

Secondary organic aerosol formation from phenolic compounds in the absence of NO_x

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Abstract. SOA formation from benzene, toluene, *m*-xylene, and their corresponding phenolic compounds were investigated using the UCR/CE-CERT Environmental Chamber to evaluate the importance of phenolic compounds as intermediate species in aromatic SOA formation. SOA formation yield measurements coupled to gas-phase yield measurements indicate that approximately 20 % of the SOA of benzene, toluene, and *m*-xylene could be ascribed to the phenolic route under low NO_x conditions. The SOA densities tend to be initially as high as approximately 1.8 g cm^{-3} and eventually reach the range of $1.3\text{--}1.4 \text{ g cm}^{-3}$. The final SOA density was found to be independent of elemental ratio (O/C) indicating that applying constant density (e.g., 1.4 g cm^{-3}) to SOA formed from different aromatic compounds tested in this study is a reasonable approximation. Results from a novel on-line PILS-TOFMS (Particle-into-Liquid Sampler coupled with Agilent Time-of-Flight Mass Spectrometer) are reported. Major signals observed by the on-line/off-line Agilent TOFMS indicated that products had the same number of carbon atoms as their parent aromatics, suggesting importance of ring-retaining products or ring-opening products following ring-cleavage.

1 Introduction

Secondary organic aerosol (SOA) is formed from oxidative processing of volatile organic compounds in the atmosphere. SOA has been suggested to contribute to climate change (IPCC, 2007; Kanakidou et al., 2005), adverse human health effects (Davidson et al., 2005; Pope and Dockery, 2006), and a reduction in visibility (Eldering and Cass, 1996). Previous

researchers have estimated approximately 70 % of organic aerosols are secondary in nature (Hallquist et al., 2009 and references therein). Aromatic hydrocarbons comprise ~ 20 % of nonmethane hydrocarbons in the urban atmosphere and are considered to be one of the major precursors to urban SOA (Calvert et al., 2002).

A number of studies have investigated gas-phase photooxidation of aromatic hydrocarbons (e.g., Arey et al., 2009; Calvert et al., 2002; Coeur-Tourneur et al., 2006; Johnson et al., 2004; Johnson et al., 2005; Olariu et al., 2002; Takekawa et al., 2003; Volkamer et al., 2002). Previously identified first generation products of aromatic compound photooxidation explain approximately 50 % of carbon balance (Calvert et al., 2002). Although multigenerational reactions have been suggested to contribute to aromatic SOA formation (Hurley et al., 2001; Ng et al., 2007; Sato et al., 2007), the extent of the contribution from the second or further reaction products to SOA is poorly understood.

Phenolic compounds are one of the major first generation products of OH reaction with aromatic hydrocarbons (Calvert et al., 2002). Previous studies suggested the major gas-phase reaction products from OH reaction of phenolics are dihydroxy compounds (e.g., 80 % catechol formation from phenol, Olariu et al., 2002). However, the mechanisms of SOA formation from phenolic compounds are highly uncertain. In addition, since phenolic compounds are significant products in wood smoke (Hawthorne et al., 1989, 1992; Schauer et al., 2001; Simoneit, 1999), the reaction mechanism of phenolic compounds leading to SOA formation is of a great interest (Chang and Thompson, 2010; Coeur-Tourneur et al., 2010a, 2010b; Grosjean, 1984; Henry et al., 2008; Iinuma et al., 2010; Sun et al., 2010).

SOA formation from individual aromatic and phenolic compounds were investigated using an environmental chamber under low NO_x (and high HO_2) conditions to evaluate the role of phenolic species in SOA formation from aromatic



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hydrocarbons. Chemical analysis was performed using on-line and off-line mass spectrometry to infer the structure of aromatic and phenolic SOA.

2 Experimental

2.1 Environmental chamber

Most of the experiments were conducted in the UC Riverside/CE-CERT environmental chamber described in detail in Carter et al. (2005). In short, this facility consists of dual 90 m³ Teflon® reactors suspended by rigid frames in a temperature controlled enclosure (27 ± 1 °C) continuously flushed with dry (a dew point below -40 °C) purified air generated by an Aadco 737 series (Cleves, Ohio) air purification system. The top frames are slowly lowered during the experiments to maintain a slight positive differential pressure (0.03''H₂O) between the reactors and enclosure to minimize dilution and possible contamination of the reactors. 272 115 W Sylvania 350 black lights are used as the light source for all the experiments reported herein.

Some of the results of dimethylphenols (DMPs) were acquired in the UCR/CE-CERT mezzanine chamber (Nakao et al., 2011). The UCR/CE-CERT mezzanine chamber is within a 2.5 m × 3 m × 7.8 m enclosure covered with reflective aluminum sheets and is illuminated with 170, 40 W blacklights with peak intensity at 350 nm (SYLVANIA, 350 BL) with the NO₂ photolysis rate of 0.6 min⁻¹. Within this enclosure is a 12 m³ volume 2 mil FEP Teflon® film reactor. A minimum of 1 m space between the reactor surface and blacklights avoids excessive heating at the surface of the film. Additionally, six fans are used to mix the air inside the enclosure with room air to minimize heating in the enclosure. Prior to each experiment, the bag is flushed overnight with purified air. Background particle concentration is below the detection limit of 0.2 cm⁻³.

