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**Simulated impact of NO_x on SOA formation from oxidation of toluene
and *m*-xylene**

by

Jialu Xu

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APPROVED, THESIS COMMITTEE

Robert J. Griffin, Chair

Professor, Civil & Environmental Engineering

Daniel Cohan, Associate Professor

Civil & Environmental Engineering

Mark Embree, Adjunct Professor

Computational and Applied Mathematics

HOUSTON, TEXAS

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Jialu Xu

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ABSTRACT

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Despite the crucial role of aromatic-derived secondary organic aerosol (SOA) in deteriorating air quality, its formation mechanism is not well understood, and the dependence of aromatic SOA formation on nitrogen oxides (NO_x) is not captured fully by most SOA formation models. In this study, NO_x-dependent mechanisms of toluene and *m*-xylene SOA formation are developed using the gas-phase Caltech Atmospheric Chemistry Mechanism (CACM) coupled to a gas/aerosol partitioning model. The updated models were optimized by comparison to eighteen chamber experiments performed under both high- and low-NO_x conditions at the University of California – Riverside. Correction factors for vapor pressures imply uncharacterized association chemistry, likely in the aerosol phase. The newly developed model can predict strong decreases of *m*-xylene SOA yield with increasing NO_x. Simulated SOA speciation implies the importance of ring-opening products in governing SOA formation (up to ~40-60% for both aromatics). Speciation distributions under varied NO_x levels imply that competition between hydroperoxide radical and NO for reaction with a bicyclic peroxide radical may not be the only factor influencing SOA formation. The reaction of aromatic peroxy radicals with NO competing with self-cyclization also affects NO_x-dependence of SOA formation. Comparison of SOA formation yield and composition between toluene and *m*-xylene suggests aldehyde/ketone chemistry from a ring-opening route and a phenolic

route play important roles in governing SOA formation, with their relative importance likely varying due to the number of methyl groups on the aromatic ring. Sensitivity studies of the NO_x /Aromatic/SOA system with a range of NO_x and hydrocarbon concentrations are carried out for toluene, *m*-xylene, and a mix of toluene and *m*-xylene. The impact of a non-aromatic hydrocarbon not expected to form SOA (propene) also is investigated. The effect of temperature variations on model predictions of the NO_x effect on SOA formation is also explored. The updated box model will be implemented into a three-dimensional model to evaluate NO_x effect on aromatic SOA formation on a larger scale.

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Chapter 1

Introduction

1.1. Background

Atmospheric particulate matter (PM) is known to have adverse impacts on human health and cause impaired visibility. Elevated PM mass concentrations also are associated with increased morbidity and mortality (Pope et al., 2009). A key constituent of atmospheric PM is organic aerosol (OA). OA can be further classified as primary organic aerosol (POA), that which is directly emitted into atmosphere, and secondary organic aerosol (SOA), that which is formed from condensation of products of the oxidation of volatile organic compounds (VOCs) emitted from various sources. Approximately half of the fine PM burden in the troposphere is constituted by OA, a majority of which could be SOA (Kanakidou et al., 2005). Substantial work has been devoted to understanding SOA formation mechanisms. The experimental community has carried out various chamber experiments to elucidate SOA formation and evolution pathway for various VOCs.

In short, the oxidation of VOCs emitted from biogenic or anthropogenic sources in the gas phase by species such as hydroxyl radical, ozone, or the nitrate radical initiates the formation of SOA (Griffin et al., 1999a). The products often contain hydroxyl, carboxyl, carbonyl, nitro and nitrate functional moieties. These products are more soluble and less volatile than the parent VOC, facilitating in partitioning into condensed aerosol phases. The product distribution and their phase partitioning depend on environmental variables such as nitrogen oxides (NO_x) concentration, temperature, relative humidity (RH), and the nature and concentration of pre-existing aerosol.

Aromatic hydrocarbons such as benzene, toluene, xylene, and trimethylbenzenes constitute an important fraction of anthropogenic reactive VOCs in the urban atmosphere, comprising up to 45% of the VOCs in urban US locations (Calvert et al., 2002). Global SOA formation from aromatic hydrocarbons is estimated to be 212 Tg yr^{-1} (Henze et al., 2008). Despite the crucial role of aromatic-derived SOA in deteriorating air quality, its complex formation mechanism is not well understood, and model simulation of SOA formation remains difficult.

NO_x plays a critical role in affecting SOA formation from aromatic hydrocarbons (Johnson et al., 2005; Song et al., 2005; Ng et al., 2007). A strong decrease in SOA yield is observed when NO_x level increases in aromatic hydrocarbon chamber studies. The most likely explanation is that NO_x governs the fate of organic peroxy radicals (RO_2). With more $\text{NO}_x + \text{RO}_2$ reactions, more volatile products are formed. Decreasing NO_x leads to production of less volatile species via $\text{RO}_2 + \text{hydroperoxide radical (HO}_2\text{)}$ reactions (Ng et al., 2007; Song et al., 2007). Therefore, models/mechanisms developed only from chamber experiments performed at high NO_x may not

be applicable to areas where the NO_x level is significantly lower than those used in chamber experiments (Carter et al., 2005).

1.2. Previous NO_x - Aromatic Simulation Studies

Previous zero-dimensional models have incorporated sophisticated mechanisms for NO_x -aromatic chemistry. Johnson et al. (2004; 2005) utilized the fully explicit gas-phase Master Chemical Mechanism (MCM) coupled to a gas/aerosol equilibrium model to simulate aromatic hydrocarbon SOA formation under both low- and high- NO_x conditions successfully after scaling absorptive partitioning coefficients. These studies strongly suggest association of reactive aldehydes species is probable in the aerosol phase for toluene and imply the important role of organic hydroperoxides in SOA formation. However, the fully explicit model has high computational demand, which is not suitable for incorporation into three-dimensional (3D) air quality models for simulation of ambient organic aerosol concentrations. Furthermore, the same species required estimated partitioning coefficients values that depended on NO_x levels, implying that the model did not capture fully the NO_x -related chemistry. This phenomenon is also a limitation for application of this model in 3D simulations.

Hu et al. (2007) adopted a kinetic model to simulate SOA formation from photooxidation of toluene over a range of toluene to NO_x ratios by setting the ratio of rate constants of condensation and evaporation equal to the gas-particle partitioning coefficient. This study theorized that the contribution of organic nitrates to the aerosol phase increases and that the contribution of total oligomers formed by glyoxal/methyl-glyoxal and organic peroxides

decreases with increasing NO_x . Speciation of simulated aerosol shows oligomers and polymers contribute $\sim 70\%$ of the aerosol mass.

An additional approach has been to modify the newly developed SAPRC-11 gas-phase mechanism to predict SOA formation from aromatic photo-oxidation and explore the role of NO_x in SOA formation (Carter et al., 2012). The aromatic SOA mechanism developed in this work lumps the various reaction routes and reactive products formed into a limited number of reactions and model species. The same kinetic approach as adopted by Hu et al. (2007) to calculate rates of condensation of gas-phase species onto existing particles is used by Carter et al. (2012). Yields and partitioning parameters of SOA model species were adjusted to fit the available data while minimizing bias (Carter et al., 2012).

1.3. Purpose of the study

This study aims to update aromatic-SOA chemistry within the Caltech Atmospheric Chemistry Mechanism (CACM) (Griffin et al., 2002) to allow for detailed composition information without overly burdensome computational demand. The approach here lies between the non-specific mechanisms used by Carter et al. (2012) and the fully explicit approach used by Johnson et al. (2004; 2005) as an intermediate approach in terms of treatment of gas phase reactions. The primary goals of this paper are to: 1. Update gas-phase oxidation mechanisms for toluene and *m*-xylene (as representative predominant aromatic hydrocarbons) under the framework of the gas-phase CACM; 2. Simulate SOA formation for toluene and *m*-xylene by coupling CACM output to a gas-particle partitioning model based on product molecular property predictions; 3. Validate both the gas-phase and gas-partitioning models using experimental data under both low- (less

than 1 ppb) and high- NO_x ($\sim 10 < \text{NO}_x < \sim 100$ ppb) conditions; and 4. Investigate the impact of NO_x level on aromatic SOA formation both quantitatively and chemically. The preliminary version of the toluene oxidation mechanism is described by Liu (2012).

Experimental Description

The models developed in this thesis were evaluated using chamber experiments performed by collaborators. Both toluene and *m*-xylene experiments were conducted in the well-characterized environmental chamber at the University of California - Riverside that was designed specifically for O₃ and organic aerosol chemistry evaluation at low hydrocarbon and NO_x concentrations under well-controlled conditions (Carter et al., 2005). The enclosure is flushed continually with purified air supplied by an Aadco (Cleves, OH) 737 series air purification system at flow rates up to 1500 liters min⁻¹. The air is further purified by supplementing the Aadco 737 with cartridges filled with Hopcalite type catalyst, Purafil[®], and secondary HEPA filtration. All experiments were carried out without seeding and under dry conditions (dew point <-40°C). The experiments with high NO_x were conducted at various initial aromatic and NO_x levels, while irradiations with limited NO_x were carried out with varying initial aromatic and hydrogen peroxide (H₂O₂, as a radical source) levels.

Ozone, NO, and total reactive nitrogen (NO_y) were monitored continuously (every minute) using commercial instruments. Toluene and *m*-xylene were analyzed approximately every 40 minutes by gas chromatography with a flame ionization detector. A scanning mobility particle sizer was utilized to monitor particle size distribution and calculate particle volume concentration. A constant density of 1.4 g/cm^3 (Nakao et al., 2013) was adopted to convert particle volume concentration to particle mass concentration. Particle mass concentrations were corrected for wall loss assuming first order wall-loss kinetics (Cocker et al., 2001). More detailed experimental information is available in Carter et al. (2012).

The initial conditions for all simulated experiments are shown in Table 2.1. Experiments were chosen for simulation based on the following criteria: an initial aromatic mixing ratio below 0.15 ppm, a maximum initial NO_x mixing ratio of 0.1 ppm, and an approximate maximum initial H_2O_2 mixing ratio of 2.0 ppm.

