Tropospheric Chemistry of Aromatic Compounds Emitted from Anthropogenic Sources

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Abstract

The kinetics and mechanisms associated with the atmospheric photooxidation of aromatic compounds emitted from anthropogenic sources are of seminal importance in the chemistry of the urban and regional atmosphere. Aromatic compounds readily react with hydroxyl radicals to lead to ozone and aerosol formation. However, over the years, difficulties have existed in unambiguously identifying the stable species formed. Thus, only 60–70% of the reacted carbon has been fully accounted for. This article summarizes the major advances that have been made towards elucidating the atmospheric chemistry of anthropogenic aromatic hydrocarbons using computational chemistry. In addition, the computational data are compared to experimental data, and areas for future advances in the community’s understanding of aromatic reactions through the use of computational chemistry calculations are discussed.

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1. INTRODUCTION

Aromatic compounds are of great abundance in the troposphere, comprising approximately 20% of the composition of non-methane volatile organic carbon [1]. It is well known that these compounds are abundant constituents of motor vehicle emissions [2], and several air sampling studies have been conducted that positively identify aromatic compounds in ambient air [1, and references therein]. Based on the data obtained, it is clear that aromatic compounds comprise a significant portion of the total non-methane organic carbon (NMOC) in many parts of the world. The percentages of aromatic hydrocarbons varies depending on the urban, suburban, or rural nature of the area.

While much research has been conducted in recent years on the reactions of biogenic ring structured hydrocarbons (i.e. α-pinene, and β-pinene, among others) [3–10], in comparison, much less work has been conducted on the reactions of aromatic hydrocarbons (i.e. toluene, m-xylene, p-xylene, etc.) [1, and references therein]. Recent modeling efforts have underscored the importance of aromatic compounds in relation to the chemistry of the free troposphere [11]. Also, recent chemical mechanism modeling work on aromatic compounds has suggested the need for additional studies to more accurately assess the reactions of aromatic compounds, since existing mechanisms cannot adequately predict the yields of products observed in experimental systems [12–15]. While laboratory data have provided some data to elucidate the mechanisms of these aromatic compounds, computational chemistry efforts have helped to further propel the understanding of these reactions. This article provides a review of the computational work that has been published regarding aromatic compounds, while simultaneously relating this information to existing experimental data to identify data gaps and areas of future need.

2. REACTIONS

2.1 Kinetic rate constants

The primary tropospheric oxidants are ‘OH, O₃, and NO₃, with ‘OH and O₃ reactions with hydrocarbons dominating primarily during daytime hours, and NO₃ reactions dominating at night. Rate constants for the reactions of many different aromatic compounds with each of the aforementioned oxidants have been determined through laboratory experiments [16]. The rate constant data as well as atmospheric lifetimes for the reactions of toluene, m-xylene, p-xylene, m-ethyltoluene, and 1,2,4-trimethylbenzene appear in Table 14.1. Only these particular aromatic compounds will be discussed in this review paper, since much of the computational chemistry efforts have focused on these compounds. When considering typical atmospheric concentrations of the major atmospheric oxidants, OH, O₃, and NO₃ of $1.5 \times 10^6$, $7 \times 10^{11}$, and $4.8 \times 10^8$ molecules cm$^{-3}$, respectively [17], combined with the rate constants, it is clear that the major atmospheric loss process for these selected aromatic compounds is reaction with the hydroxyl
Table 14.1 Overall rate constants and calculated lifetimes (τ) for the OH, O₃, and NO₃ reactions of selected aromatic compounds. Rate constant data are from Ref. [16]. Lifetimes are calculated assuming atmospheric concentrations for OH, O₃, and NO₃ of 1.5 × 10⁻⁶, 7 × 10¹¹, and 4.8 × 10⁸ molecules cm⁻³, respectively [17].

