seed aerosols stabilize, a known volume of toluene is injected into the chamber. The gas phase of H\textsubscript{2}O\textsubscript{2} is then introduced into the chamber by gently purging the nitrogen at 1 L/min over a 50% H\textsubscript{2}O\textsubscript{2} aqueous solution (Aldrich). The UV-Visible lights are turned on at the beginning of the H\textsubscript{2}O\textsubscript{2} injection. The initial H\textsubscript{2}O\textsubscript{2} concentrations in the chamber range from 3.48-3.71 ppm which are estimated by mass loss of the 50% H\textsubscript{2}O\textsubscript{2} solution between before and after H\textsubscript{2}O\textsubscript{2} injection and the mole fraction of H\textsubscript{2}O\textsubscript{2} in vapor mixture (water + H\textsubscript{2}O\textsubscript{2}) (Manatt and Manatt, 2004).

For the middle (90-105 ppb) and the high NO\textsubscript{x} (280-315 ppb) experiments, a known amount of NO and NO\textsubscript{2} are added in the chamber from a certificate NO tank (99.5% nitric oxide, Linde Gas). After the NO\textsubscript{x} concentrations stabilize, a known volume of toluene is injected and the UV lights are turned on, which marks the starting point of the SOA experiment. During the experiments, ozone and NO\textsubscript{x} concentrations are monitored with a photometric ozone analyzer (model 400E, Teledyne Instruments, San Diego, CA) and a chemiluminescence NO\textsubscript{x} detector (model 200E, Teledyne Instruments, San Diego, CA). The experimental conditions and the resulting SOA data are summarized in Table 5.1.

5.3 Results and Discussion

5.3.1 Model components

The SOA predictive model consists of two individual SOA models: OM\textsubscript{p} and OM\textsubscript{H}. The experimental variables (e.g. consumed concentration of organic precursors, humidity, temperature, seed mass concentration, seed composition) for toluene SOA formation are used
for the SOA model evaluation. The SOA model includes various submodels: a gas phase kinetic model of toluene oxidation (MCM) (Jenkin et al., 2003), an inorganic thermodynamic model (Nenes, 2006) for proton concentration and water activity, an organic thermodynamic model (Fredenslund and Sorensen, 1994) for activity coefficients of organics in SOA and water, a semiempirical model for heterogeneous rate constants (Jang et al., 1995), and an equilibrium partitioning model for absorptive partitioning coefficients (Pankow, 1994). Figure 5.1 shows the relationship among model components.

![Figure 5.1 Components of the SOA model including partitioning and heterogeneous reactions](image)

Figure 5.1 Components of the SOA model including partitioning and heterogeneous reactions
5.3.2 OM\textsubscript{P} model

The partitioning SOA model (equation 1) originally built by Schell et al. (2001) has been modified by inclusion of OM\textsubscript{H}. The OM\textsubscript{P} model of this study is developed based on mass balance of organic compounds between the gas and particle phase.

\[
OM\textsubscript{P} = \sum_{i} \left[ C_{\text{tot},i} - C_{H,i} - C_{\text{sat},i} \frac{C_{\text{aer},i}}{m_i + C_{\text{init},i}} \right] \text{(µg/m}^3) \tag{1}
\]

\(C_i\) refers to the concentration (µg/m\(^3\)) of compound \(i\) in aerosols (\(aer\)), the total product (\(tot\)) from gas phase reactions, and the concentration of compound \(i\) converted to the oligomers (\(H\)) in the particle phase. \(C^*_{\text{sat},i}\) is a saturation concentration of \(i\). \(C_{\text{init}}\) is the concentration of the preexisting absorbing materials. Unlike the Schell’s original SOA partitioning model, additional absorbing material always exists in our OM\textsubscript{P} model because OM\textsubscript{H} appears in aerosols as the preexisting absorbing materials (\(C_{\text{int}}\)).

5.3.3 OM\textsubscript{H} model

OM\textsubscript{H} model (equation 2) developed by Jang et al. (2006) has been used for heterogeneous toluene SOA prediction.

\[
OM_{\text{H}} = \sum_{i} \sum_{j} \frac{f_{\text{H}} \left( k_{H,j} M_{\text{seed}} + k_{0,j} t \right)}{1 + \left( k_{H,j} M_{\text{seed}} + k_{0,j} t \right)} \frac{\left[ \frac{10^3 \alpha_{i,j} \Delta ROG K_{\text{tot,i}} \gamma_{\text{OM,i}} V_{\text{OM}}}{MW_i \gamma_{w,i} V_w} \right]^2 \frac{MW_i}{10^3 K_{\text{tot,i}} \gamma_{w,i} V_{\text{OM}}}}{10^3 K_{\text{tot,i}} \gamma_{w,i} V_{\text{OM}}} \tag{2}
\]