<i>m</i> -xylene- H_2O_2					
Expr.	Average Temperature (K)	HC (ppm)	H_2O_2 (ppm)	SOA Yield	SOA ($\mu\text{g}/\text{m}^3$)
1134B	299.6	0.078	1.01	32.9%	99.9
1212A	298.4	0.114	2.00	29.1%	137
1212B	298.4	0.052	2.03	31.6%	72.3
1470A	297.3	0.089	1.00	38.4%	157
1472B	297.0	0.100	1.00	24.0%	111
<i>m</i> -xylene- NO_x					
Expr.	Average Temperature (K)	HC (ppm)	NO (ppm)	SOA Yield	SOA ($\mu\text{g}/\text{m}^3$)
1175A	297.7	0.085	0.0514	6.7%	23.4
1192A	297.7	0.077	0.0419	4.9%	15.0
1516A	297.5	0.095	0.026	14.5%	47.3
1530A	296.7	0.120	0.012	11.4%	35.9
<i>toluene</i> - H_2O_2					
Expr.	Average Temperature (K)	HC (ppm)	H_2O_2 (ppm)	SOA Yield	SOA ($\mu\text{g}/\text{m}^3$)
1141B	298.2	0.085	1.50	16.3%	21.2
1251B	298.2	0.084	1.01	14.9%	17.6
1266A	298.2	0.104	1.01	21.5%	17.3
1477A	297.3	0.115	1.02	48.7%	61.2
<i>toluene</i> - NO_x					
Expr.	Average Temperature (K)	HC (ppm)	NO (ppm)	SOA Yield	SOA ($\mu\text{g}/\text{m}^3$)
1499B	296.7	0.070	0.046	13.3%	37.6
1500A	296.9	0.104	0.045	44.4%	146.0
1500B	296.9	0.104	0.045	39.0%	117.0
1501B	296.9	0.101	0.043	38.9%	128.0
1504B	296.8	0.150	0.060	15.0%	73.0
1509A	296.8	0.099	0.043	41.7%	133.0
1509B	296.8	0.099	0.043	48.9%	156.0

‘HC’ refers to initial hydrocarbon concentration. ‘SOA’ refers to final SOA mass concentration (corrected for wall loss). ‘Yield’ refers to the SOA yield at the end of measurement and is calculated by $\text{Yield} = \text{SOA}/\Delta\text{HC}_{\text{mass}}$. Only experiments with valid final hydrocarbon and SOA concentration data at the same time point are used.

Table 2.1 Summary of initial conditions and relevant data for all experiments simulated

Mechanism Development

3.1. Gas-phase Chemistry

New gas-phase chemistry of *m*-xylene and toluene was incorporated into CACM, which previously included more than 200 species and 360 reactions (Chen and Griffin, 2005). In this paper, the gas-phase chemistry schemes were constructed from previous experimental and theoretical studies of benzene, toluene and *m*-xylene systems (Gery et al., 1987; Atkinson et al., 1991; Andino et al., 1996; Klotz et al., 2002; Jenkin et al., 2003; Suh et al., 2003; Hu et al., 2007). Available experimental or theoretical rate constants and branching ratio information from literature were incorporated into CACM. Where rate constant and branching ratio information for a specific species was not available, values for other better-characterized systems were taken. Where no appropriate kinetic value could be found, a structure-activity relationship technique was applied (Kwok and Atkinson, 1995).

Atmospheric oxidation of aromatic hydrocarbons begins mainly through reaction with hydroxyl radical (OH). All the reactions incorporated in this model can be found in Table 3.1 (*m*-xylene) and Table 3.2 (toluene), along with rate constants and branching ratios. Gas-phase mechanism development of *m*-xylene is described in detail in the next four paragraphs. The treatment of toluene photooxidation follows a scheme very similar to that of *m*-xylene, simply with one less methyl group and with appropriately different rate constants and stoichiometric yields.

A simplified scheme of *m*-xylene oxidation by OH is shown in Figure 3.1. Note that only the formation pathways of the first generation products are shown in this scheme. The first step in the scheme is OH-addition to the aromatic ring forming an OH-adduct (RAD31, 96%) and H-abstraction from a C-H bond of the methyl substituent forming a RO₂ (RO291, 4%) (Calvert et al., 2002). RO291 is then treated as described in Jenkin et al. (2003) by reacting with NO, NO₃, HO₂ and RO₂T, forming carbonyl, hydroperoxide, and alcohol products. *m*-Tolualdehyde (RP25) is the most abundant among these products. In the OH-addition route, OH radical mainly adds to the 2- and 4-positions (Andino et al., 1996). RAD31 represents the hydroxycyclohexadienyl radical with attack at the 2- or 4- position; it reacts with O₂ or NO₂. Addition of NO₂ to the adduct forms mainly dimethylphenols and dimethylnitrobenzenes (DMP1, UR71, and their isomers) (Klotz et al., 2002; Koch et al., 2007). The reaction with O₂ is the major pathway for RAD31 under ambient conditions, either by addition to form aromatic peroxy radical RO292 (82%) or by H-abstraction to form DMP1 or its isomer (18%) (Jenkin et al., 2003; Koch et al., 2007). The route to form dimethylphenol is named the “phenolic route.” RO292 either reacts with NO to form 2,4-dimethyl-2,4-hexadienedial (RP93) and its isomers or undergoes unimolecular rearrangement to form bicyclic radicals such as RAD38 and its isomers (Andino et

al., 1996; Lay et al., 1996; Bohn and Zetzsch, 1999). Upon reaction of RAD38 with O₂, C8-unsaturated epoxy dicarbonyls (R102, 37%) and peroxide bicyclic radical (RO299, 63%) are formed (Kwok et al., 1997; Bohn and Zetzsch, 1999). Peroxide bicyclic radical RO299 then reacts with HO₂ or RO₂T to form ring-retaining hydroperoxide (RP94), carbonyl (RP95), and alcohol (RP96) products. Under high NO_x levels, reaction of RO299 with NO becomes dominant over reaction with RO₂T and HO₂, with the formation of nitrate AP41 (14%) or bicyclic oxy radical RAD32. The bicyclic oxy radical then undergoes β-scission, leading to formation of methyl-glyoxal, glyoxal and their co-products, 1,4-unsaturated dicarbonyls (shown as RP37, RP38, and RP97 in Table 3.3). These unsaturated dicarbonyls also rearrange to form cyclic products such as methylfuranone (shown as UR72 in Table 3.3) (Smith et al., 1999; Wagner et al., 2003).

Further photooxidation reactions of phenolic compounds 2,6- and 2,4- dimethylphenol (DMP1 and DMP2) also were incorporated in detail into CACM. Figure 3.2 shows the oxidation mechanism for DMP1. DMP2 follows a similar mechanism, with the reactions listed in Table 3.2. These chemistry schemes are adapted mainly from Olariu (2001), Thüner et al. (2004) and Jørgensen (2012). The main atmospheric sinks for phenolic compounds are oxidation by OH and NO₃ radical. If reaction of phenolic compound DMP1 is initiated by NO₃ radical, only the H-abstraction reaction is expected to occur, leading to dimethylnitrophenol products (RPR4). If DMP1 reacts with OH, both H-abstraction and OH-addition routes are possible (Jørgensen, 2012). Dimethylnitrophenol (RPR4) is formed through the H-abstraction route, while dimethylbenzoquinone (UR73) and dihydroxy-dimethylbenzene (RP98) are formed through the OH-addition route. RP98 proceeds to react with OH radical to form radical RAD34, to which NO₂

adds to form UR77 (Olariu, 2001). Since ring-opening products account for only a small fraction in the phenolic compounds photooxidation system (Olariu, 2001), they were not described in this work.

Because unsaturated dicarbonyls (such as RP93) compose an important fraction of the products in aromatic oxidation systems, further reactions of these first generation products were incorporated into CACM. These reactions were mostly adapted from MCM, with a number of simplifications applied to reduce computational demand. Only reactions initiated by OH, NO₃ and photolysis are included in this model. Only reactions with NO and NO₂ are incorporated into the further reaction steps. Further reactions of C8-unsaturated epoxy dicarbonyls (R102) also were treated with simplifications. For the purpose of modeling SOA, R102 is oxidized by OH to form an acid species and one molecule of O₃, with an aldehyde group being directly converted to an acid group, similar to the treatment used in previous studies utilizing CACM as the gas-phase model (Griffin et al., 2002; Chen and Griffin, 2005).

Chemical reaction scheme showing the degradation pathways of DMP1 (2,4-dimethylphenol) initiated by OH radicals.

DMP1 reacts with OH to form a resonance-stabilized radical intermediate.

The radical intermediate can follow several pathways:

- Reaction with NO_3 leads to RAD33 (2,4-dimethylphenoxyl radical).
- Reaction with NO_2 leads to RPR4 (2,4-dimethyl-4-nitrophenol).
- Reaction with NO leads to RP98 (2,4-dimethylcatechol).
- Reaction with OH leads to RAD34 (2,4-dimethylphenoxyl radical).
- Reaction with NO_2 leads to UR77 (2,4-dimethyl-2,6-dinitrophenol).
- Reaction with NO and NO_2 leads to a cyclic intermediate, which then reacts with O_2 and HO_2 to form UR73 (2,4-dimethyl-2,6-dione).

Figure 3.2. Photooxidation of 2,6-dimethyl-phenol by OH and NO₃.

Table 3.1. Oxidation mechanism for *m*-xylene (k_i refers to rate constant of reaction *i*).

Num	Reactants	Products	Rate Constants($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Ref
493	MXYL+OH	$0.04 \cdot \text{RO291} + 0.04 \cdot \text{H2O} + 0.96 \cdot \text{RAD31} + 0.04 \cdot \text{RO2T}$	$2.31\text{E-}11$	1
494	MXYL+NO ₃	RO291+RO2T	$2.60\text{E-}16$	1
495	RO291+RO2T	$0.2 \cdot \text{RP91} + 0.8 \cdot \text{RP25} + 0.75 \text{HO}_2 + \text{RO2T}$	$1.21\text{E-}12$	2
496	RO291+NO	RP25+HO ₂ +NO ₂	$2.54\text{E-}12 \cdot \text{EXP}(360/\text{T})$	3
497	RO291+NO ₃	RP25+HO ₂ +NO ₂	$2.30\text{E-}12$	4
498	RO291+HO ₂	RP92	$1.5\text{E-}13 \cdot \text{EXP}(1310/\text{T})$	4
499	RP91+OH	RP25+HO ₂ +NO ₂	$2.70\text{E-}12$	4
500	RP92+OH	RP25+OH	$4.5\text{E-}18 \cdot \text{T}^{-2} \cdot \text{EXP}(887/\text{T})$	3,5
501	RP92+HV	RP25+OH+HO ₂	J(CH ₃ OOH)	3, a
502	RAD31+NO ₂	$0.2 \cdot (0.5 \cdot \text{UR71} + 0.5 \cdot \text{H2O} + 0.5 \cdot \text{RPR4}) + 0.8 \cdot (0.62 \cdot \text{DMP1} + 0.38 \cdot \text{DMP2} + \text{HONO})$	$3.50\text{E-}11$	6
503	RAD31+(O ₂)	$0.18 \cdot (0.62 \cdot \text{DMP1} + 0.38 \cdot \text{DMP2} + \text{HO}_2) + 0.82 \cdot (\text{RO292} + \text{RO2T})$	$3.78\text{E-}11$	6, b
504	RO292+NO	RP93+NO ₂ +HO ₂	$1.10\text{E-}11$	7
505	RO292	RAD38	$1.60\text{E+}42/\text{T}^{11.34} \cdot \text{EXP}(-9451/\text{T})$	15
506	RAD38+(O ₂)	$0.63 \cdot (\text{RO299} + \text{RO2T}) + 0.37 \cdot (\text{R102} + \text{HO}_2)$	$2.10\text{E-}12$	7, b
507	RO299+HO ₂	RP94	$2.91\text{E-}13 \cdot \text{EXP}(1300/\text{T})$	3