2.2 Gas and particle analysis

The Agilent 6890 Gas Chromatograph – Flame Ionization Detector was used to measure concentrations of reactants and products. All phenolic compounds were analyzed by a GC equipped with a thermal desorption system (CDS analytical, ACEM9305, Sorbent Tube MX062171 packed with Tenax-TA/Carbopack/Carbosieve S111) except for dimethylphenols for mezzanine chamber experiments. Aromatic hydrocarbon measurements were calibrated using a dilute gas cylinder (SCOTT-MARIN, Inc) or by introducing known amount of liquid hydrocarbons into the reactor. Calibration for phenolic compounds was performed by impregnation of the glass cartridges with known quantities of phenolic compounds in acetonitrile. The Ionicon Proton Transfer Reaction – Quadrupole Mass Spectrometer (PTR-MS) was used to measure dimethylphenol decay for mezzanine chamber experiments.

Particle size distribution between 27 nm and 686 nm was monitored by a custom built Scanning Mobility Particle Sizer (SMPS) similar to that described by Cocker et al. (2001). Particle effective density was measured with an Aerosol Particle Mass Analyzer (APM, Kanomax) (Ehara et al., 1996) and SMPS in series. The APM is located upstream of the SMPS for improved time resolution and sensitivity (S/N) over the more common configuration of Differential Mobility Analyzer (DMA) – APM (Khalizov et al., 2009; McMurry et al., 2002; Xue et al., 2009). A detailed description of the APM-SMPS system and data algorithms are described elsewhere (Malloy et al., 2009).

The high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) (DeCarlo et al., 2006) was operated in high resolution W mode. Elemental analysis (EA) was used to determine the atomic ratio (O/C) of non-refractory organic aerosols (Aiken et al., 2008).

The Agilent 6210 Accurate-Mass Time-of-Flight Mass Spectrometer equipped with multimode ionization source for electrospray and atmospheric pressure chemical ionization (ESI/APCI-TOFMS) is used to obtain accurate mass of analytes. Soft ionization by ESI and APCI provides lower fragmentation of the analytes compared to electron impact (EI) used for the HR-ToF-AMS or other conventional GC-MS techniques. Mass accuracy is routinely calibrated by standard compounds (Agilent low concentration MMI tuning mix, G1969-85020) before analysis and in most cases mass accuracy of less than 5 ppm is achieved. Occasionally higher mass errors (~30 ppm) were observed during sample analysis, which resulted in a consistent shift of mass throughout the mass range of the instrument. Since the extent of the shift can be inferred from repeatedly observed ions (e.g., pyruvic acid), formulas were carefully assigned based on tendency of shift and repeat experiments. Filter samples were collected onto Teflo® filters (2 µm, 47 mm, PALL Life Sciences) at 25 l min⁻¹ for 1 ~ 4 h. After collection, filters were stored in a freezer until extraction. Extractions were achieved by sonicating the filter in 5 ml of acetonitrile. The extract volume was reduced under a gentle stream of N₂ until near dryness and reconstituted by 300 µl of acetonitrile/water/acetic acid (50/50/0.1v). Samples were directly infused to the TOFMS. A: water (0.1 v % acetic acid) and B: acetonitrile were used as eluents (B 50 %, 0.5 ml min⁻¹). Acetonitrile was chosen as the organic solvent to reduce the solvent-analyte reaction compared to methanol (Bateman et al., 2008). Mixed mode ionization (simultaneous APCI and ESI) was used with vaporizer temperature 200 °C, nebulizer pressure 40 psig, corona current 2 µA, fragmentor voltage 100V. Although the mixed mode is used to survey a wide range of products, the resulting major signals were the same as in ESI only. APCI yielded lower sensitivity in this study. All Agilent TOFMS data was acquired in negative ion mode.

A Particle-Into-Liquid-Sampler (PILS) (Orsini et al., 2003; Weber et al., 2001) was interfaced with the TOFMS to provide an on-line accurate mass analysis of water soluble

organic compounds (Bateman et al., 2010). In order to couple the PILS (Brechtel Manufacturing Inc.) to the TOFMS, the use of HPLC pumps in addition to a commonly used peristaltic pump was critical to overcome the backpressure of the TOFMS inlet and to supply steady flow of water (18.2 M Ω , Milli-Q, Millipore) into the boiler. The PILS-TOFMS system will be described in more detail in an upcoming publication (Clark et al., 2011). The negative ESI was used as the ionization method with similar conditions as the filter analysis without the corona current.

2.3 Chamber experiments

The experimental test matrix is summarized in Table 1. A known volume of high purity liquid aromatic hydrocarbon (All purchased from Sigma-Aldrich: $\geq 99\%$ or $\geq 99.5\%$, except 2,4-DMP $\geq 98\%$) was injected through a heated glass injection manifold system and flushed into the chamber with pure N₂. Since phenolic compounds are less volatile than hydrocarbons typically used for chamber experiments, injection into the chambers were carefully performed using a heated oven (50 ~ 80 °C) through a heated transfer line maintained at a temperature higher than the oven. The glass manifold inside the oven was packed with glass wool to increase the mass transfer surface area. Since reasonable agreement between the calculated concentration of phenolics (based on injected amount) and observed concentrations were confirmed, loss of phenolics in the transfer line and to the wall was assumed to be negligible. H₂O₂ was used as an OH (and HO₂) radical source. H₂O₂ 50 wt % solution was injected through the same oven system. Since the H₂O₂ solution did not spread through glass wool, the glass wool was processed with an acid/base bath and cleaned by water and acetone which enabled the H₂O₂ solution to spread. Initial H₂O₂ concentration was not measured, but is estimated to be 1 ~ 5 ppm based on amount injected and hydrocarbon decay rate. No seed particles were used in this study. Exponential decay rates of particle number is used to calculate particle volume wall loss (Carter et al., 2005). To investigate the role of organic peroxides, additional high NO experiments were also performed and the chemical composition of SOA was compared to low NO_x condition. Initial ratio of approximately 50/50/500 ppb for phenolic/methyl nitrite/NO was used to ensure that excess NO was present to suppress RO₂ + HO₂ reaction.