<table>
<thead>
<tr>
<th>Compound</th>
<th>OH reactions k at 298 K (cm³ molecule⁻¹ s⁻¹)</th>
<th>τ (days)</th>
<th>O₃ reactions k at 298 K (cm³ molecule⁻¹ s⁻¹)</th>
<th>τ (days)</th>
<th>NO₃ reactions k at 298 K (cm³ molecule⁻¹ s⁻¹)</th>
<th>τ (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>5.63 × 10⁻¹²</td>
<td>1.37</td>
<td>&lt;1 × 10⁻²⁰</td>
<td></td>
<td>7 × 10⁻¹⁷</td>
<td>344</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>23.1 × 10⁻¹²</td>
<td>0.33</td>
<td>2.6 × 10⁻¹⁶</td>
<td>93</td>
<td>5.0 × 10⁻¹⁶</td>
<td>48</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>14.4 × 10⁻¹²</td>
<td>0.54</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-Ethyltoluene</td>
<td>18.6 × 10⁻¹²</td>
<td>0.41</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2,4-Trimethylphenol</td>
<td>32.5 × 10⁻¹²</td>
<td>0.24</td>
<td></td>
<td></td>
<td>1.8 × 10⁻¹⁵</td>
<td>13</td>
</tr>
</tbody>
</table>

radical. This same conclusion can be drawn for other aromatic compounds as well as hydrocarbons in general. Thus, much of the past work that has been published on the reactions of aromatic hydrocarbons, either from an experimental or a computational perspective, focuses on their reactions with the OH radical.

2.2 Mechanisms

Despite the prevalence of aromatic compounds in the atmosphere, much work is still required to fully elucidate the atmospheric reaction mechanisms of these compounds. Approximately 60–70% of the reacted carbon can be fully accounted for as products (either in the gas or aerosol phases) in aromatic/OH systems [1,16].

Aromatics react with OH radicals either through an abstraction mechanism to form water and eventually an aromatic aldehyde, or through addition to form an aromatic–OH adduct. The aromatic–OH adduct subsequently reacts with O₂ or NO₂ to form a series of stable ring-retained products or aromatic–OH peroxy radicals. The aromatic–OH peroxy radicals subsequently react to form intermediate radicals that eventually undergo ring fragmentation to form smaller oxygenated organic compounds. Products identified in laboratory studies of the toluene–OH, m-xylene–OH, p-xylene–OH, and 1,2,4-trimethylbenzene–OH systems appear in Table 14.2.

Several experiments have been conducted to characterize the nature, mechanism, and extent of aerosol formation from gas-to-particle conversion [18–25]. Despite all of these studies, much information has yet to be elucidated. Because of the inability to fully account for all of the reacted carbon through experimental studies, computational studies have been performed to more fully understand the possible reaction mechanisms, thereby providing guidance to experimentalists on the nature of compounds expected to form.

2.2.1 Initial OH attack on the Aromatic ring

The aromatic–OH reaction proceeds initially either by OH addition to or abstraction from the aromatic ring to form a radical (Reaction 1a) or an aromatic–OH adduct (Reaction 1b). Note that the “R” in all of the reactions presented subsequently refers either to a hydrogen atom or an alkyl group. The depiction is meant...
TABLE 14.2  Products detected in laboratory studies of the OH-initiated reactions of selected aromatic compounds [1]