508	RO299+RO2T	$0.2*RP95+0.2*RP96+0.6*RAD32+RO2T$	1.06E-12	2
509	RO299+NO	$CF(150)*RAD32+CF(150)*NO_2+CF(151)*AP41$	$2.54E-12*EXP(360/T)$	3
510	RP94+HV	RAD32+OH	J(CH ₃ OOH)	3, a
511	RP94+OH	RP95	1.17E-10	8
512	RP96+OH	RP95+HO ₂	2.50E-10	8
513	RP95+OH	RO295+MGLY+RO2T	7.93E-11	8
514	RO299+NO	$0.862*(RAD32+NO_2)+0.138*AP41$	$2.54E-12*EXP(360/T)$	3
515	RAD32+(O ₂)	$0.78*MGLY+0.26*(RP38+RP37+UR72)+0.22*RP35+0.11*(UR72+RP97)+HO_2$	1.00E+06	b
516	AP41+OH	RP95+NO ₂	7.15E-11	8
517	DMP1+OH	$0.92*(0.085*(UR73+HO_2+NO_2-NO)+0.915*RP98+0.915*HO_2)+0.08*RAD33$	6.75E-11	9
518	DMP1+NO ₃	RAD33+HNO ₃	5.01E-11	9
519	DMP2+OH	$0.92*(RP98+HO_2)+0.08*RAD33$	6.75E-11	9
520	DMP2+NO ₃	RAD33+HNO ₃	5.01E-11	9
521	RAD33+NO ₂	RPR4	2.08D-12	10
522	RP98+OH	RAD34	2.05E-11	14
523	RAD34+NO ₂	UR77	2.08D-12	10
524	RP97+OH	$0.5*RO297+0.5*RO298+RO2T$	7.00E-11	8
525	RP97+NO ₃	RO297+HNO ₃ +RO2T	$4.25*1.4E-12*EXP(-1860/T)$	8

526	RO297+NO	RAD37+NO ₂	$2.54\text{E-}12*\text{EXP}(360/T)$	3
527	RO297+NO ₂	PN12	k_{126}	
528	PN12	RO297+NO ₂ +RO2T	k_{127}	
529	RO297+HO ₂	$0.44*(\text{RAD37}+\text{OH})+0.56*\text{R101}+0.56*\text{O}_3$	$5.20\text{E-}13*\text{EXP}(980/T)$	12
530	RAD37	$0.35*\text{MGLY}+0.35*\text{RO28}+0.65*(\text{UR75}+\text{RO21})+\text{RO2T}$	$1.00\text{E}+06$	b
531	R101+OH	RO297+RO2T	$3.90\text{E-}11$	8
532	R101+HV	RAD37+OH	$J(\text{CH}_3\text{OOH})$	a
533	RO298+NO	$2*\text{MGLY}+\text{HO}_2+\text{NO}_2$	$2.54\text{E-}12*\text{EXP}(360/T)$	3
534	RP97+HV	$0.6*(\text{RO297}+\text{HO}_2+\text{RO2T})+0.4*\text{UR73}$	$2.8\text{E-}2*J(\text{NO}_2)$	3
535	RP93+OH	$0.381*\text{RP38}+0.619*\text{RP37}+\text{MGLY}+\text{HO}_2+\text{NO}_2-\text{NO}$	$7.50\text{E-}11$	13
536	R102+OH	$\text{O}_3-\text{HO}_2+\text{UR76}$	$2.12\text{E-}18*T^{-2}*\text{EXP}(-51/T)$	5

Table 3.2. Oxidation mechanism for toluene (k_i refers to rate constant of reaction i).

Num	Reactants	Products	Rate Constants ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Ref
401	TOLU+OH	$0.07*\text{RAD9}+0.93*\text{RAD10}$	$1.8\text{E-}12*\text{EXP}(338/T)$	1
402	RAD9+(O ₂)	RO275+ROT2	$1.00\text{E}+06$	b
403	RO275+RO2T	$0.2*\text{RP24}+0.8*\text{RP25}+0.6*\text{HO}_2+\text{RO2T}$	$1.21\text{E-}12$	2

404	RO275+NO	RP25 + HO ₂ + NO ₂	2.54E-12*EXP(360/T)	3
405	RO275+HO ₂	RP26	1.5E-13*EXP(1310/T)	4
406	RO275+NO ₃	RP25 + HO ₂ + NO ₂	2.30E-12	4
407	RP24 +OH	RP25 + HO ₂	2.70E-12	4
408	RP26 + OH	RP25 + OH	4.5E-18*T ² *EXP(887/T)	3, 5
409	RP26 + HV	RP25 + OH +HO ₂	J(CH ₃ OOH)	3,a
410	RAD10+NO ₂	0.2*(0.5*UR55+0.5*RP27)+0.8*(0.656*OCRE+0.172*MCRE+0.172*PCRE+HONO)	3.60E-11	6
411	RAD10+(O ₂)	0.194*(0.656*ORCE+0.172*MCRE+0.172*PCRE+HO ₂)+0.806*RO276+0.806*RO2T	1.18E-10	6, b
412	RO276+NO	RP28+NO ₂	1.10E-11	7
413	RO276	RAD15	1.60E+42/T ^{11.34} *EXP(-9451/T)	15
414	RAD15 +(O ₂)	0.867*(RO277+RO2T)+0.133*(RP33+HO ₂)	2.10E-12	7, b
415	RO277+HO ₂	RP29	2.91E-13*EXP(1300/T)	3
416	RO277+RO2T	0.2*RP30+0.2*RP31+0.6*RAD11+RO2T	1.06E-12	2
417	RO277+NO	0.889*(RAD11+NO ₂)+0.111*AP25	2.54E-12*EXP(360/T)	3
418	RP29+HV	RAD11 +OH	J(CH ₃ OOH)	3, a
419	RP29+OH	RP30	1.17E-10	8
420	RP31+OH	RP30	2.50E-10	8

421	RAD11+(O ₂)	0.6*RP35+0.2*RP38+0.2*RP37+0.2*UR72+0.4*MGLY+0.2*UR56+0.2*RP32+HO ₂	1.00E+06	b
422	AP25+OH	RP30 + NO ₂	7.15E-11	8
423	RP30 + OH	RO293 + RP35 + RO2T	7.99E-11	8
424	OCRE+OH	0.2*(RO278 + RO2T)+0.727*RP34+0.073*RAD12+0.8*HO ₂	4.10E-11	9
425	OCRE+NO ₃	RAD12+HNO ₃	1.40E-11	9
426	MCRE+OH	0.2*(RO278 + RO2T)+0.727*RP34+0.073*RAD12+0.8*HO ₂	6.80E-11	9
427	MCRE+NO ₃	RAD12+HNO ₃	1.10E-11	9
428	PCRE+OH	0.2*(RO278 + RO2T)+0.727*RP34+0.073*RAD12+0.8*HO ₂	5.00E-11	9
429	PCRE+NO ₃	RAD12+HNO ₃	1.10E-11	9
430	RAD12+NO ₂	RP27	2.08E-12	10
431	RO278+HO ₂	UR60	2.91E-13*EXP(1300/T)	3
432	RO278+NO	0.68*(UR74+RP35)+0.32*UR61+HO ₂	2.54E-12*EXP(360/T)	3
433	RP34 + OH	RAD13	1.96E-10	14
434	RAD13+NO ₂	UR57	2.08E-12	10
435	RP27+NO ₃	RAD16+HNO ₃	3.77E-12	11
436	RAD16+NO ₂	UR58	2.3E-11*EXP(151/T)	11

437	RP32+OH	$0.83 \cdot \text{RO279} + 0.83 \cdot \text{RO2T} + 0.17 \cdot \text{RO280}$	$5.20\text{E-}11$	3
438	RP32+NO ₃	$\text{RO279} + \text{RO2T} + \text{HNO}_3$	$5.6\text{E-}12 \cdot \text{EXP}(-1860/\text{T})$	8
439	RO279+NO	$\text{RAD14} + \text{NO}_2$	$2.54\text{E-}12 \cdot \text{EXP}(360/\text{T})$	3
440	RO279+NO ₂ +M	PN13	k_{126}	
441	PN13	$\text{RO279} + \text{NO}_2 + \text{RO2T}$	k_{127}	
442	RO279+HO ₂	$0.44 \cdot \text{RAD14} + 0.44 \cdot \text{OH} + 0.15 \cdot \text{UR59} + 0.15 \cdot \text{O}_3 + 0.41 \cdot \text{RP36}$	$5.20\text{E-}13 \cdot \text{EXP}(980/\text{T})$	12
443	RAD14	$0.4 \cdot \text{RP35} + 0.4 \cdot \text{CO} + 0.6 \cdot \text{UR24} + \text{HO}_2$	$1.00\text{E+}06$	b
444	RO280+NO	$2 \cdot \text{RP35} + \text{HO}_2 + \text{NO}_2$	$2.54\text{E-}12 \cdot \text{EXP}(360/\text{T})$	3
445	RP32+HV	$0.4 \cdot \text{UR56} + 0.6 \cdot (\text{RO279} + \text{RO2T} + \text{HO}_2)$	$2.8\text{E-}2 \cdot \text{J}(\text{NO}_2)$	3, a
446	RP36+OH	$\text{RO279} + \text{RO2T}$	$4.00\text{E-}11$	8
447	RP36+HV	$\text{RAD14} + \text{OH}$	$\text{J}(\text{CH}_3\text{OOH})$	a
448	RP28+OH	$\text{RP32} + \text{MGLY} + \text{HO}_2 + \text{NO}_2 - \text{NO}$	$7.50\text{E-}11$	13
449	RP33+OH	$\text{O}_3 - \text{HO}_2 + \text{UR62} + \text{H}_2\text{O}$	$2.12\text{E-}18 \cdot \text{T}^2 \cdot \text{EXP}(-51/\text{T})$	5
450	RP37+OH	$0.48 \cdot \text{RO293} + 0.52 \cdot \text{RO294} + \text{RO2T}$	$6.20\text{E-}11$	3,8
451	RP37+NO ₃	$\text{RO293} + \text{HNO}_3 + \text{RO2T}$	$2.75 \cdot 1.4\text{E-}12 \cdot \text{EXP}(-1860/\text{T})$	8
452	RO293+NO	$\text{RAD35} + \text{NO}_2$	$2.54\text{E-}12 \cdot \text{EXP}(360/\text{T})$	3
453	RO293+NO ₂ +M	PN11	k_{126}	
454	WALL + HV	HONO	$1.18\text{E-}5 \cdot 0.401$	11
455	RO293+HO ₂	$0.44 \cdot \text{RAD35} + 0.44 \cdot \text{OH} + 0.15 \cdot \text{UR74} + 0.15 \cdot \text{O}_3 + 0.41 \cdot \text{RP99}$	$5.20\text{E-}13 \cdot \text{EXP}(980/\text{T})$	12