\(f_{\text{H}}\) is a mathematical parameter to describe the degree of heterogeneous reactions linked to the ratios of consumed organic precursor (\(\Delta ROG, \mu g/m^3\)) concentration to the inorganic seed mass concentration (\(M_{\text{seed}}, \mu g/m^3\)) (details are addressed in the section “degree of heterogeneous reactions at different NO\textsubscript{x} levels”). \(k_{H,j}\) is the heterogeneous reaction rate constant (m\(^3\)µg\(^{-1}\)sec\(^{-1}\)) of oxygenated products with fast reactivity (H-f), medium reactivity
(H-m) and slow reactivity (H-s). t is the heterogeneous reaction time (60 second). $\alpha_{i,H;j}$ is the mass fraction stoichiometric coefficient for the lumped group based on volatility ($i$=1, 2, 3, 4, 5) and reactivity ($j$=H-f, H-m, H-s). Values for $\alpha_{i,H;j}$ are obtained from the gas phase kinetics model (MCM) (Jenkin et al., 2003) (details are addressed in the section “lumping structures of gas phase products”). $K_{om,i}$ is the partitioning coefficient (m$^3$/µg) for each lumped group with different vapor pressure ($i$=1, 2, 3, 4, 5). $V_{om}$ and $V_w$ denote the molar volume of OM and water (ml/mol). $\gamma_{om,i}$ and $\gamma_{w,i}$ are the activity coefficients of $i$ in organic matter and in water.
Table 5.1 Experimental conditions and resulting SOA data from photooxidation of toluene\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Exp #\textsuperscript{c}</th>
<th>% RH (µg/m\textsuperscript{3})</th>
<th>Initial NO (ppb)</th>
<th>Initial NO\textsubscript{2} (ppb)</th>
<th>ΔTOI (ppm)</th>
<th>V\textsubscript{seed} (nL/m\textsuperscript{3})</th>
<th>V\textsubscript{mix} (nL/m\textsuperscript{3})</th>
<th>OM (µg/m\textsuperscript{3})</th>
<th>M\textsubscript{org}/M\textsubscript{inorg}</th>
<th>Yield\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNO\textsubscript{x}-NA-LRH</td>
<td>18.4</td>
<td>0.01</td>
<td>&lt;1.5</td>
<td>&lt;1.5</td>
<td>0.10</td>
<td>169</td>
<td>245</td>
<td>106.3</td>
<td>0.45</td>
</tr>
<tr>
<td>LNO\textsubscript{x}-NA-HRH</td>
<td>48.2</td>
<td>0.01</td>
<td>&lt;1.5</td>
<td>&lt;1.5</td>
<td>0.09</td>
<td>179</td>
<td>229</td>
<td>70.5</td>
<td>0.28</td>
</tr>
<tr>
<td>LNO\textsubscript{x}-A-LRH</td>
<td>17.0</td>
<td>0.80</td>
<td>&lt;1.5</td>
<td>&lt;1.5</td>
<td>0.13</td>
<td>153</td>
<td>285</td>
<td>183.2</td>
<td>0.86</td>
</tr>
<tr>
<td>LNO\textsubscript{x}-A-HRH</td>
<td>48.2</td>
<td>0.69</td>
<td>&lt;1.5</td>
<td>&lt;1.5</td>
<td>0.10</td>
<td>185</td>
<td>249</td>
<td>89.4</td>
<td>0.35</td>
</tr>
<tr>
<td>MNO\textsubscript{x}-NA-LRH</td>
<td>15.8</td>
<td>0.01</td>
<td>66.2</td>
<td>28.6</td>
<td>0.13</td>
<td>218</td>
<td>263</td>
<td>66.5</td>
<td>0.22</td>
</tr>
<tr>
<td>MNO\textsubscript{x}-NA-HRH</td>
<td>41.0</td>
<td>0.02</td>
<td>78.1</td>
<td>14.8</td>
<td>0.10</td>
<td>215</td>
<td>262</td>
<td>65.3</td>
<td>0.22</td>
</tr>
<tr>
<td>MNO\textsubscript{x}-A-LRH</td>
<td>21.1</td>
<td>1.05</td>
<td>69.2</td>
<td>30.0</td>
<td>0.12</td>
<td>203</td>
<td>292</td>
<td>124.4</td>
<td>0.44</td>
</tr>
<tr>
<td>MNO\textsubscript{x}-A-HRH</td>
<td>38.5</td>
<td>0.87</td>
<td>82.7</td>
<td>22.0</td>
<td>0.12</td>
<td>212</td>
<td>295</td>
<td>116.5</td>
<td>0.39</td>
</tr>
<tr>
<td>HNO\textsubscript{x}-NA-LRH</td>
<td>14.6</td>
<td>0.01</td>
<td>241.4</td>
<td>70.4</td>
<td>0.30</td>
<td>246</td>
<td>340</td>
<td>130.9</td>
<td>0.38</td>
</tr>
<tr>
<td>HNO\textsubscript{x}-NA-HRH</td>
<td>42.7</td>
<td>0.02</td>
<td>229.4</td>
<td>85.1</td>
<td>0.29</td>
<td>210</td>
<td>309</td>
<td>138.0</td>
<td>0.47</td>
</tr>
<tr>
<td>HNO\textsubscript{x}-A-LRH</td>
<td>19.9</td>
<td>1.19</td>
<td>226.1</td>
<td>62.0</td>
<td>0.28</td>
<td>227</td>
<td>328</td>
<td>141.4</td>
<td>0.44</td>
</tr>
<tr>
<td>HNO\textsubscript{x}-A-HRH</td>
<td>40.9</td>
<td>0.94</td>
<td>222.2</td>
<td>81.6</td>
<td>0.31</td>
<td>235</td>
<td>336</td>
<td>142.0</td>
<td>0.43</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Temperature: 295 -299 K. \textsuperscript{b} Initial toluene concentrations range from 0.63-0.88 ppm. \textsuperscript{c} LNO\textsubscript{x}: low NO\textsubscript{x} level (OH radical source: photolysis of H\textsubscript{2}O\textsubscript{2}); MNO\textsubscript{x}: middle NO\textsubscript{x} level ([NO\textsubscript{x}]=90-135 ppb); HNO\textsubscript{x}: high NO\textsubscript{x} level ([NO\textsubscript{x}]=280-315 ppb); NA: in the presence of non acidic seed; A: in the presence of acidic sulfate seed; LRH: low %RH level; HRH: high %RH level. \textsuperscript{d} SOA yield was calculated with the density of organic matter of 1.4 g/mL. The uncertainties of the resulting SOA yields were calculated using the uncertainties of OM and ∆ROG through the propagation of uncertainty for divisions (Levie, 1997).
5.3.4 Gas phase product distribution from a gas phase model of toluene oxidation (MCM)

A gas phase model of toluene oxidation is described using the master chemical
mechanism version 3.1 (MCM) (Jenkin et al., 2003) to determine gas product distribution
\( \alpha_i, H_j \) and \( \Delta ROG \) that is used for the predictive SOA model. The MCM of toluene oxidation
is available on the website of University of Leeds
(http://mcm.leeds.ac.uk/MCM/browse.html?species=TOLUENE). A chemical solver, Morpho
developed by Jeffries et al. (1998), is used to run the MCM. Consistent with findings from
other studies (Bloss et al., 2005; Hu et al., 2007), the slow toluene decay is observed with
MCM simulation compared to the experimentally measured toluene decay in our chamber.
According to Bloss et al. (2005), an artificial OH source was added in the toluene oxidation
mechanisms to constantly provide the additional OH radicals throughout the simulated
chamber experiments. The generation rate of the artificial OH radical source was determined
by comparing the modeled toluene loss rate to the measured toluene decay rate. The artificial
OH rate of this study is \( 4 \times 10^8 \) molecule cm\(^{-3}\) s\(^{-1}\). Interestingly, the same rate was also
employed in the study of Bloss et al. (2005). Figure 5.2 shows the comparison between the
experimental data and model simulations of toluene decay, NO\(_x\) conversion, and ozone
formation at low NO\(_x\) (toluene decay only), middle NO\(_x\) and high NO\(_x\) conditions. The model
appears to reasonably track the NO-NO\(_2\) conversion but tends to overpredict ozone
concentrations. The resulting gas product composition and consumption of toluene from the
gas phase model using MCM are applied to the SOA model as addressed in the following
sections.
Figure 5.2 Comparison of model simulated and measured concentrations of toluene, NO, NO₂ and O₃ for experiments at middle NOₓ and high NOₓ levels (with an artificial OH radical source incorporated in the model). Low NOₓ: 6/9/06 NA; Mid NOₓ: 1/24/08; High NOₓ: 1/28/08 (Table 5.1).
5.3.5 Lumping structures of gas phase products

Using MCM, there are total 147 organic products from photooxidation of toluene. In our toluene SOA model, these explicit organic products are lumped into 20 groups according to their vapor pressure and reactivity for heterogeneous reactions. The vapor pressure is estimated by equation 3 (Mackay et al., 1982).