<table>
<thead>
<tr>
<th>Parent aromatic compound</th>
<th>Ring retained products</th>
<th>Ring fragmented products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>o-Cresol</td>
<td>Glyoxal</td>
</tr>
<tr>
<td></td>
<td>m-Cresol</td>
<td>Methyl glyoxal</td>
</tr>
<tr>
<td></td>
<td>p-Cresol</td>
<td>Methylbutenedial</td>
</tr>
<tr>
<td></td>
<td>m-Nitrotoluene</td>
<td>Hydroxymethylbutenedial</td>
</tr>
<tr>
<td></td>
<td>o-Nitrotoluene</td>
<td>Oxoheptadienal</td>
</tr>
<tr>
<td></td>
<td>p-Nitrotoluene</td>
<td>Methylhydroperoxide</td>
</tr>
<tr>
<td></td>
<td>Benzaldehyde</td>
<td>Formaldehyde</td>
</tr>
<tr>
<td></td>
<td>2-Methyl-p-benzoquinone</td>
<td>Hexadienyl</td>
</tr>
<tr>
<td></td>
<td>Benzyl alcohol</td>
<td>Hydroxyoxoheptadienyl</td>
</tr>
<tr>
<td></td>
<td>Benzyl nitrate</td>
<td>Maleic anhydride</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>2,4-Dimethylphenol</td>
<td>Glyoxal</td>
</tr>
<tr>
<td></td>
<td>2,6-Dimethylphenol</td>
<td>Methylglyoxal</td>
</tr>
<tr>
<td></td>
<td>4-Nitro-m-xylene</td>
<td>Formaldehyde</td>
</tr>
<tr>
<td></td>
<td>5-Nitro-m-xylene</td>
<td>3-Methyl-5-furanone</td>
</tr>
<tr>
<td></td>
<td>m-Tolualdehyde</td>
<td>4-Oxo-2-pentenal</td>
</tr>
<tr>
<td></td>
<td>3-Methylbenzyl nitrate</td>
<td></td>
</tr>
<tr>
<td>p-Xylene</td>
<td>2,5-Dimethylphenol</td>
<td>Glyoxal</td>
</tr>
<tr>
<td></td>
<td>2-Nitro-p-xylene</td>
<td>Methylglyoxal</td>
</tr>
<tr>
<td></td>
<td>p-Tolualdehyde</td>
<td>3-Hexene-2,5-dione</td>
</tr>
<tr>
<td></td>
<td>4-Methylbenzyl nitrate</td>
<td>Formaldehyde</td>
</tr>
<tr>
<td></td>
<td>2,5-Dimethyl p-benzoquinone</td>
<td>2-Methylbutenedial</td>
</tr>
<tr>
<td></td>
<td>2,5-Dimethylfuran</td>
<td></td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>2,4-Dimethylbenzaldehyde</td>
<td>3-Hexene-2,5-dione</td>
</tr>
<tr>
<td></td>
<td>2,5-Dimethylbenzaldehyde</td>
<td>3-Methyl-3-hexene-2,5-dione</td>
</tr>
<tr>
<td></td>
<td>3,4-Dimethylbenzaldehyde</td>
<td>2-Methylbutenedial</td>
</tr>
<tr>
<td></td>
<td>2,4,5-Trimethylphenol</td>
<td>Biacetyl</td>
</tr>
<tr>
<td></td>
<td>2,3,5-Trimethylphenol</td>
<td>Methylglyoxal</td>
</tr>
<tr>
<td></td>
<td>2,3,6-Trimethylphenol</td>
<td>Glyoxal</td>
</tr>
</tbody>
</table>

to allow for discussion of a generalized mechanism:
FIGURE 14.1 MP2/6-311G** optimized OH–toluene pre-reactive complex. The indicated interatomic distances are in units of Angstroms.

The OH interaction (either via an addition or abstraction route) with toluene has been studied using computational chemistry [26–29]. Uc et al. [28] specifically showed that the mechanism for OH interaction with toluene involves the formation of a stable pre-reactive complex (depicted in Figure 14.1) when the radical approaches the aromatic ring at a van der Waals distance.

Many radical-molecule reaction mechanisms have been shown to be complex and to involve a fast equilibrium between the reactants and the pre-reactive complex, followed by the irreversible formation of products. An example of this mechanism for toluene is shown in Reactions 1bi and 1bii, respectively,

\[
C_6H_5CH_3 + OH \rightleftharpoons \frac{k_1}{k^{-1}} [C_6H_5CH_3 \cdot \cdot \cdot OH], \quad \text{(Reaction 1bi)}
\]

\[
[C_6H_5CH_3 \cdot \cdot \cdot OH] \rightarrow C_6H_5(OH)CH_3. \quad \text{(Reaction 1bii)}
\]

The formation of these complexes has often been discussed [30], especially in radical–molecule reactions where their existence is needed to explain observed negative activation energies. It has been shown [31] that pre-reactive complexes are fundamental in that they guide the reaction from the beginning, and also have a strong effect on the reaction barrier height. Pre-reactive complexes may be expected to be responsible for the selectivity of the aromatic–OH adducts formed in (Reaction 1bii). Indeed, considerable spin density is transferred from the radical to the complex [32]. Smith and Ravishankara [33] have described these complexes, which are generally too short-lived to be detected, and whose existence can only be inferred by the way they affect the overall behavior of the reaction. However, in recent work by Davey et al. [34], a π-type hydrogen-bonded complex between the hydroxyl radical and acetylene leading to the addition reaction has been stabilized in the reactant channel well. This complex has been
characterized by infrared action spectroscopy in the OH overtone region spectrum.