456	RAD35	$0.83*(UR24+RO21+RO2T)+0.17*(MGLY+HO_2+CO)$	1.00E+06	b
457	RP99+OH	RO293+RO2T	3.60E-12	8
458	RP99+HV	RAD35+OH	J(CH ₃ OOH)	a
459	RO294+NO	MGLY+RP35+HO ₂ +NO ₂	$2.54E-12*EXP(360/T)$	3
460	RP37+HV	$0.6*(RO293+HO_2+RO2T)+0.4*UR72$	$2.8E-2*J(NO_2)$	3
461	RP38+OH	$0.77*RO295+0.23*RO296+RO2T$	4.40E-11	3,8
462	RP38+NO ₃	RO295+HNO ₃	$4.25*1.4E-12*EXP(-1860/T)$	16
463	RO295+NO	RAD36+NO ₂	$2.54E-12*EXP(360/T)$	3
464	RO295+NO ₂	PN11	k ₁₂₆	
465	PN11	$0.53*RO295+0.47*RO293+NO_2+RO2T$	k ₁₂₇	
466	RO295+HO ₂	$0.44*RAD36+0.485*(R100+O_3)+0.075UR82$	$5.20E-13*EXP(980/T)$	12
467	RAD36	$0.65*UR75+0.175*MGLY+0.825*HO_2+0.175*(RP35+RO21+RO2T)+0.35*CO$	1.00E+06	b
468	R100+OH	RO295+RO2T	4.73E-11	8
469	R100+HV	RAD36+OH	J(CH ₃ OOH)	a
470	RO296+NO	RP35+MGLY+HO ₂ +NO ₂	$2.54E-12*EXP(360/T)$	3
471	RP38+HV	$0.6RO295+0.4UR72+0.6*RO2T$	$2.8E-2*J(NO_2)$	3
472	Wall	HCHO	$1.0E-5*0.401$	11

473	O ₃	Loss	1.08E-4	11
474	RP25 + OH	RO281 + RO2T	5.9E-12*EXP(225/T)	8
475	RP25 + NO ₃	RO281 + RO2T + HNO ₃	2.40E-15	8
476	RO281 + HO ₂	0.41*UR63 + 0.44*(RO282 + RO2T + OH) + 0.15*UR64	5.2E-13*EXP(980/T)	8
477	RO281 + NO	RO282 + RO2T + NO ₂	7.5E-12*EXP(290/T)	8
478	RO282 + HO ₂	UR65	2.91E-13*EXP(1300/T)*0.77	8
479	RO282 + NO	RAD17 + NO ₂	2.7E-12*EXP(360/T)	8
480	RAD17 + NO ₂	UR66	k ₄₃₄	8
481	RAD17 + O ₃	RO282 + RO2T	2.86E-13	8
482	RP35 + OH	0.6*(2*CO+HO ₂)+0.4*(RO283+RO2T)	3.1E-12*EXP(340/T)	8
483	RO283+HO ₂	0.15*UR68+0.41*UR69+0.44*(HO ₂ +CO +CO ₂ +OH)	k ₄₇₆	8
484	RO283+NO ₂	PN14	k ₁₂₆	
485	PN14	RO283 + NO ₂ + RO2T	k ₁₂₇	
486	RP35 + HV	2*(CO + HO ₂)	0.01258*J(NO ₂)	11
487	RP35 + HV	HCHO + CO	0.00466*J(NO ₂)	11

Notes for Tables 3.1 and 3.2:

^aJ(CH₃OOH) refers to the photolysis rate of methyl-hydroperoxide (CH₃OOH) and J(NO₂) refers to the photolysis rate of NO₂. ^bOxygen concentration was already incorporated into rate constants. Rate constant references: 1. Calvert et al. (2002); 2. Jenkin et al. (1997); 3. Saunders et al. (2003); 4. IUPAC recommended, <http://www.iupac-kinetic.ch.cam.ac.uk/> 5. Kwok and Atkinson, (1995); 6. Koch et al. (2007); 7. Bohn and Zetzsch (1999); 8. MCM version 3.2, <http://mcm.leeds.ac.uk/MCM/>; 9.

Thüner et al. (2004); 10. Platz et al. (1998); 11. SAPRC-07, <http://www.engr.ucr.edu/~carter/SAPRC/>; 12. Jenkin et al. (2007); 13. Klotz et al. (1999); 14. Atkinson et al. (2006); 15. Lay et al. (1996); 16. Olariu (2001).

Table 3.3. Chemical species in the aromatic oxidation mechanism.

Label	Structure	Name/Description	Label	Structure	Name/Description
TOLU		toluene	UR74		4-oxopent-2-enoic acid
OCRE		<i>o</i> -cresol	UR75		3-methylfuran-2,5-dione
MCRE		<i>m</i> -cresol	AP25		nitrate species from RO ₂ 77 and NO reaction
PCRE		<i>p</i> -cresol	PN11		peroxy acyl nitrate species from RP37 and RP38 oxidation

RP35	CHO-CHO	glyoxal	PN13		peroxy acyl nitrate species from RP32 oxidation
RP24		phenylmethanol	PN14		peroxy acyl nitrate species from glyoxal oxidation
RP25		benzaldehyde	UR63		benzoperoxoic acid
RP26		1-(hydroperoxymethyl)-benzene	UR64		benzoic acid
RP27		2-methyl-6-nitrophenol	UR65		hydroperoxybenzene
RP28		ring opening species from OH addition reaction	UR66		2-nitrophenol

RP29		hydroperoxide species from peroxide-bicyclic route	UR67		2-hydroperoxy-3-methylphenol
RP30		ketone species from peroxide-bicyclic route	UR68		acid species from oxidation of glyoxal
RP31		hydroxy species from peroxide-bicyclic route	UR69		peroxy acid species from oxidation of glyoxal
RP32		butenedial	MXYL		<i>m</i> -xylene
RP33		epoxydicarbonylenes from epoxy-oxy route	DMP1		2,6-dimethylphenol
RP34		methylbenzene-1,2-diol	DMP2		2,4-dimethylphenol

RP36		peroxide acid species from oxidation of butenedial	RP91		<i>m</i> -tolylmethanol
RP37		4-oxo-2-pentenal	RP92		1-(hydroperoxymethyl)- 3-methylbenzene
RP38		2-methylfumarylaldehyde	RP93		2,4-dimethylhexa- 2,4-dienal
RP99		peroxy acid species from H abstraction route of RP37	RP94		hydroperoxide species from peroxide-bicyclic route
R100		peroxy acid species from H abstraction route of RP38	RP95		ketone species from peroxide-bicyclic route
UR71		1,3-dimethyl-5- nitrobenzene	RP96		hydroxy species from peroxide-bicyclic route

UR24		furan-2,5-dione	RP97		2-methyl-4-oxopentenal
UR55		1-methyl-3-nitrobenzene	RP98		2,6-dimethylbenzene-1,4-diol
UR56		furan-2(5H)-one	R101		peroxy acid species from H abstraction route of RP97
UR57		3-methyl-6-nitrobenzene-1,2-diol	R102		epoxydicarbonylenes from epoxy-oxy route
UR58		2-methyl-4,6-dinitrophenol	UR73		dimethyl-1,4-benzoquinone

UR59		acid species from oxidation of butenedial	UR76		acid species from H abstraction from aldehyde group in R102
UR60		hydroperoxide species from peroxide-bicyclic route for cresols	UR77		3,5-dimethyl-2-nitrobenzene-1,4-diol
UR61		methyl-benzoquinone	AP41		nitrate species from RO ₂ 93 and NO reaction
UR62		acid species from H abstraction from aldehyde group in RP33	PN12		peroxy acyl nitrate species from RP97 oxidation
UR72		3-methylfuran-2(5H)-one			

3.2. Wall reaction and Photolysis

A wall reaction is incorporated into the gas-phase mechanism as a source of HONO in the chamber:

The wall reaction rate is based on the chamber characterization information utilized to develop the most recent version of SAPRC model (Carter et al., 2012). This reaction will not be included in 3D applications of these models.

To minimize variability caused by different conditions in different experiments, only experiments employing the same light source (“BL2”) are used. Information regarding the light source can be found in Carter et al. (2012). A value 0.802 for UVFAC (photolysis parameter in CACM) is derived based on light intensity in the chamber (where value of 1 for UVFAC refers to clear sky at the top of boundary layer at noon in Los Angeles summer). Furthermore, photolysis rates for 16 species were updated based on values adopted by SAPRC. These chamber-specific rates will not be used in the 3D applications as well.

3.2. Equilibrium Absorptive Model

An equilibrium gas/particle partitioning model first developed by Colville and Griffin (2004) is linked to CACM to calculate SOA formation. Since particle-phase water is excluded in the simulated chamber system, only the partitioning of secondary products between gas and condensed organic phases is necessary. Condensed organic material (om) is assumed to be liquid and capable of absorbing gas-phase organic molecules. The equilibrium partitioning coefficient $K_{om,i}$ ($\text{m}^3\mu\text{g}^{-1}$) for an individual compound i is described by (Pankow, 1994):

$$K_{om,i} = \frac{RT}{MW_{om} 10^6 \gamma_i P_{L,i}^\circ} = \frac{A_i}{G_i M_o} \quad (2)$$

where R is the ideal gas constant ($8.206 \times 10^{-5} \text{m}^3 \text{atm mol}^{-1} \text{K}^{-1}$), T is temperature (K), MW_{om} is the average molecular weight of the organic phase (g mol^{-1}), γ_i is the activity coefficient of compound i , and $p_{L,i}^\circ$ is the sub-cooled liquid vapor pressure (atm) of compound i at temperature T . The factor of 10^6 is used to convert grams to micrograms. A_i ($\mu\text{g m}^{-3}$) and G_i ($\mu\text{g m}^{-3}$) are the aerosol- and gas-phase concentrations of compound i , respectively, while M_o ($\mu\text{g m}^{-3}$) is the total aerosol-phase organic mass concentration (including primary organic aerosol, or POA, if present).