\[
\ln P^0 = \frac{\Delta S_{vap}(T_b)}{R} \left[ (1.8)(1 - \frac{T_b}{T}) + (0.8)(\ln \frac{T_b}{T}) \right]
\]  (3)

where \(\Delta S_{vap}\) is the entropy of vaporization, R is a gas constant (8.314 JK\(^{-1}\)mol\(^{-1}\)), \(T_b\) is the boiling point (K) and \(T\) is the ambient temperature (K). \(\Delta S_{vap}\) of an organic compound is calculated by modified Trouton’s method developed by Zhao et al. (1999) with parameters related to molecular geometry and association. The boiling points of organic compounds are calculated by a group contribution method originally developed by Joback and Reid (1987) with a modified equation and group contribution parameters (Stein and Brown, 1994). The vapor pressures of gas phase organic products are categorized into five groups: \(10^{-6}\), \(10^{-5}\), \(10^{-4}\), \(10^{-3}\), \(10^{-2}\) mmHg (in the order of \(i=1\) to \(i=5\)). Each of five groups \((i=1, 2, 3, 4, 5)\) then is divided into four subgroups \((j)\) according to the reactivity of organic products for heterogeneous reactions: high reactivity \((H-f)\), medium reactivity \((H-m)\), low reactivity \((H-s)\) and no reactivity \((P,\ partitioning\ only)\). The reactivity order of organic compounds is multifunctional aldehydes > aldehydes > ketones > carboxylic acids, which is applied to sort out the organic products. Then, the gas phase toluene reaction can be described as

\[
\text{Toluene} + OH \rightarrow \alpha_{1,p}S_{1,p} + \alpha_{2,p}S_{2,p} + \ldots + \alpha_{1,H-f}S_{1,H-f} + \alpha_{2,H-f}S_{2,H-f} + \ldots + \alpha_{1,H-s}S_{1,H-s} + \alpha_{2,H-s}S_{2,H-s} + \ldots
\]  (4)
$S$ denotes the substrate produced by oxidation. $\alpha_{i,j}$ is stoichiometric coefficient based on mass fraction for each lumped group. Table 5.2 shows the corresponding $\alpha_{i,j}$ values for the lumped groups at different NO$_x$ levels.

Table 5.2 Stoichiometric coefficient ($\alpha$) based on mass fraction for each lumped group obtained from MCM simulations of three experiments at different NO$_x$ levels. Reactivity category H-F: high reactivity; H-M: medium reactivity; H-S: slow reactivity and PO: partitioning only.

**Low NO$_x$**

<table>
<thead>
<tr>
<th>Vapor pressure (mmHg)</th>
<th>Reactivity in heterogeneous reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PO</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>0.0086</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>0.0000</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>0.0000</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>0.0274</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>0.1187</td>
</tr>
</tbody>
</table>

**Mid NO$_x$**

<table>
<thead>
<tr>
<th>Vapor pressure (mmHg)</th>
<th>Reactivity in heterogeneous reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PO</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>0.0825</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>0.0542</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>0.0932</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>0.2257</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>0.2305</td>
</tr>
</tbody>
</table>
High NO\textsubscript{x}

<table>
<thead>
<tr>
<th>Vapor pressure (mmHg)</th>
<th>Reactivity in heterogeneous reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PO</td>
</tr>
<tr>
<td>10\textsuperscript{-6}</td>
<td>0.0373</td>
</tr>
<tr>
<td>10\textsuperscript{-5}</td>
<td>0.1001</td>
</tr>
<tr>
<td>10\textsuperscript{-4}</td>
<td>0.2225</td>
</tr>
<tr>
<td>10\textsuperscript{-3}</td>
<td>0.2112</td>
</tr>
<tr>
<td>10\textsuperscript{-2}</td>
<td>0.3150</td>
</tr>
</tbody>
</table>

5.3.6 Degree of heterogeneous reactions at different NO\textsubscript{x} levels

According to our previous studies of toluene SOA formation (Cao and Jang, 2008), heterogeneous acid-catalyzed reactions occur rapidly in the beginning when inorganic acid is abundant in aerosols and then proceed slowly. The possible explanations for such tendency have been provided in the previous study by Jang et al (2006). For example, (1) insoluble oligomers build up at the boundary between inorganic and organic phases resulting in the unavailability of inorganic acid to organic compounds; (2) oligomers may be insoluble in inorganic phase and hence cannot further react through heterogeneous acid-catalyzed reactions; (3) organic sulfate formation (Jang et al., 2008; Liggio et al., 2005) consumes acidic sulfates reducing the proton concentrations in SOA. To consider such dynamic changes in heterogeneous reactions, parameter “degree of reactions (f_H)” (equation 5) is employed in the OM\textsubscript{H} model (Jang et al., 2006).

$$f_H = \frac{1}{1 + a(\Delta ROG/M_{seed})}$$  \hspace{1cm} (5)
where \( a \) is a fitting parameter that is semi-empirically obtained by fitting the modeled total SOA mass (\( \text{OM}_T = \text{OM}_H + \text{OM}_P \)) to the experimentally measured SOA mass using two experiments at each of different \( \text{NO}_x \) levels (Table 5.1). The resulting \( a \) values vary with \( \text{NO}_x \) levels, which is not surprising, because different \( \text{NO}_x \) concentrations lead to different compositions of gas phase toluene oxygenated products and thus differently affect heterogeneous chemistry of organic products in SOA formation. In our model, the \( a \) values are 0.3, 3 and 4 for low \( \text{NO}_x \), mid \( \text{NO}_x \) and high \( \text{NO}_x \) levels, respectively.

Figure 5.3 Comparison of the predicted \( \text{OM}_T \) and the measured \( \text{OM}_T \) (Table 5.1) at three \( \text{NO}_x \) levels in the non-acidic and acidic toluene systems (low \( [\text{NO}_x] < 1.5 \) ppb; mid \( [\text{NO}_x] = 90-105 \) ppb; high \( [\text{NO}_x] = 280-315 \) ppb; Low RH=15-22%; High RH=38-49%).

5.4 Simulation results

Experimental conditions and resulting SOA data used for model simulations are listed in Table 5.1. Figure 5.3 shows that the modeled \( \text{OM}_T \) at both low and high humidity reasonably matches the experimental \( \text{OM}_T \) within \( \pm 25\% \) except one experiment labeled as “*” at high humidity. The model overpredicted 40% of the marked experimental SOA mass (*) at low \( \text{NO}_x \) and high RH% levels in the presence of acidic seed.
Figure 5.4 Predicted heterogeneous SOA mass fraction (OM$_H$/OM$_T$) at three NO$_x$ levels in the non-acidic and acidic toluene systems (low [NO$_x$] < 1.5 ppb; middle [NO$_x$] = 90-105 ppb; high [NO$_x$] = 280-315 ppb; low RH = 15-22%; high RH = 38-49%). Experimental data used for the simulation is listed in Table 5.1.