A recent theoretical study by Uc et al. [29] on the abstraction pathway for toluene (Reaction 1a), utilized DFT-BHandHLYP calculations with a 6-311++G(d,p) basis set to determine the energetics followed by rate constant determinations using transition state theory. These results indicated a theoretical rate constant for abstraction of an H atom from toluene of $2.4 \times 10^{-13}$ molecules cm$^{-3}$ s$^{-1}$ at 298.15 K. As expected, the results indicated that abstraction of the hydrogen atom preferentially occurred at the substituent methyl group, rather than on the aromatic ring. This calculated theoretical value for abstraction of a hydrogen atom from toluene is consistent with the determination (from experimental studies) that abstraction is a relatively minor pathway for the OH/toluene system, occurring less than approximately 10% of the time for methyl benzenes [1,16,17].

Several computational studies have been conducted on (Reaction 1b) to examine the relative importance of the initial OH addition to the ipso, ortho, meta, and para sites on the aromatic ring. A summary of the computational approaches used by different authors and the reaction energies calculated for the OH-adduct formation for the case of toluene appear in Table 14.3. The data indicate that (a) there are several possible likely sites of attack, (b) energy differences between the adduct isomers are very small (i.e. in general less than 2 kcal mol$^{-1}$), (c) the level of theory used to perform the geometry optimizations and energy calculations may influence results considerably, and (d) the inclusion of zero point energy corrections may change the predicted dominance of a particular OH attack site.

Addition at the ipso site had been assumed to be unlikely because of steric hindrance arguments. Therefore, past studies by Bartolotti and Edney [26] and Andino et al. [27] had not focused on this pathway. For comparison, ortho and ipso toluene–OH adducts are represented in Figure 14.2 as calculated at the MP2/6-311++G** level. Several recent calculations have emphasized the possible role of ipso adducts in toluene [29,36,37] in xylene [38,39], and in another aromatic (phenol [40]). Rather than a steric hindrance, a stabilization due to interactions between the lone pair on the oxygen atom and two methyl hydrogen atoms is observed in some of the recent studies.

To place the results of Table 14.3 into context, it is important to consider experimental data. Based on temperature dependent rate constants, an experimental value for the reaction energy associated with OH radical addition to the toluene ring is $-16.5 \pm 5$ kcal mol$^{-1}$ [41]. With the exception of the data of Bartolotti and Edney [26], all of the computational results fall within the range of values determined in a laboratory setting. It is well known that there is experimental evidence for the formation of O-, m-, and p-cresol from the toluene–OH adduct, with o-cresol dominating formation. Given that the formation pathway for the cresols proceeds through the formation of the toluene–OH adduct in (Reaction 1b), as discussed subsequently, the dominance of o-cresol suggests the dominance of attack at the or-
TABLE 14.3 Reaction energies (kcal mol\(^{-1}\)) for the formation of the ipso-, ortho-, meta-, and para-toluene/OH adducts

<table>
<thead>
<tr>
<th>Method basis set</th>
<th>Reaction energies (kcal mol(^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ipso</td>
<td>Ortho</td>
</tr>
<tr>
<td>DFT (DMOL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Modified basis set)</td>
<td>Not calculated</td>
<td>43.480*</td>
</tr>
<tr>
<td>UHF-PM3//B3LYP-DFT 6-31G(d,p)</td>
<td>Not calculated</td>
<td>-18.4*</td>
</tr>
<tr>
<td>B3LYP 6-31G(d,p)</td>
<td>-19.47*</td>
<td>-20.91*</td>
</tr>
<tr>
<td></td>
<td>-16.33</td>
<td>-17.56</td>
</tr>
<tr>
<td>PMP2 6-31G(d,p)</td>
<td>-19.65*</td>
<td>-19.03*</td>
</tr>
<tr>
<td>CCSD(T)/6-31G(d)//B3LYP/6-31G(d,p)</td>
<td>-15.54</td>
<td>-14.09</td>
</tr>
<tr>
<td>BHandHLYP 6-311G(d,p)</td>
<td>-13.41</td>
<td>-13.74</td>
</tr>
<tr>
<td>CCSD(T)/6-311G(d,p)//MP2/6-311G(d,p)</td>
<td>-14.71</td>
<td>-13.50</td>
</tr>
</tbody>
</table>

* Numbers marked with an asterisk do not include zero-point corrections.