Based on mass balance and lack of POA in chamber experiments, M_o can be found from (Colville and Griffin, 2004)

$$\sum_{i=1}^N \frac{K_{om,i} G_i}{1 + K_{om,i} M_o} = 1 \quad (3)$$

where C_i is the total concentration ($\mu\text{g m}^{-3}$) of the compound i and N is the total number of compounds present in the aerosol phase.

Given the temperature and the total concentration of each partitioning compound predicted using the gas- phase model, the iteration method to calculate SOA is performed as follows: In Equation (2), unit activity coefficients are assumed (Seinfeld and Pankow, 2003). If an initial value of MW_{om} is assumed for a specified temperature, the partitioning coefficient of each species can be estimated using Equation (2) if vapor pressure information is available. The total concentrations from CACM output at each time step are used in conjunction with these values to estimate M_o using Equation (3). The second part of Equation (2) combined with a mass balance allows for estimation of each A_i , which together will allow for an updated value of MW_{om} . In this way, MW_{om} is the variable upon which iteration is performed. When the iteration performance criterion is met, the result is the phase distribution of each individual species as well as the total concentration of SOA formed.

It is necessary to estimate sub-cooled liquid vapor pressures of compounds when data are unavailable experimentally. The group contribution method of Nannoolal et al. (2004), a refinement of the approach of Cordes and Rarey (2002), is used in this study to estimate the boiling points of organic species because it yields more accurate predictions compared to other methods (Clegg et al., 2008). The method of Myrdal and Yalkowsky (1997) is then employed to estimate the sub-cooled liquid vapor pressure. This approach is used for consistency with previous CACM-based SOA modeling (Colville and Griffin, 2004; Chen and Griffin, 2005; Jordan et al., 2008).

Implementing estimated sub-cooled vapor pressures in the model described above leads to a

strong underestimation of SOA concentration. Thus, correction factors were applied to estimated sub-cooled vapor pressures of major oxidation products in the toluene and *m*-xylene photooxidation systems to better fit with the experimental SOA formation temporal profile, as has been done previously (Colville and Griffin, 2004; Chen and Griffin, 2005; Jordan et al., 2008). The necessity of applying correction factors could be due to inaccuracy in estimating vapor pressures or a lack of association chemistry in the model. Correction factors were determined based on four experimental base cases (1141B, 1500A, 1134B and 1516A), representing four simulation conditions: toluene-H₂O₂, toluene-NO_x, *m*-xylene-H₂O₂, and *m*-xylene-NO_x. Factors were then used in other experiments listed in Table 1. Only one set of correction factors is employed to simulate both high- and low-NO_x situations for an individual aromatic so that NO_x-independent partitioning coefficients are developed. In addition, for the purpose of developing a unique model incorporating toluene and *m*-xylene systems for application in 3D air pollution episodes, the same correction factors were applied to the shared oxidation products between these two systems. This represents a significant improvement over previous modeling efforts.

Using the toluene system as an example, adjustment of sub-cooled vapor pressure is applied mainly to three major categories of oxidation products: ring-retaining products from oxidation of phenolic compounds (UR57 and UR58), ring-retaining products from “peroxide-bicyclic” route, and ring-opening products from “peroxide-bicyclic” route. Correction factors of 0.0012, 0.0006 and 0.0006 were applied to these three categories, respectively, while temperature dependence of the vapor pressures from the estimation method is retained. Similarly, correction factors in the *m*-xylene oxidation system follow the same pattern, but specific values are different between the systems. Correction factors employed in *m*-xylene system lie in the range of 0.0006 to 0.2.

Applying smaller correction factors (0.0006) for 1,4-unsaturated dicarbonyls (RP37, RP38 and RP97 in both systems) than for phenols (0.0012 for UR58 in the toluene system, 0.2 for UR77 in the *m*-xylene system) is consistent with the observation from Jang and Kamens (2001) that partitioning coefficients of aldehydes are larger and deviated more from predicted values than those for phenols, suggesting polymerization of volatile low-MW aldehydes (with carbon number smaller than five) or heterogeneous reactions between volatile aldehydes and high-MW compounds already in the aerosol phase (Johnson et al., 2004).

Chapter 4

Results

4.1. Gas-phase Chemistry simulations

The toluene and *m*-xylene mechanisms developed here describe gas-phase species concentration profiles reasonably for aromatic-H₂O₂ situations. Sample simulation output of aromatic and O₃ temporal profiles for experiment EPA 1141B (toluene- H₂O₂) and EPA 1212B (*m*-xylene- H₂O₂) are shown in Fig. 4.1(a) and (b). The fact that “measured” NO₂ is estimated by taking the difference between NO_y and NO instead of being measured directly combined with the low NO_x levels (under 1 ppb) in the aromatic-H₂O₂ experiments cause large uncertainties in NO and NO₂ measurement (Dodge, 2000). For low-NO_x experiments, strong fluctuation is observed for measured NO and NO₂ concentration profiles; thus, NO and NO₂ concentration profiles are not shown in these experiments.

For *m*-xylene-H₂O₂ simulations, excellent agreement between predicted and observed *m*-xylene is achieved, though the model simulation yields slightly more O₃ than measured, especially later

in the experiment. Excellent agreement of O_3 formation and aromatic decay between modeled and measured data for toluene- H_2O_2 runs are achieved. The fact that the discrepancy in O_3 simulation for *m*-xylene- H_2O_2 runs is bigger than that in toluene- H_2O_2 runs likely results from assuming that *m*-xylene chemistry is analogous to benzene or toluene when insufficient information is available. These results suggest that the mechanisms can describe the main characteristics of aromatic photooxidation chemistry under low- NO_x conditions adequately.

For high- NO_x experiments, both *m*-xylene and toluene mechanisms underestimate oxidation reactivity and OH levels due to underestimation of radical sources, as reported in other aromatic modeling studies (Wagner et al., 2003; Johnson et al., 2004; Hu et al., 2007). Light intensity is increased by 0.5-fold to achieve agreement between measured and modeled aromatic profiles, so that a qualitative foundation for SOA calculations is built. All 16 photolysis rates were increased except that of for H_2O_2 so that modeled aromatic decay profiles are fit to experimental data in both high- and low- NO_x simulations.

To validate the approach in fitting aromatic decay profiles taken in this study, a comparison study between this light intensity adjustment approach and the OH adjustment approach adopted by Carter et al. (2012) is carried out in Figure 4.2 (runs EPA 1509A (toluene) and EPA 1516A (*m*-xylene) under high- NO_x conditions). Time profiles of OH levels are adjusted specifically for different runs in OH adjustment approach. To achieve a unified model non-specific to different runs to make it more convenient to carry out different runs under various conditions and interpolate to conditions not represented in simulated experiments, the approach of altering light intensity is adopted over the OH adjustment approach. In OH adjustment approach, OH concentration at each time point with experimental aromatic mixing ratio is calculated by

assuming that OH concentration remains constant between two neighboring time points. The OH concentration can be calculated with the measured aromatic data and the appropriate reaction rate constant. The example for toluene shows a very good match between these two approaches. The approach of increasing light intensity predicts slightly slower *m*-xylene decay than the method of OH adjustment. The relative agreement supports the approach of altering light intensity.

Sample simulations with output of aromatic hydrocarbons, NO_x , and O_3 temporal profiles for EPA1509A (toluene) and EPA1516A (*m*-xylene) are shown in Fig. 4.1. (c) and (d). The profile of NO being converted to NO_2 is predicted well by this model. A more rapid decrease of NO_2 is predicted by the model compared to the experiments, likely due to estimation of NO_2 as $\text{NO}_y - \text{NO}$ instead of use of direct NO_2 measurement. Simulated $\text{NO}_y - \text{NO}$ is also plotted in Fig. 4.1. (c) and (d) for comparison with measured NO_2 .

Figure 4.1. Observed (points) and predicted (lines) mixing ratios of NO (blue square), NO₂ (pink open triangles), O₃ (green filled triangles) and aromatic hydrocarbons (red dots) for photooxidation experiments EPA1141B, EPA1212B, EPA1509A and EPA1516A. The dashed pink line represent predicted mixing ratio of NO_y-NO.

Figure 4.2. Aromatic decay profiles and SOA formation profiles from experiment data, original model prediction, OH adjusted model prediction and light adjusted model prediction for EPA 1509A (toluene) and EPA 1516A (*m*-xylene) respectively.

4.2. SOA Simulations

All chamber experiments shown in Table 2.1 are simulated using the updated CACM and partitioning module. Information regarding observed SOA formation yield and final SOA mass concentration also is available in Table 2.1.

Comparison of observed and predicted final SOA concentration for all *m*-xylene and toluene experiments simulated is shown in Fig. 4.3. Sensitivities to varying partitioning coefficients are shown in the form of ‘error bars’ in the figure. For *m*-xylene, the model can predict final SOA concentration precisely when aerosol loading exceeds $40 \mu\text{g}/\text{m}^3$. The model is less accurate as loading decreases toward more atmospherically relevant levels, potentially due to increased interaction of partitioning species with the chamber walls (not included in the model) at decreased loadings. Sensitivities to varying partitioning coefficients are enhanced under low aerosol loading conditions. Similar phenomena were observed in previous SOA modeling studies (Chen and Griffin, 2005). The model prediction of SOA for toluene tends to have less variability than for *m*-xylene. Similar observations are made between the two aromatic systems regarding the sensitivities to partitioning and the prediction error with decreasing aerosol loading. The performance of the model for both *m*-xylene and toluene is acceptable (prediction errors typically within 50%).

Sample simulated *m*-xylene and toluene SOA temporal profiles are shown in Fig. 4.4. For *m*-xylene, the model does not do well for the evolution of SOA with time, with a time lag in producing SOA and underprediction of SOA during the first few hours for both high- and low- NO_x runs. This could result from the lack of consideration of nucleation (Hu et al., 2007; Carter et al., 2012) and the Kelvin effect (Chen and Griffin, 2005) or from wall effects at smaller

loadings, as mentioned previously. However, considering the difficulty of optimizing the model for four different kinds of conditions without considering these effects, performance of this model is deemed acceptable. SOA evolution over time qualitatively matches observations for the experiment run of 1509A (toluene-NO_x), forming a plateau at the end of experiment. No plateau is observed in 1477A (toluene-H₂O₂), but the model predicts the profile of SOA formation adequately given that it is more difficult to simulate experiments under low aerosol loading and that only one consistent set of sub-cooled vapor pressures is used. As with *m*-xylene, the model underestimates the initial aerosol growth for these two experiments even after correction factors for vapor pressures were applied, which is also reported in other aromatic SOA partitioning modeling studies (Johnson et al., 2004).