Figure 5.4 demonstrates the simulated OM$_H$ fractions of OM$_T$ under various experimental conditions. According to the OM$_H$ model simulations, the NO$_x$ concentrations and the particle acidity considerably influence OM$_H$ fractions of OM$_T$ but humidity appears not effective. The OM$_H$ fractions of OM$_T$ are the highest at low NO$_x$ levels ranging from 0.73-0.83, and the lowest at high NO$_x$ levels in the range of 0.17-0.26. The SOA model simulations agree with our recent experimental results observed for NO$_x$ effects on SOA formation (Cao and Jang, 2008). The absolute increases in OM$_H$ fraction of OM$_T$ by the presence of acidic seed are in the range of -0.01—0.13 under all experimental conditions. The effects of particle acidity in the model simulation are maximized with middle NO$_x$ at low RH%, which is consistent with the findings from our previous chamber experiments for toluene SOA (Cao and Jang, 2008).
Table 5.3 SOA experiments conducted under the atmospheric relevant conditions at middle NO\textsubscript{x} level ([NO\textsubscript{x}] ~100-115 ppb) and high NO\textsubscript{x} level (270-290 ppb)\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Exp #\textsuperscript{c}</th>
<th>%RH</th>
<th>[H\textsuperscript{+}] (µg/m\textsuperscript{3})</th>
<th>NO\textsubscript{d} (ppb)</th>
<th>NO\textsubscript{x}\textsuperscript{d} (ppb)</th>
<th>ΔTOl (ppm)</th>
<th>V\textsubscript{seed} (nL/m\textsuperscript{3})</th>
<th>V\textsubscript{mix} (nL/m\textsuperscript{3})</th>
<th>OM (µg/m\textsuperscript{3})</th>
<th>M\textsubscript{org}/M\textsubscript{inorg}</th>
<th>Yield\textsuperscript{e}</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNO\textsubscript{x}-NA-HRH</td>
<td>42.7</td>
<td>0.001</td>
<td>83.8</td>
<td>29.9</td>
<td>0.012</td>
<td>9.78</td>
<td>20.1</td>
<td>14.5</td>
<td>1.06</td>
<td>0.32±0.026</td>
</tr>
<tr>
<td>MNO\textsubscript{x}-A-HRH</td>
<td>41.9</td>
<td>0.03</td>
<td>85.3</td>
<td>15.4</td>
<td>0.012</td>
<td>9.38</td>
<td>21.0</td>
<td>16.3</td>
<td>1.24</td>
<td>0.36±0.028</td>
</tr>
<tr>
<td>MNO\textsubscript{x}-NA-HRH</td>
<td>42.5</td>
<td>0.001</td>
<td>88.9</td>
<td>31.5</td>
<td>0.010</td>
<td>11.8</td>
<td>20.1</td>
<td>11.6</td>
<td>0.70</td>
<td>0.31±0.024</td>
</tr>
<tr>
<td>MNO\textsubscript{x}-A-HRH</td>
<td>43.7</td>
<td>0.03</td>
<td>92.5</td>
<td>20.7</td>
<td>0.013</td>
<td>10.4</td>
<td>23.7</td>
<td>18.6</td>
<td>1.28</td>
<td>0.38±0.028</td>
</tr>
<tr>
<td>MNO\textsubscript{x}-NA-LRH</td>
<td>17.7</td>
<td>0.001</td>
<td>80.6</td>
<td>27.5</td>
<td>0.016</td>
<td>9.92</td>
<td>24.7</td>
<td>20.7</td>
<td>1.49</td>
<td>0.34±0.026</td>
</tr>
<tr>
<td>MNO\textsubscript{x}-A-LRH</td>
<td>18.9</td>
<td>0.05</td>
<td>78.3</td>
<td>22.6</td>
<td>0.014</td>
<td>9.46</td>
<td>26.0</td>
<td>23.2</td>
<td>1.75</td>
<td>0.44±0.034</td>
</tr>
<tr>
<td>HNO\textsubscript{x}-NA-LRH</td>
<td>19.8</td>
<td>0.001</td>
<td>221.5</td>
<td>52.9</td>
<td>0.034</td>
<td>14.8</td>
<td>42</td>
<td>38.1</td>
<td>1.84</td>
<td>0.29±0.022</td>
</tr>
<tr>
<td>HNO\textsubscript{x}-A-LRH</td>
<td>16.2</td>
<td>0.05</td>
<td>231.7</td>
<td>50.3</td>
<td>0.034</td>
<td>18.6</td>
<td>44.8</td>
<td>36.7</td>
<td>1.41</td>
<td>0.28±0.022</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Temperature =299 K. \textsuperscript{b} Initial toluene concentration is 0.04 ppm. \textsuperscript{c} MNO\textsubscript{x}: middle NO\textsubscript{x} level; HNO\textsubscript{x}: high NO\textsubscript{x} level; NA: in the presence of non acidic seed; A: in the presence of acidic sulfate seed; HRH: high %RH level; LRH: low %RH level. \textsuperscript{d} initial concentrations. \textsuperscript{e} Yield was calculated with the density of organic matter of 1.4 g/mL. The uncertainties of the resulting SOA yields were calculated using the uncertainties of OM and ΔROG through the propagation of uncertainty for divisions (Levie, 1997)

In order to demonstrate the model performance in atmospheric relevant conditions, SOA experiments (shown in Table 5.3) conducted with low initial toluene concentrations (~40 ppb) and the low concentration of weak acidic inorganic seed aerosols (~ 10 µg/m\textsuperscript{3}) are also simulated by our SOA model (Figure 5.5). Overall, the SOA model appears to underpredict the observed SOA mass by 2-22% under atmospheric relevant conditions. The OM\textsubscript{H} fractions of OM\textsubscript{T} under atmospheric relevant conditions (as shown in Figure 5.6) range from 0.6-0.83 at middle NO\textsubscript{x} and 0.54-0.64 at high NO\textsubscript{x}, which are 1.5-3 times larger than those simulated for the experiments with high initial toluene concentrations (Figure 5.4) at

108
the same NO\textsubscript{x} levels. Such difference in heterogeneous SOA mass fractions due to different initial toluene concentrations provides important implication for SOA formation mechanisms. In the presence of high concentrations of toluene (Table 5.1), the first generation oxidation products are dominant in the system. Although rate constants of the first generation oxidation products with OH radicals are generally one order of magnitude greater than that of toluene (Finalyson-Pitts and Pitts, 2000), the OH radical reactions with toluene at high concentrations are relatively important compared to those with the first generation products. However, when the initial toluene concentration is low (Table 5.3), the first generation products can be further oxidized and produce the second generation products which are often more oxidized than the first generation products. Our modeled OM\textsubscript{H} under the atmospheric relevant conditions indicates that heterogeneous reactions of the second generation products can considerably contribute OM\textsubscript{T}.

![Figure 5.5 Comparison of the predicted OM\textsubscript{T} and the measured OM\textsubscript{T} (Table 5.3) at middle NO\textsubscript{x} and high NO\textsubscript{x} levels under atmospheric relevant conditions in the non-acidic and acidic toluene systems (mid [NO\textsubscript{x}] = 100-115 ppb; high [NO\textsubscript{x}] = 270-290 ppb; Low RH=16-20%; High RH=41-44%). Two experiments at high NO\textsubscript{x} levels were highlighted in a box.](image-url)
Figure 5.6 also shows that the effects of particle acidity on SOA formation in the atmospheric relevant conditions (low toluene and low seed concentrations) are not significant. The possible explanation for this result is the low seed concentrations and the high mass ratios of organic to inorganic seed (Table 5.3) in our experimental conditions. We expect that the actual particle acidity effects in the ambient air are probably higher than the results in our experimental conditions due to lower mass ratios of organic to inorganic species in ambient aerosols. The mass ratios of organic to inorganic compounds are the important factor to determine the degree and the rates of heterogeneous acid-catalyzed reactions of organic species in aerosols. However, another possibility to explain the weak particle acidity effects on SOA formation with low initial toluene concentrations is reactivity of the second generation products. The highly oxidized second generation products are probably very reactive so that their heterogeneous reactions occur even with no acid catalyst. Therefore, SOA formation through heterogeneous reactions of the second generation products at low toluene concentrations is less sensitive to the particle acidity. Future studies that vary mass ratios of organic to inorganic compounds for SOA formation with low initial toluene concentrations are needed.
Figure 5.6 Predicted heterogeneous SOA mass fraction (OM\textsubscript{H}/OM\textsubscript{T}) at middle NO\textsubscript{x} and high NO\textsubscript{x} levels in the non-acidic and acidic toluene systems (middle [NO\textsubscript{x}] = 100-115 ppb; high [NO\textsubscript{x}] = 270-290 ppb; low RH = 16-20%; high RH = 41-44%). Experimental data used for the simulation is listed in Table 5.3.