3 Results and discussion

3.1 SOA formation

SOA yield (Y) is defined as the mass of aerosol formed (wall-loss-corrected) (M_o) divided by mass of hydrocarbon reacted (ΔHC)

$$Y = \frac{M_o}{\Delta\text{HC}} \quad (1)$$

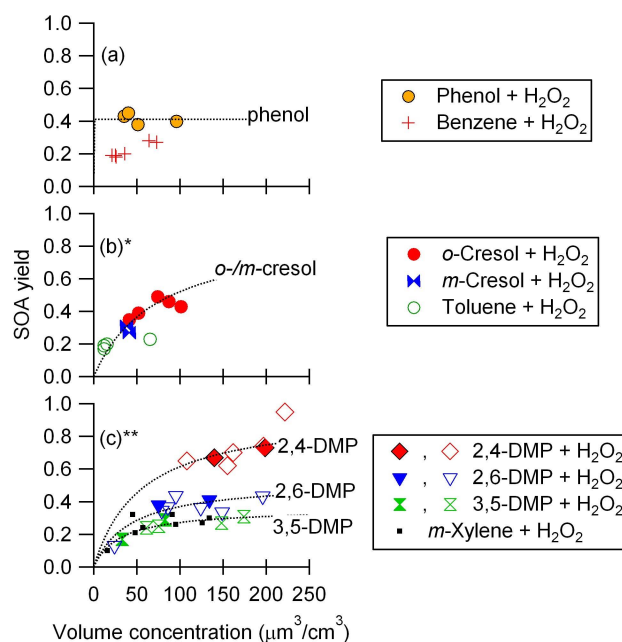


Fig. 1. SOA yield of benzene, toluene, *m*-xylene, and their phenolic compounds in the absence of NO_x (Dotted lines are one product model fit for phenolic compounds). * SOA yields from cresol isomers are combined. ** Open symbols are data acquired in CE-CERT mezzanine chamber.

Its dependence on aerosol mass loading has been traditionally parameterized by as shown below: (Odum et al., 1996)

$$Y = \sum Y_i = M_o \sum_i \frac{\alpha_i K_i}{1 + M_o K_i} \quad (2)$$

where α_i is the mass-based stoichiometric coefficient for the reaction generating product i , K_i is the partitioning coefficient of product i . Equations (1) and (2) were applied for the SOA yields obtained (Fig. 1). Particle density of 1.4 g cm⁻³ was used. 2,4-DMP had the highest SOA formation potential of the three DMP isomers, with a SOA yield approximately twice as high as the other DMP isomers. SOA yield from phenol was higher than benzene.

SOA from aromatic hydrocarbons formed under low NO_x conditions was previously reported to be effectively non-volatile (Ng et al., 2007), in which case SOA yield would be independent of particle mass concentration (flat SOA yield curves). However, for benzene, *o*/*m*-cresol, and possibly DMPs, the SOA yield was observed to be slightly dependent on particle concentration. Therefore, in this study, constant SOA yield was not assumed and a one product model fit was applied to perform calculation of the contribution of phenolic route in the following section.

Table 1. Experimental test matrix (low NO_x).


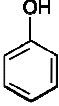

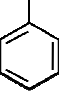


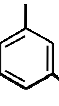


	Run ID	HC _i (ppb)	HC _f (ppb)	ΔHC (μg m ⁻³)	Mo (μm ³ cm ⁻³)	SOA yield ^c
	benzene + H ₂ O ₂					
	EPA1141A	491	434	182	25	0.19
	EPA1149A	490	429	195	26	0.18
	EPA1161A	1031	929	326	64	0.28
	EPA1161B	528	478	160	21	0.19
	EPA1225A	953	833	383	73	0.27
	EPA1225B	959	882	246	36	0.20
	phenol + H ₂ O ₂					
	EPA1206A	51	21	115	35	0.43
	EPA1206B	52	20	122	40	0.45
	EPA1217A	138	49	338	96	0.40
	EPA1217B	76	28	184	51	0.38
	catechol + H ₂ O ₂					
	EPA1293A	71 ^a	0	318	89	0.39
	toluene + H ₂ O ₂					
	EPA1266A	104	77	100	12	0.17
	EPA1251B	84	59	93	12	0.19
	EPA1141B	85	57	108	15	0.20
	EPA1290B	432	326	397	65	0.23
	o-cresol + H ₂ O ₂					
	EPA1251A	75	27	210	74	0.49
	EPA1252A	54	12	184	52	0.39
	EPA1252B	45	8	166	41	0.35
	EPA1266B	101	41	263	87	0.46
	EPA1427A	105	29	333	101	0.43
	m-cresol + H ₂ O ₂					
	EPA1255A	67	18	212	41	0.27
	EPA1255B	55	16	174	38	0.31
	m-xylene + H ₂ O ₂					
	EPA1244A	124	47	333	57	0.24
	EPA1180B	234	90	621	134	0.30
	EPA1209A	229	77	656	126	0.27
	EPA1209B	177	59	509	95	0.26
	EPA1212A	114	21	401	91	0.32
	EPA1212B	52	6	197	45	0.32
	EPA1248A	315	262	229	16	0.10
	EPA1248B	121	48	318	48	0.21
		2,4-DMP + H ₂ O ₂				
EPA1238A		83	6	381	199	0.73
EPA1238B		62	2	293	140	0.67
EPA1412A		184	41	710	340	0.67
	mezzanine chamber runs ^b					
	mez100809	68	2.2	327	222	0.9
	mez100909	131	4.9	628	331	0.74
	mez101009	48	1	234	108	0.65
	mez101109	72	2	349	155	0.62
	mez101309	77	1.9	373	197	0.74
	mez102109	66	1	322	162	0.70

Table 1. Continued.