Figure 4.3. Comparison of the final observed and modeled toluene SOA concentrations for all the simulated high- NO_x and low- NO_x experiments. Error bars reflect the corresponding predicted/observed SOA ratio values when partitioning coefficients of all compounds are adjusted by $\pm 20\%$.

Figure 4.4. Observed and predicted SOA concentration profiles versus time. Open circles represent observed SOA temporal profiles for EPA1212B (*m*-xylene) and EPA1477A (toluene) (limited NO_x); Open diamonds represent observed SOA temporal profiles for EPA1516A (*m*-xylene, with 26 ppb of NO_x) and EPA1509A (toluene, with 43 ppb of NO_x). Lines represent the corresponding simulated profiles.

4.3. NO_x Effect on SOA yields

Before exploring the NO_x effect on SOA yields, experimental and simulated SOA yields under different NO_x conditions are made comparable by converting the observed final yields to adjusted yields at a reference level using the method described by Carter et al. (2012):

$$Y_{adj} = Y_{obs} \cdot \frac{(1 + K_p \cdot PM_{massCorr})}{PM_{massCorr}} \cdot \frac{PM_{ref}}{(1 + K_p \cdot PM_{ref})} \quad (3)$$

where Y_{obs} refers to the final observed SOA yield, Y_{adj} refers to the adjusted SOA yield at the reference level, PM_{ref} refers to the reference SOA level of 50 µg/m³, which is the same as adopted by Carter et al. (2012), and K_p refers to a fixed ‘one model’ partitioning coefficient of 0.02 m³/µg calculated and verified by Carter et al. (2012). Y_{obs} is calculated by dividing final observed SOA mass concentration by the consumed mass concentration of hydrocarbon. Assuming the model can predict SOA evolution profiles adequately, simulated yields can be treated as “observed” values and adjusted using Equation (3) and the same parameters.

With a series of adjusted yields over time (both observed and predicted), Fig. 4.5 shows the SOA yield dependence on NO_x level for both *m*-xylene and toluene. The *m*-xylene plot shows an obvious decreasing trend of SOA yield with increasing NO_x concentration, while the decreasing trend for toluene is present though less obvious. Johnson et al. (2004) observed a decreasing trend of toluene SOA yield with decreasing toluene to NO_x ratio by combining several research groups’ toluene chamber experiments with NO_x concentration ranging from 45 ppb to 1300 ppb

and toluene concentration ranging from 500 ppb to 6600 ppb. The less obvious decreasing trend for the experimental toluene system shown here might be due to the limited number of runs chosen and a much lower concentration of NO_x in the present study. The trend of predicted SOA yields as a function of NO_x levels indicates that the newly developed CACM/gas-aerosol partitioning adequately can capture SOA yield dependence on NO_x level for both *m*-xylene and toluene systems when NO_x levels are closer to those typically encountered in the atmosphere. It is noticeable that the toluene system tends to have higher yields than *m*-xylene system, which also was observed by Johnson et al. (2005), who postulated that unsaturated aldehydes, which are produced through a ring-opening route, have higher SOA formation potential than unsaturated ketones, which are produced to a greater extent in the *m*-xylene system due to the second methyl group present on the aromatic ring. The simulated yield difference between toluene and *m*-xylene is affected by the correction factors for vapor pressures of peroxide-bicyclic route products and ring-retaining “phenolic route” organic nitrates.

Figure 4.5. Plot of observed SOA yield and predicted SOA yield (adjusted) for all simulated runs. The color scale represents corresponding initial NO_x levels in ppm. Different shapes represent corresponding initial HC levels of simulated experiments. The black cross represents the average observed/predicted yield with limited presence of NO_x.

The sensitivity of the SOA-aromatic-NO_x system is explored based on 150 simulations for each aromatic, with concentrations of aromatic hydrocarbon ranging from 0.01 to 0.15 ppm and NO_x concentrations ranging from 0.01 to 0.10 ppm. Figure 4.6(a) and (b) show the simulated SOA yield as a function of NO_x level and initial loading of aromatic hydrocarbon for *m*-xylene and toluene, respectively. SOA yield here refers to the yield at the point in time when 80% of the initial hydrocarbon loading has been consumed. While these sensitivity plots are not able precisely to represent real scenarios, they can provide basic information on SOA-aromatic-NO_x systems and the differences between *m*-xylene and toluene. As discussed earlier, higher yields are observed for toluene than for *m*-xylene. However, it is worth noting that it usually takes significantly more time to consume 80% of the initial toluene. Thus, under ambient conditions, SOA yield for toluene could be much smaller than those predicted here.

A strong increase in SOA yield with decreasing NO_x at *m*-xylene concentration around 0.1 ppm and NO_x concentration under 0.08 ppm (representative of ambient conditions) is illustrated in the simulated sensitivity plot. This feature originates mainly from ring-opening unsaturated products like furanones produced under low-NO_x conditions. By observing further reaction pathways of peroxide bicyclic radical (RO299) in Figure 2.1, one would expect fewer ring-opening products to be formed under low-NO_x conditions. However, production of ring-opening products also is affected by the pathway to form RP93, which depends greatly on NO_x concentration. The net effect of NO_x leads to a greater amount of ring-opening products produced under low-NO_x conditions. The simulation of Hu et al. (2007) indicates increasing ring-opening products (e.g. glyoxal/methyl glyoxal) with increasing NO_x, which is inconsistent with this study. This

inconsistency originates from the fact that pathway to form RO93 is dependent on NO_x concentration in this study, while this branch is NO_x -independent in Hu et al. (2007).

For toluene, the feature of decreasing SOA yield with increasing NO_x is largely offset by the effect of highly condensable nitrates from the phenolic route. In the *m*-xylene system, this effect is not strong due to the adopted vapor pressures of nitrates from the phenolic route. Thus, this simulation might indicate that nitrates from the phenolic route in *m*-xylene are not as important as those in the toluene SOA formation. One explanation is that it is more difficult to add -OH or - NO_2 groups on to aromatic ring with more methyl groups, thus reducing the importance of nitrates from the phenolic route in SOA formation for *m*-xylene. The greater importance of phenolic route nitrates and of peroxide bicyclic compounds in the toluene system at least partially explains higher SOA yields.

Figure 4.6. Yield (when 80% of aromatic hydrocarbon consumed) as a function of NO_x level and initial loading of aromatic hydrocarbon.

To provide insight into aromatic SOA formation under somewhat more relevant atmospheric conditions, the sensitivity of the SOA-aromatic-NO_x system with a mixture (60% toluene carbon and 40% *m*-xylene carbon) was studied and plotted in Figure 4.7(a). The split of 60% toluene carbon and 40% *m*-xylene carbon is based on Tran et al. (2000). The total concentration of aromatic hydrocarbons is expressed as ppmC, with a range of 0.2-1.2 ppmC. The resulting plot shows behavior representative of both *m*-xylene and toluene in terms of ranges of SOA yield and sensitivity behavior. Similar to the SOA-toluene-NO_x system, SOA yield with increases with except under high-NO_x, low-aromatic conditions. However, it is worth noting that the decreasing trend of SOA yield with increasing NO_x is weak under most conditions. This trend is weaker than that observed in the SOA-toluene-NO_x system, showing the influence of *m*-xylene chemistry. A similar sensitivity plot of a scenario in which propene (as a representative species of alkene) is included is shown in Figure 4.7(b). This scenario represents a potential profile of aromatic SOA formation when different levels of aromatics, other VOCs, and NO_x are mixed. Similar to the SOA-*m*-xylene-NO_x system, increasing SOA yield with decreasing NO_x is observed under low-NO_x, high-aromatic conditions, indicating reactions with *m*-xylene are playing a more important role when propene is included. The presence of propene in the system leads to an initial increase in OH concentration followed by a lower OH concentration until the end of simulations when compared to simulations without propene. Thus the behavior of Figure 4.7 (b) can be explained as followed: with less OH available due to the presence of propene, a greater portion of the consumed aromatics would be *m*-xylene due to larger *m*-xylene-OH reaction rate constant. Thus, the behavior in Figure 4.7 (b) resembles more closely the *m*-xylene system.

Figure 4.7. Aromatic SOA yield (when 80% of total aromatic hydrocarbon consumed) as a function of NO_x level and initial loading of mixture of hydrocarbons. a.) toluene carbon (60%) + *m*-xylene carbon (40%). b: toluene carbon (60%) + *m*-xylene carbon (40%) + propene (same carbon concentration as aromatics).

4.4. Speciation of Simulated SOA

4.4.1. Speciation of Simulated SOA under varying NO_x levels

The simulated aerosol species composition at the end of the simulation (with ending points of 400 min and 800 min for *m*-xylene and toluene, respectively) is grouped into five major categories and shown as a function of NO_x level (0.1-50 ppm) in Fig. 4.8. Ring opening species are the most dominant species in aerosol for both aromatic hydrocarbons and both low and high NO_x levels, corresponding to the idea that furanones, furaniones, and other products related to glyoxal and methyl-glyoxal are major products and SOA components (Forstner et al., 1997). Due to the method used for sub-cooled vapor pressure estimation, there is considerable uncertainty in the finding that furanones and furaniones exist as a large portion of SOA. However, it is fairly certain that the pathway to form furanones, furaniones, methyl-glyoxal, glyoxal, 1,4-unsaturated dicarbonyls, and other ring-opening products is a critical process for SOA formation, at least in the latter part of SOA evolution, implied from the fact that very small correction factors were needed for products (except for glyoxal and methyl-glyoxal which have documented sub-cooled vapor pressure) produced from this pathway. The small scaling factors also imply there is some aerosol phase chemistry for ring-opening, highly oxidized compounds uncharacterized in the model (Johnson et al., 2004; Hu et al., 2007).