5.5 Uncertainty and implication

A few assumptions and parameters need to be revisited when experimental data become available or when our understanding on SOA formation is improved. For example, in this study, an artificial OH source is added in the gas phase chemistry mechanisms of toluene oxidation (MCM) to reduce the significant discrepancy of toluene decay between model simulations and experimental measurements. Also, the activity coefficient of compound \(i\) in water (\(\gamma_{w,i}\)) for each lumped group is obtained using UNIFAC calculations for toluene oxygenated products. The impact of water soluble inorganic species on solubility of organic compounds in water is not considered when \(\gamma_{w,i}\) is calculated using UNIFAC. In addition, because the parameters (e.g. group surface areas and group volumes of functional groups) required by UNIFAC calculation for organic nitrates are not available, \(\gamma_{w,i}\) for organic nitrates is assumed as 100 on the basis of \(\gamma_{w,i}=1\) for water soluble organic products.
The SOA model including both OM$_{p}$ and OM$_{H}$ has been demonstrated for the toluene system in this study and also for the terpene systems in previous study (Northcross, 2008). Both studies have shown that the SOA model successfully simulated the chamber SOA data produced under various experimental conditions, which indicates that our OM$_{H}$ model can be integrated into the current SOA model used in the regional air quality model.

Acknowledgements

This work was supported by a Grant from National Science Foundation (ATM0703941).
Reference


Cao, G., Jang, M., 2008. Secondary organic aerosol formation from toluene photooxidation under the various NOx conditions and particle acidity. Atmospheric Chemistry and Physics Discussion 8, 14467–14495.


secondary organic aerosol formation from toluene oxidation in the presence of NOx and natural sunlight. Atmospheric Environment 41(31), 6478-6496.


Chapter VI

Summary of Research Findings and Recommendation for Future Studies

6.1 Summary of research findings

This dissertation not only demonstrates comprehensive laboratory chamber studies but also explores a predictive SOA model for SOA formation from oxidation of toluene in the presence of inorganic seed under various experimental conditions. The entire dissertation work includes four important investigations.

Investigation 1 (Chapter II): A number of chamber experiments have been conducted to estimate the effects of particle acidity and UV light on SOA yields from oxidation of toluene and 1,3,5-trimethylbenzene (135-TMB) under dark and UV-Visible light conditions in the absence of NO\textsubscript{x}. Overall, acidic aerosols lead to higher SOA yield than non-acidic aerosols for both the toluene and 135-TMB systems. Under dark, the effects of particle acidity appear to be much stronger with toluene SOA than 135-TMB SOA. In the presence of UV light, the effects of particle acidity on the SOA yields remain for both aromatic systems, although the magnitude of acidity impacts is less compared to the dark experiments. UV light suppresses the SOA formation for both aromatic systems. However, after the completion of SOA formation, the changes in either SOA mass or the particle size distribution are negligible by alternating UV irradiation condition for both aromatic systems.
Investigation 2 (Chapter III): A number of chamber experiments have been performed under different NO\textsubscript{x} levels and humidity levels in the presence of inorganic neutral seed and acidic seed to study how toluene SOA yields respond to various NO\textsubscript{x} concentrations, humidity and particle acidity. The results show that NO\textsubscript{x} concentrations influence the effects of particle acidity and humidity on toluene SOA formation, because NO\textsubscript{x} concentrations affect the types of gas phase products from toluene photooxidation and influence the contribution of possible mechanisms to SOA formation. Humidity effects addressed in this study include the particle phase water effect and the gas phase water effect. The magnitude of these water effects depends on the main mechanisms at different NO\textsubscript{x} levels. The results also indicate that particle acidity effects on SOA formation are strongest at intermediate NO\textsubscript{x} compared to those at low and high NO\textsubscript{x}. Insignificant effects of particle acidity and humidity are observed at high NO\textsubscript{x}. The possible mechanisms for SOA formation at different NO\textsubscript{x} levels have been addressed along with the effects of particle acidity and humidity on toluene SOA formation.

Investigation 3 (Chapter IV): An approach using two deturated alkanes is employed to semiempirically determine the hypothesized SOA compositions consisting of different numbers of various function groups in oligomers. The molecular weight of oligomers ranges from 285-446 Da and the O: C ratios, 0.23-0.47. Impacts of heterogeneous chemistry on partitioning of semivolatile organic compounds onto toluene SOA formed in the absence of NO\textsubscript{x} have been examined based on the hypothesized SOA compositions under both neutral and acidic conditions. The results show the huge discrepancy between the measured partitioning coefficients and the calculated partitioning coefficients for a majority of toluene oxygenated products, indicating that these compounds are highly reactive for heterogeneous
reactions. However, the discrepancy for organic acids is negligible, showing that the partitioning process is the dominant pathway for the contribution of organic acids to the toluene SOA.

Investigation 4 (Chapter V): An SOA model including heterogeneous reactions and partitioning processes is developed to simulate SOA formation from toluene photooxidation at different NO\textsubscript{x} levels in the presence of inorganic neutral and acidic seed. Comparisons between experimental measurements and model simulations for the gas phase chemistry (O\textsubscript{3} formation, NO and NO\textsubscript{2} conversion and toluene decay) and the SOA formation in the toluene system show that our SOA model provides reasonable predictivity. The model simulation results show that depending on different NO\textsubscript{x} concentrations in the system, about 73-83\% of the total toluene SOA mass at low NO\textsubscript{x} levels and 17%-47\% at middle and high NO\textsubscript{x} levels are from heterogeneous reactions for the SOA experiments with high initial toluene concentrations. However, for the SOA experiments with low initial toluene concentrations, the heterogeneous SOA mass accounted for 54%-83\% of the total SOA mass at middle and high NO\textsubscript{x} levels. Such significant increases in the heterogeneous SOA mass fractions may imply important mechanisms for toluene SOA formation under atmospheric relevant conditions.

**6.2 Recommendation for future studies**

Three areas need to be addressed in future studies:

1. Characterize gas and particle products obtained from SOA experiments in the presence of NO\textsubscript{x} using advanced mass spectrometer such as GC-ion trap MS for simple low molecular weight products and LC-MS for high molecular weight products (oligomers).
2. Quantify oligomer fraction. Research efforts are required for development of new methods that can experimentally measure the actual oligomer fraction in toluene SOA without introducing artifacts during the sample preparation and sample analysis. The measured oligomer fraction can be used to modify the hypothesis SOA compositions proposed in Chapter IV. The measured oligomer fraction can also be compared with the modeled values for the SOA model evaluation (Chapter V).