FIGURE 14.2 MP2/6-311++G** optimized OH–toluene ortho and ipso adducts. Indicated interatomic distances are in Angstroms.

The ipso site. It is important to note that attack at the ipso site cannot lead to the prompt formation of a cresol. Therefore, simply looking at cresol yields is insufficient to examine the relative importance of addition at each of the sites on the aromatic
TABLE 14.4  Summary of published work on aromatic systems other than toluene studied using computational approaches

<table>
<thead>
<tr>
<th>System</th>
<th>Predicted initial OH attack site (percentages, if stated)</th>
<th>Method</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Xylene + OH</td>
<td>Ipso (0.99)</td>
<td>MP2</td>
<td>Uc et al. [38]</td>
</tr>
<tr>
<td></td>
<td>Ipso (0.78), ortho (0.07), para (0.13)</td>
<td>B3LYP</td>
<td>Uc et al. [38]</td>
</tr>
<tr>
<td>m-Xylene + OH</td>
<td>Ortho</td>
<td>B3LYP</td>
<td>Andino et al. [27]</td>
</tr>
<tr>
<td></td>
<td>Ortho (0.61), ipso (0.30)</td>
<td>B3LYP and MP2</td>
<td>Uc et al. [38]</td>
</tr>
<tr>
<td>p-Xylene + OH</td>
<td>Ortho</td>
<td>B3LYP</td>
<td>Andino et al. [27]</td>
</tr>
<tr>
<td></td>
<td>Ortho (0.23), ipso (0.77)</td>
<td>MP2</td>
<td>Uc et al. [38]</td>
</tr>
<tr>
<td></td>
<td>Ortho (0.81), ipso (0.19)</td>
<td>B3LYP</td>
<td>Uc et al. [38]</td>
</tr>
<tr>
<td></td>
<td>Ortho (0.8), ipso (0.2)</td>
<td>B3LYP</td>
<td>Fan and Zhang [39]</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene + OH</td>
<td>Ipso</td>
<td>B3LYP</td>
<td>Andino et al. [27]</td>
</tr>
<tr>
<td>m-Ethyltoluene</td>
<td>Ortho</td>
<td>B3LYP</td>
<td>Andino et al. [27]</td>
</tr>
</tbody>
</table>

ring. However, it is important to also emphasize that a 100% carbon balance on the reacted aromatic and products has not yet been achieved in laboratory studies for any of the aromatic/OH systems.

New reaction pathways for the ipso toluene–OH adduct have been proposed [28]. Elimination of the methyl group on toluene is not an expected route, and, in order to stabilize, the ipso adduct probably transforms. Hydroxyl radical addition at the ipso site of toluene has been postulated to lead to formation of o-cresol through an OH shift from the ipso to the ortho position on the ring [28]. This formation might be used to explain the relatively large amount of observed products that originate from the ortho toluene–OH adduct. Calculations were performed using the MP2/6-311G** method to examine the direct migration of OH from the ipso to the ortho position on the ring [32]. A large barrier, of 22 kcal mol$^{-1}$ was obtained, suggesting that this is not a likely pathway and that migration, if it occurs, must be catalyzed, perhaps, by another molecule (such as oxygen). Tiecco [42] has suggested that in addition to a shift of the OH from the ipso to the ortho position, radical ipso intermediates could evolve in several ways: ipso substitution, return to the starting products, coupling with other radicals, and the rearrangement and fragmentation of a group remote from the ipso position. Additional computational work is needed to further examine these theories.
Formation of \( o \)-cresol is consistent with the primary products that have been identified in toluene–OH chamber studies. It is important to note, however, that cresols quickly react with NO\(_3\), thus leading to the prompt formation of additional ring-retained components. Thus, additional computational studies that specifically examine the formation of products from the subsequent reactions of the primary products with OH and NO\(_3\) are needed.