The next important class of compounds for both *m*-xylene and toluene is the ring-retaining organic nitrates from the phenolic route, implying the importance of the phenolic route in aromatic photooxidation and SOA formation, especially under high NO_x conditions. Other important components include peroxide bicyclic ring-retaining products under toluene-low NO_x conditions and acylperoxyl nitrate-like compounds (PAN-like) for both aromatics under high

NO_x conditions. PAN-like compounds also are predicted to be important in the kinetic modeling study of Hu et al. (2007). By comparing speciation under varied NO_x levels, a strong decrease in the peroxide bicyclic route with increasing NO_x is observed, especially for toluene. The simulated result with more significant contribution from peroxide bicyclic ring-retaining compounds for toluene than *m*-xylene is a result of a lower required correction factor for vapor pressures of toluene peroxide bicyclic ring-retaining. This fact indicates that peroxide bicyclic ring-retaining compounds might be more involved in the association effect in SOA formation for toluene compared to *m*-xylene. This supports the hypothesis of Johnson et al. (2005) that unsaturated aldehydes formed from oxidation of toluene (due to one less methyl group existing on toluene structure than *m*-xylene) participate in association reactions with peroxide bicyclic ring-retaining compounds.

Figure 4.8. Simulated composition of *m*-xylene and toluene SOA as a function of NO_x level for simulations carried out with an initial aromatic loading of 0.1ppm for both *m*-xylene and toluene.

4.4.2. Time evolution of SOA species

Time evolution profiles of important groups of SOA species for both aromatic hydrocarbons under high and low NO_x levels are plotted in Figure 4.9. With the exception of the bicyclic products, toluene and m-xylene share a similar pattern of temporal evolution of SOA species. Under high- NO_x levels, the group of furanone, furandione and ring-opening species becomes less important as time proceeds, while nitrates from the phenolic route and PAN-like species becoming more important. This stems from the fact that formation of nitrates from phenolic route and PAN-like species requires multiple reaction steps. Under low- NO_x levels, the group of furanone, furandione and ring-opening species becomes more important as time proceeds, with the contribution from peroxide bicyclic ring-retaining species decreasing especially for toluene. Under NO_x -limited conditions, more and more HONO being released from wall with increasing irradiation time leads to the slight increase of organic nitrates from phenolic route and PAN-like species.

Figure 4.9. Time evolution of simulated SOA composition with an initial loading of 0.1ppm *m*-xylene or toluene under low- and high (50ppb)- NO_x levels.

4.5. Temperature Impact on Aromatic/NO_x/SOA System

The effect of temperature variations on SOA yield at varying NO_x levels also has been explored, with results shown in Figure 4.9. Reaction rate constants in CACM are temperature dependent, and based on partitioning theory and the vapor pressure estimation method adopted by this study, phase transitions also are impacted significantly by temperature. Figure 4.10 shows a large shift in SOA yield for both aromatics over a change in temperature of 40K (from 280K to 320K).

For the *m*-xylene system, the range of SOA yields at low temperature (0.4 to 0.5) is larger than at high temperature at 280K. This is because at low temperature, the contribution of PAN-like species increases greatly from low-NO_x to high-NO_x conditions. At high temperature, PAN-like species are not a major component of SOA regardless of NO_x level due to their vapor pressures. When temperature increases from 280K to the middle of temperature range 300K, a switch in the behavior is observed with regard to SOA yield change with increasing NO_x. This results from PAN-like species becoming less important in SOA formation as temperature increases and ring-opening species becoming more important. Ring-opening species decrease with increasing NO_x according to the discussions in previous sections in this chapter.

The major difference between the *m*-xylene and toluene systems lies in this switching behavior, as no switch behavior is observed in toluene system. This can be explained by the fact that nitrates from the phenolic route are major species in toluene system, and that nitrates are positively correlated to NO_x levels. This simulation supports experimental observations of large transition in *m*-xylene SOA composition from 278K to 292K by (Qi et al., 2010).

Figure 4.10. The effect of temperature variations on SOA yield under varying NO_x concentration with initial aromatic hydrocarbon loading of 0.1ppm

Chapter 5

Conclusion and Future Research

5.1. Conclusion

Gas-phase oxidation mechanisms for toluene and *m*-xylene have been updated within the CACM framework. A gas-particle partitioning model is optimized and linked to CACM to predict SOA formation from toluene and *m*-xylene photooxidation systems under high- and low-NO_x conditions for a series of chamber experiments. The SOA formation models developed in this study simulate well both *m*-xylene and toluene SOA formation simultaneously under various NO_x levels without the need to change model parameters and with state-of-art and appropriately detailed aromatic gas-phase chemistry. These represent great improvements over previous efforts.

Gas-phase modeling shows an over prediction of O₃ concentration. SOA simulations generally generate acceptable agreement between predicted and observed SOA formation, especially for the latter part of SOA evolution, with underestimation at the onset of SOA formation, especially for low-NO_x conditions. SOA simulations predict a strong decreasing yield trend with increasing

NO_x levels in the *m*-xylene system, with a less obvious decreasing trend in the toluene system. Simulated speciation of SOA helps confirm the hypothesis that low NO_x levels lead to more products produced from the peroxide bicyclic route, resulting in more peroxide bicyclic compounds partitioning into aerosol phase in NO_x -limited situations. The differences in simulated speciation between toluene and *m*-xylene suggest more theoretical or experimental research is needed regarding the phenolic route in aromatic oxidation chemistry. Simulated speciation of SOA also indicates that products from ring-opening routes are the major source of SOA formation and that association of aldehyde species in the SOA phase is probable. Sensitivities of aromatic/ NO_x /SOA systems under representative ambient conditions with a mixture of toluene, *m*-xylene, and propene show the potential trend of increasing aromatic SOA yield with decreasing NO_x . Results also imply that increasing temperature decreases *m*-xylene SOA yield quantitatively and leads to a switch in NO_x sensitivity of SOA formation. Such a switch in the NO_x sensitivity of SOA yield is not obviously observed in the toluene system, as toluene SOA yield increases with increasing NO_x over the range of temperature 280K-320K.

5.2. Future Research

5.2.1. Future chamber studies

New experiments with a larger NO_x concentration range and with longer irradiation time are suggested to evaluate the model more extensively. More detailed real-time chemistry analysis of important gas- and aerosol-phase products also would be incredibly useful.

5.2.2. Future box model studies

Gas-phase and aerosol partitioning mechanisms for other aromatics, such as *p*-xylene and 1,3,5-trimethylbenzene should be implemented into this model and validated by chamber experiments results. Comparison of SOA formation from oxidation of various aromatic hydrocarbons is suggested to evaluate the impact of different numbers and positions of methyl groups on SOA formation chemically.

5.2.3. 3D model

These box modules currently are being implemented into a 3D model to investigate the impact of changing NO_x emissions on aromatic-derived SOA in highly urbanized region of South Coast Air Basin of California (SoCAB). The model used in this study would be the UCI-CIT airshed model, a regional air quality model with a state-of-art chemical mechanism and gas-particle transport modules accounting for organic species partitioning into both the organic and aqueous phases (Chang et al., 2010). The goals of this work are to:

1. Develop a new emission inventory for the SoCAB for August 2005 that includes *m*-xylene and toluene emissions specifically in addition to the previous aromatic proxies AROH (representative of high SOA yield aromatics species) and AROL (representative of low SOA yield aromatics species). Toluene is assumed to be 80% of AROH and *m*-xylene 100% of AROL based on data generated from California emission inventory from California Air Resources Board. This emission inventory development work is complete.

2. Implement updated CACM with the new toluene and *m*-xylene chemistry into UCI-CIT; this is complete. A sample O₃ concentration difference plot between the new and old models at 23:00 on Aug 27, 2005 is shown in Figure 5.1.
3. Update the Model to Predict the Multiphase Partitioning of Organics (MPMPO), the module that treats organic aerosols in the 3D model (Griffin et al., 2003); this will include lumping species from the zero-dimensional model into a smaller number of surrogates, calculating activity coefficients, and allowing species to partition into aerosol aqueous phases. This work is in progress;
4. Simulate an August 2005 pollution episode with varying NO_x emissions and unaltered aromatic emission to evaluate temporally, spatially, and chemically the NO_x effect on SOA formation from oxidation of aromatic hydrocarbons in the SoCAB. This will occur upon completion of the above steps.

Figure 5.1. O₃ concentration difference plot at 23:00 Aug 27th, 2005(UCI-CIT with toluene and *m*-xylene updated – old version of UCI-CIT).

5.3. Publication and Presentations

A paper named “Simulated impact of NO_x on SOA formation from oxidation of toluene and *m*-xylene” based on this study was recently submitted to *Atmospheric Environment*. Presentations about this work were made at 2013 American Geophysical Union (AGU) Fall Meeting and NASA Air Quality Applied Sciences Team (AQAST) 6th Biannual Meeting (January 2014).

References

- Andino, J.M., Smith, J.N., Flagan, R.C., Goddard, W.A., Seinfeld, John H, 1996. Mechanism of atmospheric photooxidation of aromatics : A theoretical study. *Journal of Physical and Chemistry* 100, 10967-10980.
- Atkinson, R., Aschmann, S.M., Arey, J., 1991. Formation of ring-retaining products from the OH radical-initiated reactions of *o*-, *m*-, and *p*-xylene. *International Journal of Chemical Kinetics* 23, 77-97.
- Atkinson, R., Baulch, D.L., Cox, R.A., Crowley, J.N., Hampson, R.F., Hynes, R.G., Jenkin, M. E., Rossi, M.J., Troe, J., 2006. Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species. *Atmospheric Chemistry and Physics* 6, 3625–4055.
- Bohn, B., Zetzsch, C., 1999. Gas-phase reaction of the OH-benzene adduct with O₂: Reversibility and secondary formation of HO₂. *Physical Chemistry Chemical Physics* 1, 5097-5107.
- Calvert, J. G., Atkinson, R., Becker, K.H., Kamens, R.M., Seinfeld, J.H., Wallington, T. J., and Yarwood, G., 2002. *The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons*. Oxford University Press, New York.
- Carter, W.P.L., Cocker, D.R., Fitz, D.R., Malkina, I.L., Bumiller, K., Sauer, C.G., Pisano, J.T., Bufalino, C., Song, C., 2005. A new environmental chamber for evaluation of gas-phase chemical mechanisms and secondary aerosol formation. *Atmospheric Environment* 39, 7768–7788.