3. Revisit assumptions and parameters used for the SOA model when experimental data become available or when our understanding on SOA formation is improved. The gas phase chemistry mechanisms of toluene oxidation (MCM) need to be improved to decrease the significant discrepancy of toluene decay between model simulation and experimental measurement (in this dissertation, an artificial OH source was added in MCM to reduce such discrepancy). Also, a possibility of calculating the activity coefficients of compound $i$ in water ($\gamma_{w,i}$) for organic nitrates should be explored. Moreover, great research effort for future SOA model development should be focused on how the time concept can be integrated into the SOA model in order to provide predicted SOA mass to the regional air quality model systems for each input time step.
Appendix A

NO$_x$ Meter and O$_3$ Meter Calibration

A.1 Equipments and supplies used for the calibration

O$_3$ meter (photometric O$_3$ analyzer-model 400E) with an internal pump

NO$_x$ meter (chemiluminescence NO/NO$_x$ analyzer-model 200E) with an external pump

Zero air tank (airgas)

Certified 50 ppm NO tank balanced with N$_2$ (airgas)

O$_3$ generator (ozone producing double-bore lamps, Jelight Company, Inc)

Mass flow controller

Bubbler for the gas flow rate measurement

Stop watch

GPT

Venting system

A.2 Principle of the GPT calibration

The GPT calibration method is based on the reaction (equation 1) between nitric oxide (NO) and ozone (O$_3$) and can be used for dynamic calibration for NO$_x$ and O$_3$ meters.

\[ NO + O_3 \rightarrow NO_2 + O_2 \]  \quad (1)
Figure A.1 shows the experimental setup of the GPT calibration system for calibrating NO\textsubscript{x} meter and O\textsubscript{3} meter.

Figure A.1 shows the experimental setup of the GPT calibration system. A steady flow of zero air controlled by a mass flow controller is provided to flow through the O\textsubscript{3} generator (the low pressure Hg-vapor UV lamp), GPT mixing chamber and to waste. A very low flow of standard NO balanced in N\textsubscript{2} is controlled by a needle valve of a pressure regulator on the tank. The NO flow and zero air flow first mix in front of the GPT mixing chamber. The mixed two streams then flow through the GPT and get to the sampling ports for the NO\textsubscript{x} and O\textsubscript{3} meters.

NO\textsubscript{x} meter is usually calibrated first. The NO\textsubscript{x} meter zero point is set when only the zero air flow through the entire GPT system. The span point is set when the known concentration of NO is added in the system. The obtained NO concentration depends on the mixing ratio (dilution factor) of NO and zero air. Therefore, by changing the mixing ratios of NO and zero air, a five-point calibration curve between the calculated NO concentrations and
measured ones (NO\textsubscript{x} meter readings) is obtained. The slope of the calibration curve is used as the correction factor to adjust the meter readings to the actual values.

After the NO\textsubscript{x} meter is calibrated, the O\textsubscript{3} meter can be calibrated based on the calibrated NO\textsubscript{x} meter readings. Steady NO\textsubscript{x} flow and zero air flow are added in the GPT system until the NO reading is stable ([NO]\textsubscript{0, average}, usually the last ten points are taken for the average). Then the O\textsubscript{3} generator is turned on. Due to the reaction of O\textsubscript{3} and NO, a decay of NO is observed. The O\textsubscript{3} and NO readings are recorded during this time until the readings of NO and O\textsubscript{3} are stable ([NO]\textsubscript{ss, average}, [O\textsubscript{3}]\textsubscript{ss, average}, usually the last ten points are taken for the average). Then NO tank is closed to remove the NO flow from the system. Therefore, the total measured O\textsubscript{3} in the system ([O\textsubscript{3}]\textsubscript{0, average}, usually the last ten points are taken for the average) can be known. Equations 2–4 are the mathematical expression for the calibration principle. Based on the comparison between the results from equation 2 and equation 4, the calibration factor for the O\textsubscript{3} meter is obtained.

\[
\Delta O_3 = [O_3]_{0, \text{average}} - [O_3]_{\text{ss, average}} \tag{2}
\]

(equation 2: O\textsubscript{3} consumption according to the O\textsubscript{3} meter readings)

\[
\Delta NO = [NO]_{0, \text{average}} - [NO]_{\text{ss, average}} \tag{3}
\]

\[
\Delta O_3 = \Delta NO \tag{4}
\]

(equation 4: actual O\textsubscript{3} consumption according to the actual NO consumption)

For the calibration, therefore, it is necessary to know the flow rates of the zero air and NO, the NO concentration in the certificated gas tank.
A.3 Procedure

Before starting the calibration, turn on the NO\textsubscript{x} meter (and its external pump) and the O\textsubscript{3} meter.

A. NO\textsubscript{x} meter calibration

(I) set the zero point of the NO\textsubscript{x} meter

1) turn on the zero air tank

2) adjust the mass flow controller for the zero air stream at a certain value (e.g. 3 L/min)

3) wait for 5 mins and record the NO\textsubscript{x} reading (more than five data points for average)

(II) set the span point of the NO\textsubscript{x} meter (There are two spans in the NO\textsubscript{x} meter (chemiluminescence NO/NO\textsubscript{x} analyzer-model 200E): 0-0.5 ppm and 0-1 ppm. The target NO concentrations used to set the span point should be around 80% of the maximum concentration of the span, which are 0.4 ppm for 0-0.5 ppm and 0.8 ppm for 0-1 ppm).

1) remain the zero air tank on and turn on the NO standard tank

2) measure the flow rate of NO stream directly from the outlet of the tank

3) calculate the NO concentration based on the flow rates of zero air and the NO as well as the NO concentration of the tank (make the NO concentration around 0.4 ppm or 0.8 ppm)

4) connect the NO in the GPT system

5) record the NO readings until they are stable

6) measure the flow rate of NO one more time to ensure the NO flow remains stable
It is not necessary to perform (II) very frequently, unless the parts in the NO<sub>x</sub> meter are replaced or the setting parameters for the meter are changed.

(III) make a calibration curve between the calculated actual NO concentrations and the NO meter readings

1) adjust either the flow of zero air or the flow of NO to change the mixing ratios in order to have five different concentrations of NO in the GPT system

2) for each NO concentration, follow the procedure in A (II)

3) turn off the NO tank

4) flush the GPT system by remaining the zero air tank on for 5 mins

5) turn off the zero air tank

6) make a calibration curve with five data points and obtain the slope as the correction factor to adjust the NO meter readings to the actual values

B. O<sub>3</sub> meter calibration

1) turn on the zero air tank and set the air flow by the mass flow controller

2) record the O<sub>3</sub> meter readings as the zero offset for the O<sub>3</sub> meter

3) turn on the NO tank

4) measure the NO flow from the outlet of the NO tank

5) connect NO to the GPT system

6) check the NO readings until they are stable

7) disconnect NO and measure the NO flow rate to ensure the NO flow is stable

8) connect the NO stream in the GPT system

9) turn on the O<sub>3</sub> generator

10) record the NO<sub>x</sub> and O<sub>3</sub> readings until the readings are stable
11) disconnect NO and measure the flow rate to ensure the NO flow is stable and turn off the NO tank

12) remain O₃ generator on and record the O₃ readings until they are stable

13) turn off the O₃ generator

14) flush the GPT system with zero air for 5 mins and turn off the zero air tank

**After the calibration of NOₓ and O₃ meters is done, turn off the NOₓ meter (and its external pump) and O₃ meter.**

Figure A.2 and Figure A.3 show examples of experimental data for the calibration of NOₓ and O₃ meters.