Run ID	HC _i (ppb)	HC _f (ppb)	ΔHC (μg m ⁻³)	Mo (μm ³ cm ⁻³)	SOA yield ^c
2,6-DMP + H ₂ O ₂					
EPA1240A	98	6	457	134	0.41
EPA1240B	58	2	278	75	0.38
mezzanine chamber runs ^b					
mez081409	64	0	319	79	0.35
mez081609	66	0	327	86	0.37
mez081809	67	16	255	24	0.13
mez100609	64	2.8	305	95	0.44
mez100709	130	2.7	632	196	0.43
mez120309	125	0	621	149	0.34
mez120409	96	0	478	124	0.36
3,5-DMP + H ₂ O ₂					
EPA1243A	90	9	400	83	0.29
EPA1243B	60	7	262	33	0.17
mezzanine chamber runs ^b					
mez051910	72.24	0	359	61	0.24
mez052010	85.09	0	422	75	0.25
mez052310	154.1	0	765	148	0.27
mez060210	160.5	0	797	174	0.31

^a Initial concentration calculated by amount injected. Injection done with oven temperature ~ 120 °C. ^b Initial DMPs concentrations calculated based on injection. Final concentration obtained by the PTR-MS. ^c yields calculated using SOA density 1.4 g cm⁻³.

3.2 Contribution of phenolic route

The formation yields of phenolics from aromatics were obtained. An example for *o*-cresol and *m/p*-cresol formation from toluene is shown in Fig. 2. The cresol formation yields from toluene were calculated from measured cresol by correcting for the further reaction of cresols with OH. Equations in Atkinson et al. (1982) and rate constants from Calvert et al. (2002) were used for the correction. Phenol, cresols, and DMPs formation yields are in reasonable agreement with previous studies (Table 2) (Atkinson, 1989; Atkinson et al., 1991; Berndt and Böge, 2006; Klotz et al., 1998; Noda et al., 2009; Smith et al., 1999; Smith et al., 1998; Volkamer et al., 2002).

Contributions of the phenolic route to aromatic SOA formation in the low NO_x system were estimated by combining SOA yield measurement (Fig. 1), phenolic yields, and consumption of phenolics (e.g., Fig. 2). The amount of phenolics (as products) reacted is calculated as the gap between the observed concentration of phenolic compounds and the concentration corrected for the secondary reaction. Phenolic route SOA is calculated by multiplying reacted phenolics and their SOA yield at appropriate mass loading using the phenolic SOA yield curves in Fig. 1. SOA yields from cresol isomers (*o*-, *m*-, and *p*-) were assumed to be the same (Henry et al., 2008). The ratio of 2,4-DMP and 2,6-DMP produced from

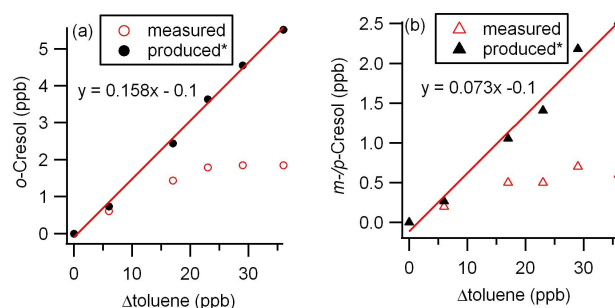


Fig. 2. Formation of cresols from OH reaction with toluene. *measured cresol concentrations were corrected for secondary reaction.

OH reaction of *m*-xylene was assumed to be the same as that reported by Smith et al. (1999). Formation of 3,5-DMP is assumed to be insignificant (Smith et al., 1999). Contribution of the phenolic route in the no NO_x system is summarized in Table 3. The contribution was approximately 20% for benzene, toluene, and *m*-xylene in low NO_x conditions.

Table 2. Phenolic formation yield from OH reaction with benzene, toluene, and *m*-xylene.

	Phenolic formation yield (%)		NO _x (ppm)
	<i>o</i> -Cresol	(<i>m</i> + <i>p</i>)-Cresol	
	Phenol		
This study	41.3		0
Berndt and Böge (2006)	61 ± 6		0
Volkamer et al. (2002)	53.1 ± 6		0.002–2
	<i>o</i> -Cresol	(<i>m</i> + <i>p</i>)-Cresol	
This study	15.8	7.3	0
Atkinson et al. (1989)	20.4 ± 2.7	4.8 ± 0.9	0–10
Klotz et al. (1998)	12.0 ± 1.4	5.9 ± 0.9	0.003–0.3
Smith et al. (1998)	12.3 ± 0.6	5.6 ± 0.4	0.10–0.42
	(2,4 + 2,6 + 3,5)-DMP		
This study*	8.2 ± 1.3		0
Smith et al. (1999)	10.9 ± 0.5		0.157–1.081
Atkinson et al. (1991)	21.0 ± 5.6		0–10
Noda et al. (2009)	14.1 ± 2.6		0.01–0.1

* Acquired in mezzanine chamber using PTR-MS.