- Carter, W.P.L., Heo, G., Cocker, D.R., Nakao, S., 2012. SOA Formation: Chamber study and model development. Final Report to the California Air Resources Board, Contract No. 08-326.
- Chang, W.L., Griffin, R.J., Dabdub, D., 2010. Partitioning phase preference for secondary organic aerosol in an urban atmosphere. *Proceedings of National Academy of Science* 107, 6705-6710.
- Chen, J., Griffin, R.J., 2005. Modeling secondary organic aerosol formation from oxidation of α -pinene, β -pinene, and d-limonene. *Atmospheric Environment* 39, 7731–7744.
- Clegg, S.L., Kleeman, M.J., Griffin, R.J., Seinfeld, J.H., 2008. Effects of uncertainties in the thermodynamic properties of aerosol components in an air quality model - Part 2: Predictions of the vapour pressures of organic compounds. *Atmospheric Chemistry and Physics* 8, 1087–1103.
- Cocker, D.R., Flagan, R.C., Seinfeld, J.H., 2001. State-of-the-art chamber facility for studying atmospheric aerosol chemistry. *Environmental Science and Technology* 35, 2594-2601.
- Cordes, W., Rarey, J., 2002. A new method for the estimation of the normal boiling point of non-electrolyte organic compounds. *Fluid Phase Equilibria* 201, 409-433.
- Colville, C.J., Griffin, R.J., 2004. The roles of individual oxidants in secondary organic aerosol formation from Δ^3 -carene: 2. SOA formation and oxidant contribution. *Atmospheric Environment* 38, 4013-4023.
- Dodge, M., 2000. Chemical oxidant mechanisms for air quality modeling: critical review. *Atmospheric Environment* 34, 2103-2130.

- Forstner, H.J.L., Flagan, R.C., Seinfeld, J.H., 1997. Secondary organic aerosol from the photooxidation of aromatic hydrocarbons: molecular composition. *Environmental Science and Technology* 31, 1345–1358.
- Gery, M.W., Fox, D.L., Kamens, R.M., Stockburger, L., 1987. Investigation of hydroxyl radical reactions with *o*-xylene and *m*-xylene in a continuous stirred tank reactor. *Environmental Science and Technology* 21, 339–48.
- Griffin, R.J., Cocker, D.R., Flagan, R.C., Seinfeld, J.H., 1999. Organic aerosol formation from the oxidation of biogenic hydrocarbons. *Journal of Geophysical Research* 104, 3555-3567.
- Griffin, R.J., Dabdub, D., Seinfeld, J. H., 2002. Secondary organic aerosol 1. Atmospheric chemical mechanism for production of molecular constituents. *Journal of Geophysical Research: Atmospheres* 107, 4332.
- Griffin, R.J., Nguyen, K., Dabdub, D. , Seinfeld, J. H., 2003. A combined hydrophobic-hydrophilic module for predicting secondary organic aerosol formation. *Journal of Atmospheric Chemistry* 44, 171-190.
- Henze, D.K., Seinfeld, J.H., Ng, N.L., Kroll, J.H., Fu, T.-M., Jacob, D.J., Heald, C.L., 2008. Global modeling of secondary organic aerosol formation from aromatic hydrocarbons: high- vs low- yield pathways. *Atmospheric Chemistry and Physics* 8, 2405-2421.
- Hammond, D., Cook, J.P., 1993. Evaluation of ambient non-methan hydrocarbon measurements taken during the winter of 1991-92 in Sacramento, California. Air & Waste Management Association 86th annual Meeting & Exhibition.

- Hu, D., Tolocka, M., Li, Q., Kamens, R.M., 2007. A kinetic mechanism for predicting secondary organic aerosol formation from toluene oxidation in the presence of NO_x and natural sunlight. *Atmospheric Environment* 41, 6478–6496.
- Jang, M., Kamens, R.M., 2001. Characterization of secondary aerosol from the photooxidation of toluene in the presence of NO_x and 1-propene. *Environmental Science and Technology* 35, 3626–39.
- Jenkin, M. E., Saunders, S. M., Pilling, M.J., 1997. The tropospheric degradation of volatile organic compounds: a protocol for mechanism development. *Atmospheric Environment* 31, 81–104.
- Jenkin, M. E., Hurley, M.D., Wallington, T.J., 2007. Investigation of the radical product channel of the $\text{CH}_3\text{COO}_2 + \text{HO}_2$ reaction in the gas phase. *Physical Chemistry Chemical Physics* 9, 3149–62.
- Jenkin, M.E., Saunders, S. M., Wagner, V., Pilling, M.J., 2003. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): Tropospheric degradation of aromatic volatile organic compounds. *Atmospheric Chemistry and Physics* 3, 181-193.
- Johnson, D., Jenkin, M.E., Wirtz, K., Martin-Reviejo, M., 2004. Simulating the formation of secondary organic aerosol from the photooxidation of toluene. *Environmental Chemistry* 1, 150-165.
- Johnson, D., Jenkin, M., Wirtz, K., Martin-Reviejo, M., 2005. Simulating the formation of secondary organic aerosol from the photooxidation of aromatic hydrocarbons. *Environmental Chemistry* 2, 35–48.

- Jordan, C.E., Ziemann, P.J., Griffin, R.J., Lim, Y.B., Atkinson, R., Arey, J., 2008. Modeling SOA formation from OH reactions with C₈-C₁₇ *n*-alkanes. *Atmospheric Environment* 42, 8015–8026.
- Jørgensen, S., 2012. Gas-phase oxidation of cresol isomers initiated by OH or NO₃ radicals in the presence of NO₂. *International Journal of Chemical Kinetics* 44, 165–178.
- Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C.J., Swietlicki, E., Putaud, J.P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati, E., Stephanou, E.G., Wilson, J., 2005. Organic aerosol and global climate modelling: a review. *Atmospheric Chemistry and Physics* 5, 1053–1123.
- Klotz, B., Volkamer, R., Hurley, M.D., Andersen, M.P.S., Nielsen, O.J., Barnes, I., Imamura, T., Wirtz, K., Becker, K.H., Platt, U., Wallington, T.J., Washida, N., 2002. OH-initiated oxidation of benzene. *Physical Chemistry Chemical Physics* 4, 4399–4411.
- Koch, R., Knispel, R., Elend, M., Siese, M., Zetzsch, C., 2007. Consecutive reactions of aromatic-OH adducts with NO, NO₂ and O₂: Benzene, naphthalene, toluene, *m*- and *p*-xylene, hexamethylbenzene, phenol, *m*-cresol and aniline. *Atmospheric Chemistry and Physics* 7, 2057–2071.
- Kwok, E.S.C., Atkinson, R., 1995. Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: An update. *Atmospheric Environment* 29, 1685–1695.

- Kwok, E.S.C., Aschmann, S.M., Atkinson, R., Arey, J., 1997. Products of the gas-phase reactions of *o*-, *m*- and *p*-xylene with the OH radical in the presence and absence of NO_x. Journal of the Chemical Society, Faraday Transactions 93, 2847-2854.
- Lay, T.H., Bozzelli, J.W., Seinfeld, J.H., 1996. Atmospheric photochemical oxidation of benzene : Benzene + OH and the benzene-OH Adduct (hydroxyl-2,4-cyclohexadienyl) + O₂. Journal of Physical and Chemistry 100, 6543-6554.
- Liu, Y., 2012. Computational simulation of Secondary Organic Aerosol (SOA) formation from toluene oxidation. Rice University.
- Myrdal, P.B., Yalkowsky, S.H., 1997. Estimating pure component vapor pressures of complex organic molecules. Industrial and Engineering Chemistry Research 36, 2494–2499.
- Nakao, S., Tang, P., Tang, X., Clark, C.H., Qi, L., Seo, E., Asa-Awuku, A., Cocker, D.R., 2013. Density and elemental ratios of secondary organic aerosol: Application of a density prediction method. Atmospheric Environment 68, 273-277.
- Nannoolal, Y., Rarey, J., Ramjugernath, D., Cordes, W., 2004. Estimation of pure component properties. Fluid Phase Equilibria 226, 45–63.
- Ng, N.L., Kroll, J.H., Chan, A.W.H., Chhabra, P.S., Flagan, R. C., Seinfeld, J. H., 2007. Secondary organic aerosol formation from *m*-xylene, toluene, and benzene. Atmospheric Chemistry and Physics 7, 3909–3922.
- Olariu, R.I., 2001. Atmospheric oxidation of selected aromatic hydrocarbons. University of Wuppertal.

Pankow, J.F., 1994. An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmospheric Environment* 28, 185–188.

Platz, J., Nielsen, O.J., Wallington, T.J., Ball, J.C., Hurley, M.D., Straccia, a. M., Schneider, W.F., Sehested, J., 1998. Atmospheric chemistry of the phenoxy radical, $C_6H_5O(\bullet)$: UV spectrum and kinetics of its reaction with NO, NO₂, and O₂. *Journal of Physical Chemistry A* 102, 7964–7974.

Pope, C.A., Ezzati, M., and Dockery, D.W., 2009. Fine particulate air pollution and life expectancy in the United States. *N.E.J. Med.* 260, 376–386.

Saunders, Sandra M., Jenkin, Michael E., Derwent, R.G., Pilling, M.J., 2003. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds. *Atmospheric Chemistry and Physics* 3, 161–180.

Qi, L., Nakao, S., Tang, P., and Cocker III, D. R., 2010. Temperature effect on physical and chemical properties of secondary organic aerosol from *m*-xylene photooxidation, *Atmospheric Chemistry and Physics* 10, 3847–3854.

Seinfeld, J.H., Pankow, J.F., 2003. Organic atmospheric particulate material. *Annual Review of Physical Chemistry* 54, 121–140.

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

Song, C., Na, K., Cocker, D.R., 2005. Impact of the hydrocarbon to NO_x ratio on secondary organic aerosol formation. *Environmental Science and Technology* 39, 3143–3149.

- Song, C., Na, K., Warren, B., Malloy, Q., Cocker, D.R., 2007. Secondary organic aerosol formation from *m*-xylene in the absence of NO_x. *Environmental Science and Technology* 41, 7409-7416.
- Suh, I., Zhang, R., Molina, L.T., Molina, M.J., 2003. Oxidation mechanism of aromatic peroxy and bicyclic radicals from OH-toluene reactions. *Journal of the American Chemical Society* 125, 12655-12665.
- Thüner, L.P., Bardini, P., Rea, G.J., Wenger, J.C., 2004. Kinetics of the gas-phase reactions of OH and NO₃ radicals with dimethylphenols. *Journal of Physical Chemistry A* 108, 11019-11025.
- Tran, N.K., Steinberg, S.M., Johnson, B.J., 2000. Volatile aromatic hydrocarbons and dicarboxylic acid concentrations in air at an urban site in the Southwestern US, *Atmospheric Environment* 34, 1845-1852.
- Wagner, V., Jenkin, M.E., Saunders, S. M., Stanton, J., Wirtz, K., Pilling, M.J., 2003. Modelling of the photooxidation of toluene: conceptual ideas for validating detailed mechanisms. *Atmospheric Chemistry and Physics* 3, 89-106.