Figure A.2 The calibration curve for the NOₓ meter (Jan 06, 2008). The correction factor is 0.9472.
Figure A.3 Gas phase titration (GPT) chart for the calibration of the O₃ meter. A: NO on and O₃ off; B: NO on and O₃ on; C: NO off and O₃ on.
Appendix B
Chamber Characterization

A 2 m$^3$ indoor Teflon film photoirradiation chamber has been used to study the SOA formation from oxidation of toluene. The indoor chamber has been characterized in terms of particle wall loss, chamber leak, light spectra and light intensity.

B.1 Particle wall loss

Particle wall loss is an inevitable problem of using Teflon film chambers. We assume that the size-dependent particle lost to the chamber wall is controlled under a first order decay (McMurry and Grosjean, 1985). The data for the particle lost to the chamber wall is obtained from (NH$_4$)$_2$SO$_4$ aerosol atomized into the chamber by monitoring its decay over time for each particle size bin. Figure B.1 shows the particle wall loss rate as a function of particle size. All SOA data is corrected empirically for the wall loss using the first order rate constant for each particle size bin. On average, 15% SOA mass of this study increases after wall loss correction.
Figure B.1 Particle wall loss rate as a function of particle size

### B.2 Chamber leak rate

The chamber leak rate is measured by injecting 6 ppm carbon tetrachloride (CCl₄) into the chamber and monitoring the concentrations of CCl₄ for four hours with a gas chromatography-flame ionization detector (GC-FID). No appreciable CCl₄ concentration change over time is detected by GC-FID, indicating the chamber leak is negligible.

### B.3 Light characterization

Light characterization is required for evaluating the photolysis of organics during the SOA experiments and for modeling gas phase kinetics of photolysis. Two measurements are needed to determine the UV-Visible irradiation in the chamber: one is the spectral distribution of the UV-Visible irradiation and the other is the NO₂ photolysis rate. Basically, the spectral distribution is a relative intensity spectrum. An absolute intensity spectrum is obtained by correcting the relative intensity spectrum with a factor obtained from the comparison of the relative NO₂ photolysis rate against the measured NO₂ photolysis rate.
Various NO₂ photolysis rates are tested in an inorganic gas phase chemistry model for NO₂ actinometry experiments at the given initial NO and NO₂ concentrations. The actual absolute NO₂ photolysis rate is determined as the one which provides the smallest deviation between the modeled and measured values for the final NO and NO₂ concentrations. In the present study, the spectral distribution (Figure B.2) is measured directly using a LI-COR 1800 spectroradiometer from Dr. Jeffries’ group (my sincere appreciation to Dr. Ken Sexton for the help on the spectral measurement). In future studies, the spectral distribution will be measured with a spectroradiometer PS-300 (UV/NIR)(newly purchased from apogee instruments inc.). This document mainly discusses about the NO₂ actinometry experiment in the indoor chamber and the determination of the absolute UV-Visible irradiation from the lamps surrounding our chamber.

![Graph showing fluorescence light spectrum compared with solar spectra for zenith angle of 51°](image_url)

**Figure B.2 Fluorescence light spectrum compared with solar spectra for zenith angle of 51°**
B.3.1 Experimental measurement

The light characterization experiment is conducted in the presence of a low concentration of O\textsubscript{2}. Our 2m\textsuperscript{3} indoor chamber is half-way evacuable chamber. To make the low O\textsubscript{2} concentration, the chamber is flushed with N\textsubscript{2} from an ultra high purity N\textsubscript{2} tank in the way of the half chamber completely “squeezing in and pulling out” for several times. The exact initial O\textsubscript{2} concentration in the system is necessary to be known for the calculation of NO\textsubscript{2} photolysis rate. The instruments for the measurement of O\textsubscript{2} concentration are not available in our laboratory. Therefore the initial O\textsubscript{2} concentrations in the chamber are estimated indirectly. CCl\textsubscript{4} is used to monitor the dilution during the chamber flushing with N\textsubscript{2}. The known amount of CCl\textsubscript{4} is injected in the chamber in the beginning of the dilution. In order to keep the low CCl\textsubscript{4} concentration in the chamber, instead of adding very high concentration of CCl\textsubscript{4} one time, we inject small amount of CCl\textsubscript{4} (e.g. 100 µL) each time for several times during the N\textsubscript{2} chamber flushing. The obtained dilution factor is used to calculate the O\textsubscript{2} concentration in the chamber.

B.3.2 Experimental procedures

1. flush the chamber completely prior to the experiments.
2. inject an known amount of CCl\textsubscript{4} into the chamber for the calculation of the dilution factor that will be used to calculate the final O\textsubscript{2} concentration.
3. add N\textsubscript{2} from a high purity N\textsubscript{2} tank to make the O\textsubscript{2} concentration in the chamber as low as possible with the reasonable amount of time and effort taken.
4. add an known amount of NO\textsubscript{2} into the chamber.
5. record NO, NO\textsubscript{2}, NO\textsubscript{x} readings from a NO\textsubscript{x} meter.
6. turn on the UV lights and record NO, NO\textsubscript{2}, NO\textsubscript{x} readings from the NO\textsubscript{x} meter.
7.  Turn off the light and record the NOx, NO, NO2 readings.

8.  Repeat step 6-7 several times.

B.3.3 Model simulation

A model of inorganic gas phase chemistry is used to find the NO2 photolysis rate that leads to simulation results with the smallest deviation from the measured NO and NO2 concentrations. The model includes all possible reactions in the chamber during the photolysis of NO2 (Figure B.3). The model is executed in a chemical solver—Morpho. The input for the model is the initial concentrations of O2, NO and NO2. Because the experiment is performed in the UV light on-off mode, the model is operated for both UV light and dark conditions.