Table 3. Estimated contribution of phenolic route to benzene, toluene, and *m*-xylene SOA.

	Benzene	Toluene	<i>m</i> -Xylene
Phenolic route (%)	23.5 ± 4.7*	15.8 ± 3.8*	16.9 ± 3.4 (<i>n</i> = 4)

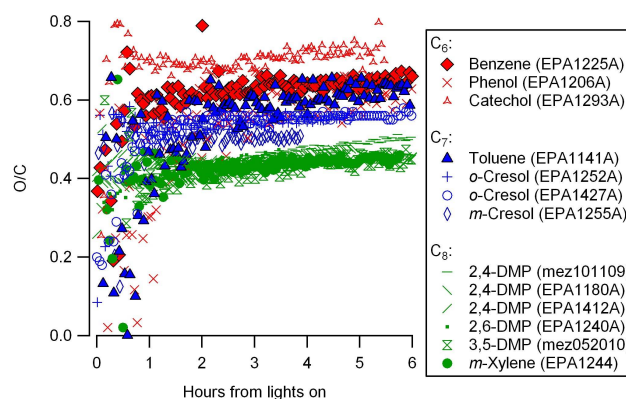
* Error estimated based on repeated *m*-xylene experiments and phenolic route calculations.

3.3 Particle chemical composition

3.3.1 SOA elemental ratio and density

The results of elemental analysis of HR-ToF-AMS data (O/C ratio) are shown in Fig. 3. The O/C ratios during the experiments were nearly constant with only a small increase in O/C observed over time. The O/C ratio decreased as the number of methyl substituents on the parent aromatic ring increased; ~0.6 for C₆ species (benzene, phenol, and catechol), ~0.5 for C₇ species (toluene and cresols), and ~0.4 for C₈ species (*m*-xylene and dimethylphenols). The decrease in O/C is approximately consistent with the increasing number of carbons in the parent aromatics, indicating that the methyl substituents did not play a major role in the SOA formation mechanism. Therefore the H-abstraction from methyl substituents is not likely to be an important route to aromatic SOA formation under low NO_x conditions. The O/C ratios of SOA between aromatic hydrocarbons and corresponding phenolics were similar, suggesting the significance of multi-generational reactions.

Real-time SOA density measured by the APM-SMPS is shown in Fig. 4. The SOA densities were observed to be

**Fig. 3.** Time series of the O/C ratio of SOA formed from aromatic hydrocarbons and phenolic compounds.

initially high (~1.8 g cm⁻³), which could be due to high density of nucleating species. The final SOA densities were in the range of 1.3–1.4 g cm⁻³, in reasonable agreement with previous studies (Ng et al., 2007; Sato et al., 2010). Although Bahreini et al. (2005) observed weak correlation between effective density and relative contribution of *m/z* 44 signal to total organic signal of AMS, the final SOA densities were found to be independent of elemental composition of SOA from aromatics tested in this study (Fig. 5). Therefore a constant SOA density (1.4 g cm⁻³) is applied to all the experiments in this study.

3.3.2 Filter analysis

Chemical composition of SOA was analyzed by off-line filter analysis. Samples were directly infused to the

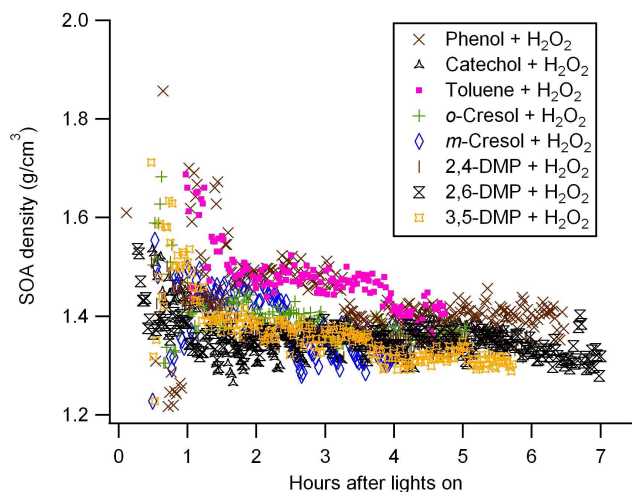


Fig. 4. Time series of the density of SOA formed from aromatic hydrocarbons and phenolic compounds.

ESI/APCI-TOFMS. Although direct infusion of SOA extract into ESI-MS is often done (e.g., Altieri et al., 2006; Camredon et al., 2010; De Haan et al., 2009; Heaton et al., 2009), caution must be taken in interpreting the mass spectrums due to possible formation of adducts or analyte-solvent reaction products (Bateman et al., 2008; Pratt and Prather, 2011). Mass spectra obtained by ESI/APCI-TOFMS are shown in Fig. 6. High mass accuracy measurements enabled determination of empirical formula typically within 5 ppm mass error. Inclusion of nitrogen or halogens in the formula calculation did not yield reasonable formulae. Major ions in each spectrum contained the same number of carbon as reactants (e.g., $C_6H_8O_6$ from phenol, $C_7H_{10}O_6$ from *o*-cresol, and $C_8H_{12}O_6$ from 2,4-DMP).

The possibility of adduct formation between acetic acid mobile phase modifier and analytes was investigated by changing acetic acid to formic acid; however, the major signals were still the same, indicating that the observed products are not adducts of the acid modifier. Acetonitrile was used in this study instead of methanol to reduce the risk of analyte-solvent reactions (particularly reactions of methanol and carbonyls or carboxylic acids) (Bateman et al., 2008). Tests substituting methanol as an organic solvent did not alter the major MS signal distribution indicating those MS signals did not result from analyte-solvent reaction. The agreement of carbon number and apparent CH_2 shift with increasing number of methyl substituents on the aromatic precursor suggests that these major signals are not likely to be adducts formed during ionization.

Since only formulae were determined and no structural information is available in this study, there are a number of possible structures such as unsaturated multi-functional ring-opening products (e.g., diacids, polyols). Although column separation using different types of reverse-phase column was

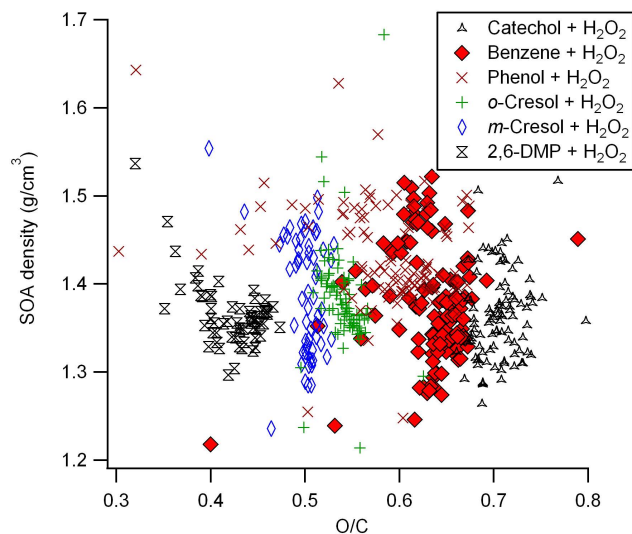


Fig. 5. The relationship between density and elemental compositions of SOA formed from aromatic hydrocarbons and phenolic compounds.

attempted, most of the major signals appeared in the non-retained peak, indicating that these species were too polar to be retained by conventional reversed-phase columns.

Another possible reaction products consistent with these formulae of the major signals are the bicyclic hydroperoxides formed from the reaction of HO_2 and bicyclic peroxy radicals (Fig. 7). The formation of bicyclic peroxy radical intermediate from OH-initiated reaction of aromatic hydrocarbons in gas-phase has been reported experimentally and theoretically (Andino et al., 1996; Birdsall et al., 2010; Birdsall and Elrod, 2011; Glowacki et al., 2009; Huang et al., 2008; Wyche et al., 2009). Johnson et al. (2004, 2005) predicted bicyclic hydroperoxides as one of the predominant aerosol species from aromatic hydrocarbons. Currently, organic peroxides such as hydroperoxides and peroxyhemiacetals have been suggested to be important component of SOA (e.g., monoterpene ozonolysis; Docherty et al., 2005, isoprene photooxidation; Surratt et al., 2006, naphthalene photooxidation; Kautzman et al., 2010, and toluene photooxidation; Sato et al., 2007). Reinnig et al. (2008) reported that the parent ion from two hydroperoxide surrogates, cumene hydroperoxide and tert-butylhydroperoxide were not seen by either negative or positive mode ESI and APCI. Further, only fragments for cumene hydroperoxide were observed for ESI and APCI operating only in the positive mode and for tert-butylhydroperoxide only in the positive APCI mode. This poses an uncertainty in our detection of bicyclic hydroperoxide in this study; however, since the tentatively proposed bicyclic hydroperoxide are highly oxidized and multi-functional (with an oxygen-bridge), other functional groups may enable the ionization.