Figure B.3 All reactions included in the inorganic gas phase model

\[
\begin{align*}
\text{NO}_2 & \rightarrow \text{NO} + \text{O}_3\text{P} & \text{NO}_2 \rightarrow \text{NO} + \text{O}_3\text{P} & @ j[\text{NO}_2\rightarrow\text{O}_3\text{P}]; \\
\text{O}_3\text{P} + \text{O} + \text{M} & \rightarrow \text{O}_3 + \text{M} & \text{NO} + \text{NO} + \text{O}_2 & \rightarrow 2.0\text{NO}_2 & @ 3.30E-39*\exp(530.0/TK) \\
\text{O}_3 + \text{NO} & \rightarrow \text{NO}_2 + \text{O}_2 & \text{NO} + \text{NO} + \text{O}_2 & \rightarrow 2.0\text{NO}_2 & @ 1.50E-11*\exp(170.0/TK) \\
\text{O}_3\text{P} + \text{NO}_2 & \rightarrow \text{NO} + \text{O}_2 & \text{NO}_3 + \text{NO} & \rightarrow 2.0\text{NO}_2 & @ 4.50E-14*\exp(-1260.0/TK) \\
\text{O}_3\text{P} + \text{NO}_2 & \rightarrow \text{NO}_3 + \text{O}_2 & \text{NO}_3 + \text{NO}_2 & \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2 & @ 6.5E-12*\exp(120.0/TK) \\
\text{O}_3\text{P} + \text{NO} & \rightarrow \text{NO}_2 & \text{NO}_3 + \text{NO}_2 & \rightarrow \text{NO}_3 + \text{O}_2 & @ 6.5E-12*\exp(120.0/TK) \\
\text{NO} + \text{NO} + \text{O}_2 & \rightarrow 2.0\text{NO}_2 & \text{NO} + \text{NO} + \text{O}_2 & \rightarrow 2.0\text{NO}_2 & @ 3.30E-39*\exp(530.0/TK) \\
\text{O}_3 + \text{NO}_2 & \rightarrow \text{NO}_3 + \text{O}_2 & \text{O}_3 + \text{NO}_2 & \rightarrow \text{NO}_3 + \text{O}_2 & @ 1.2E-13*\exp(-2450.0/TK) \\
\text{NO}_3 & \rightarrow \text{NO}_2 & \text{NO}_3 & \rightarrow \text{NO}_2 & @ 1.50E-11*\exp(170.0/TK) \\
\text{NO}_3 + \text{NO} & \rightarrow 2.0\text{NO}_2 & \text{NO}_3 + \text{NO}_2 & \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2 & @ 4.50E-14*\exp(-1260.0/TK) \\
\text{NO}_3 + \text{NO}_2 & \rightarrow \text{N}_2\text{O}_5 & \text{NO}_3 + \text{NO}_2 & \rightarrow \text{NO}_3 + \text{NO}_2 & @ 1.50E-12*\exp(-0.7, b[M], 0.6) \\
\text{N}_2\text{O}_5 & \rightarrow \text{NO}_3 + \text{NO}_2 & \text{N}_2\text{O}_5 & \rightarrow \text{N}_2\text{O}_5 & @ 1.5E-21; \\
\text{O}_3 & \rightarrow \text{O}_3 + \text{O}_2 & \text{O}_3 & \rightarrow \text{O}_3 + \text{O}_2 & @ j[\text{O}_3\rightarrow\text{O}_3+\text{O}_2]; \\
\text{O}_3 + \text{O}_2 & \rightarrow \text{O}_3 + \text{O}_2 & \text{O}_3 + \text{O}_2 & \rightarrow \text{O}_3 + \text{O}_2 & @ j[\text{O}_3\rightarrow\text{O}_3+\text{O}_2]; \\
\text{O}_3 + \text{NO}_2 & \rightarrow \text{NO}_3 + \text{O}_2 & \text{O}_3 + \text{NO}_2 & \rightarrow \text{NO}_3 + \text{O}_2 & @ j[\text{O}_3\rightarrow\text{O}_3+\text{O}_2]; \\
\text{N}_2\text{O}_5 + \text{H}_2\text{O} & \rightarrow 2.0\text{HNO}_3 & \text{N}_2\text{O}_5 + \text{H}_2\text{O} & \rightarrow 2.0\text{HNO}_3 & @ 1.5E-21; \\
\text{O}_3 + \text{H}_2\text{O} & \rightarrow \text{O}_3 + \text{H}_2\text{O} & \text{O}_3 + \text{H}_2\text{O} & \rightarrow \text{O}_3 + \text{H}_2\text{O} & @ j[\text{O}_3\rightarrow\text{O}_3+\text{O}_2]; \\
\text{O}_3 + \text{H}_2\text{O} & \rightarrow \text{OH} + \text{NO}_2 & \text{O}_3 + \text{H}_2\text{O} & \rightarrow \text{OH} + \text{NO}_2 & @ 2.0E-10; \\
\text{O}_3 + \text{NO}_2 & \rightarrow \text{OH} + \text{NO}_2 & \text{O}_3 + \text{NO}_2 & \rightarrow \text{OH} + \text{NO}_2 & @ 1.60E-12*\exp(-940.0/TK) \\
\text{OH} + \text{OH} + \text{H}_2\text{O} & \rightarrow 2.0\text{HONO} & \text{OH} + \text{OH} + \text{H}_2\text{O} & \rightarrow 2.0\text{HONO} & @ 4.4E-40; \\
\text{HONO} + \text{HONO} & \rightarrow \text{NO} + \text{NO}_2 + \text{H}_2\text{O} & \text{HONO} + \text{HONO} & \rightarrow \text{NO} + \text{NO}_2 + \text{H}_2\text{O} & @ 1.0E-20; \\
\text{OH} + \text{NO} & \rightarrow \text{HONO} & \text{OH} + \text{NO} & \rightarrow \text{HONO} & @ j[\text{HONO}\rightarrow\text{NO}]; \\
\text{HONO} & \rightarrow \text{OH} + \text{NO} & \text{HONO} & \rightarrow \text{OH} + \text{NO} & @ 1.80E-11*\exp(-390.0/TK); \\
\text{OH} + \text{HONO} & \rightarrow \text{NO}_2 + \text{H}_2\text{O} & \text{OH} + \text{HONO} & \rightarrow \text{NO}_2 + \text{H}_2\text{O} & @ 1.80E-11*\exp(-390.0/TK); \\
\end{align*}
\]
In this model, several things need to be modified according to characteristics of our indoor chamber and the experimental conditions: (1) $O_2$ concentration—in the original model, the $O_2$ concentration is set at 20%. This value should be changed based on the actual experimental $O_2$ concentration in the chamber. This change is done in the file “StdVarNames.minc” under the directory of mechanisms/sources/stdinclude (Figure B.4). The mixing ratio of $N_2$: $O_2$ used in this study is 0.995:0.005. (2) Other parameters such as the deposition rate of $H_2O_2$ and $O_3$ on the chamber wall need to be updated for our chamber condition accordingly in the file “UNCAuxInorgStd_d.rxn” under the directory of mechanisms/sources/stdinclude (Figure B.4). The $H_2O_2$ deposition rate is $1.1 \times 10^{-3}$ sec$^{-1}$ and $O_3$ deposition rate is $9.6 \times 10^{-5}$ sec$^{-1}$. Because the humidity in the chamber is very low (~ 5%), the deposition of $N_2O_5$, $HNO_3$ and $HONO$ on the wall is negligible. (3) Because the organics in the chamber are negligible, all reactions involved with organics are removed from the original mechanism (e.g. the reactions of background VOC in the file “UNCAuxOrgStd_a.rxn” under the directory of mechanisms/sources/stdinclude (Figure B.4)).
The determined NO\textsubscript{2} photolysis rate is 0.0585 min\textsuperscript{-1} and the resulting factor is 2.11. Figure B.5 shows comparison results between the experiment measurements and the model simulations for NO\textsubscript{2} actinometry experiments.

Figure B.5 Comparison between measured and modeled values for NO, NO\textsubscript{2} and NO\textsubscript{x} for NO\textsubscript{2} actinometry experiments (NO\textsubscript{2} photolysis rate is 0.0585 min\textsuperscript{-1}). UV light is operated in on-off mode. The grey boxes indicate the dark conditions.
The photolysis rates of compounds (jtable) are generated in Morpho using the absolute light intensity, quantum yields and cross sections of compounds. Figure B.6 demonstrates a flow chart for generation of photolysis rate files in Morpho. The detailed procedure is addressed in FLUX User’s Guide to the In-chamber Actinic Flux Simulation Programs (Jeffries).

Figure B.6 A flow chart for generation of photolysis rate files in Morpho. Square box denotes input files; ellipse, output files and rhombus, executable files.
Reference


Jeffries, H. A microcomputer system for testing kinetics mechanisms with chamber data. Volume 3: FLUX user’s guide to the in-chamber actinic flux simulation programs. Project report to Atmospheric Research and Exposure Assessment Laboratory