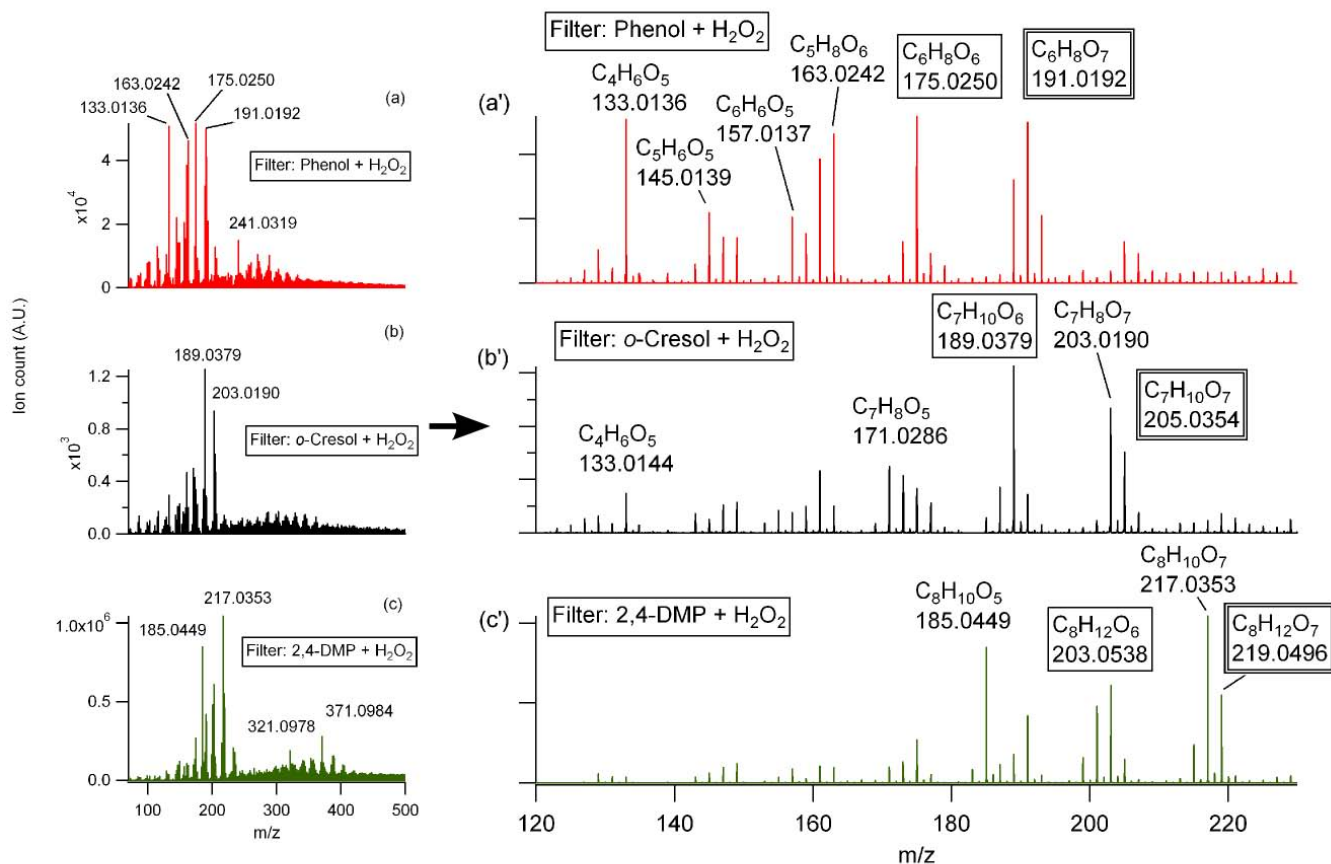


Fig. 6. ESI/APCI-ToF mass spectra of SOA formed by OH reaction with phenolic compounds.

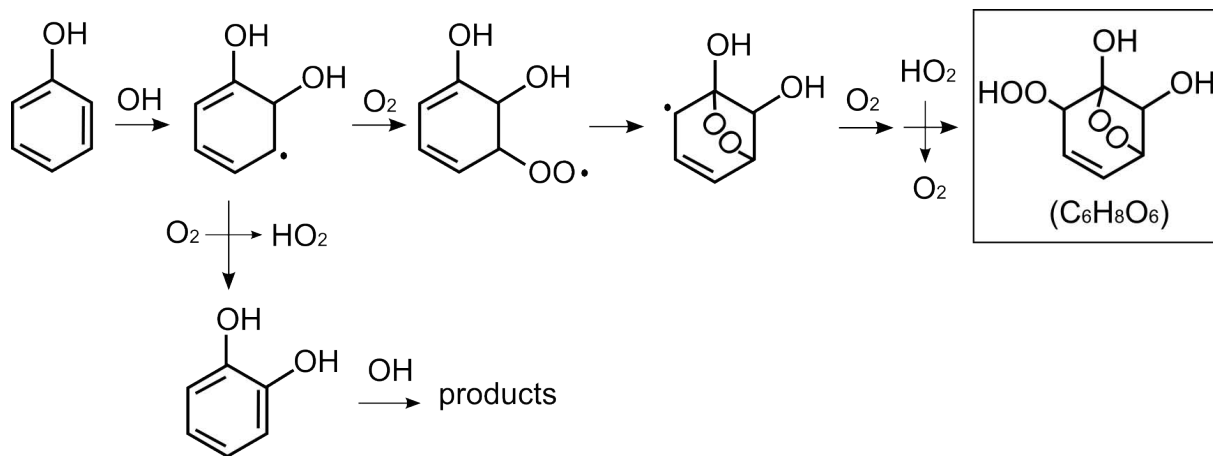


Fig. 7. Possible formation pathway of a bicyclic hydroperoxide ($C_6H_8O_6$) from OH reaction with phenol in the absence of NO_x inferred from aromatics oxidation mechanisms (e.g., Calvert et al., 2002; Johnson et al., 2005). Catechol formation from phenol is reported to be approximately 80% (Olariu et al., 2002).

The presence of peroxides was investigated by conducting phenol photooxidation experiments under excess NO. In excess NO condition, the (bicyclic) peroxy radicals rapidly react with NO to form the alkoxy radical, which is suggested

to undergo decomposition (Atkinson, 2000; Calvert et al., 2002). The resulting mass spectrum (after separating nitrophenolic species by a reverse phase column; not shown) indicated $C_6H_8O_6$ and $C_6H_8O_7$ were still present, suggesting

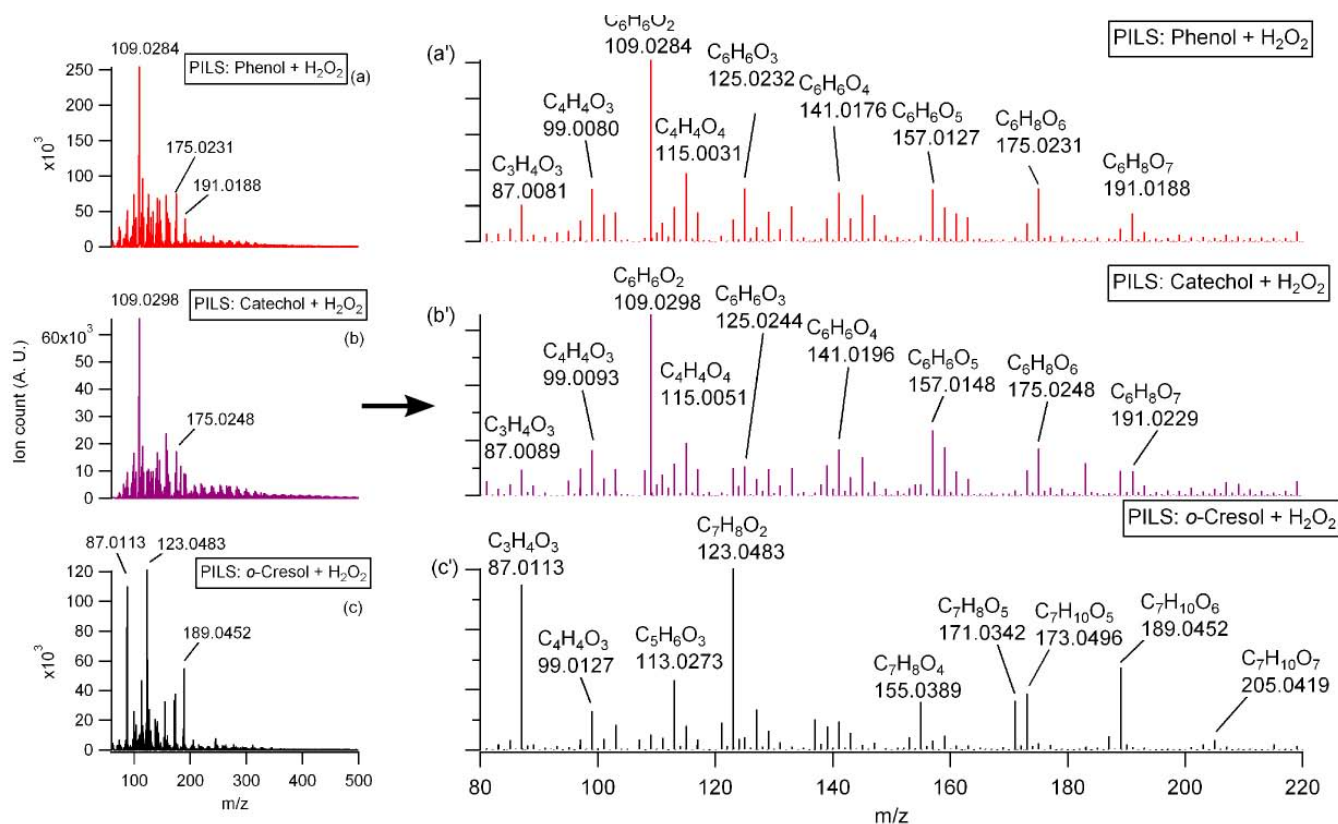


Fig. 8. PILS-ESI-ToF mass spectrums of SOA formed by OH reaction with phenolic compounds. (The spectrum for phenol (a) and catechol (b) is taken when SOA concentration was highest. For *o*-cresol (c), spectrum at highest C₇H₈O₂ is shown.)

that at least some fraction of C₆H₈O₆ and C₆H₈O₇ are formed via a non-peroxy radical route. Although uncertainty remains, it is still interesting that major signals in ESI/APCI-TOFMS matched the widely recognized bicyclic hydroperoxides. Additional analytical techniques, such as column separation of the highly polar species, derivatization, MS/MS or NMR, are necessary for unambiguous identification of the products.

3.3.3 PILS-TOFMS

Mass spectra obtained by PILS-ESI-TOFMS of SOA formed from OH reaction with phenol, catechol, and *o*-cresol are shown in Fig. 8. Major signals observed from off-line filter analysis were also observed by the on-line PILS-TOFMS such as *m/z* 175 and 191 from the phenol SOA mass spectrum (Fig. 8a). Since the PILS-TOFMS was operated without a denuder upstream, water soluble gas-phase compounds can potentially be collected by the PILS system. The highest signal in Fig. 8a (mass spectrum when SOA was highest), *m/z* 109 is catechol (C₆H₆O₂), which is consistent with previous gas-phase studies (80.4 % yield from phenol, Olariu et al., 2002). From *o*-cresol, methylcatechol (*m/z* 123) was observed. Although further reaction mechanisms of catechol

species is highly uncertain, a series of signals consistent with –OH addition to catechol was observed (C₆H₆O₂, C₆H₆O₃, C₆H₆O₄, C₆H₆O₅), which could imply successive addition of –OH group to the aromatic ring. Although the absence of column separation before TOFMS may introduce adduct formation, the agreement between carbon number of major products and reactants is obvious, and hence the major signals are unlikely to be artifacts. Additionally, the agreement between off-line filter samples and on-line PILS indicates that the major signals from off-line filter analysis are not likely to be artifacts formed during filter collection.

4 Conclusions

The significance of phenolic compounds as intermediate species of aromatic SOA and possible SOA formation mechanism in the absence of NO_x was investigated using the UCR/CE-CERT Environmental Chamber. SOA formation yield measurements coupled to gas-phase yield measurements indicate that approximately 20 % of the SOA of benzene, toluene, and *m*-xylene could be ascribed to the phenolic route. Initial SOA densities were as high as approximately 1.8 g cm⁻³ and eventually reached the range of 1.3–1.4 g cm⁻³, independent of elemental ratio (O/C) of

SOA tested in this study. The major products observed by ESI/APCI-TOFMS contained the same number of carbons as parent aromatics. Major signals from on-line PILS-TOFMS and off-line filter analysis agreed, with some additional possible water soluble gas phase products observed by PILS-TOFMS such as catechol.

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