Computational studies of the OH interactions with other methyl substituted aromatic compounds have been performed by only a few research groups [27,32,38,39]. Table 14.4 details the systems studied and the major results published in the literature.

Based on the data in Table 14.4, OH radical attack appears to occur at either the *ortho* or the *ipso* positions on the aromatic rings. The predicted position of attack appears to vary based on the method used to calculate the energies (i.e. MP2 versus B3LYP), as is clearly evident in the \( o \)-xylene/OH and \( p \)-xylene/OH systems. In all cases, the MP2 method tends to favor the *ipso* adduct much more than DFT.

### 2.2.2 Aromatic–OH adduct reaction with O\(_2\)

Under atmospheric conditions, oxygen is expected to rapidly react with the aromatic–OH adduct, forming either an alcohol (Reaction 2a) or a peroxy radical (Reaction 2b):

\[
\begin{align*}
\text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R} \\
\cdot & \quad \cdot & \quad \cdot & \quad \cdot \\
\text{H} & \quad \text{OH} & \quad \text{HO}_2 & \quad \text{HO}_2 \\
\end{align*}
\]

Several computational chemistry studies have focused on the reactions of O\(_2\) with aromatic–OH adducts [27,43–45]. These studies are in good agreement, indicating that the aromatic–OH adduct will add O\(_2\) to form the corresponding peroxy radical, as seen in (Reaction 2b).

### 2.2.3 Reactions of the OH–aromatic adduct with NO and NO\(_2\)

The aromatic OH adduct formed in (Reaction 1b) can react with NO\(_2\) according to a series of different pathways (Reactions 3a–3e). Experimental data have indicated the formation of stable nitroaromatic products (stable product formed in
(Reaction 3a)) from chamber studies:

While several studies have also pointed out that nitroaromatic products are more characteristic of laboratory studies where high NO\textsubscript{x} mixing ratios are employed rather than the ambient environments where lower NO\textsubscript{x} mixing ratios exist, understanding the formation mechanisms of these nitroaromatic compounds is critical to properly defining the reaction mechanisms for aromatic compounds. The only computational study to date that probed the NO\textsubscript{2} reaction with the aromatic–OH adducts is that of Andino et al. [27], and their work considered only the reactions of the most likely aromatic–OH adduct, as predicted from the computational results. However, theoretical work involving NO\textsubscript{2} tends to be complicated by symmetry problems, so that reaction energy profiles are difficult to obtain.

2.2.4 Reactions of the peroxy radical
The peroxy radical formed in (Reaction 2b) is expected to cyclicize to form a corresponding bicyclic radical (Reaction 4) or react with nitric oxide via an abstraction mechanism to form the corresponding aromatic oxy radicals (Reaction 5a):

The only studies to date that examined the competing pathways for the peroxy radical are those of Andino et al. [27] (focused on the peroxy radicals from toluene, \textit{m}-xylene, \textit{p}-xylene, 1,2,4-trimethylbenzene, and \textit{m}-ethyltoluene), García...
Cruz et al. [43] and Suh et al. [46] (focused on toluene), and Fan and Zhang [39] focused on p-xylene). Computational chemistry studies predict the preferential cyclization of the peroxy radical over reaction with NO to form the aromatic oxy radical. Cyclization to specifically form a 5-member ring structure is highly preferred, as might be expected by considering the potential ring strain that would form with a 4-member ring, or the relatively large ring that would form with a 6-member structure. It is important to point out that past studies of the reactions of the aromatic peroxy radicals considered addition of NO to the peroxy radical to form an aromatic nitrate species. For completeness, computational chemistry studies to examine the potential formation of aromatic nitrate species through addition of NO to the peroxy radical according to (Reaction 5b) would be important:

2.2.5 Reactions of the bicyclic radical

The bicyclic radical is expected to quickly add O2 (Reaction 6) to form a bicyclic peroxy radical which subsequently reacts with NO to form a bicyclic oxy radical (Reaction 7). It is the subsequent reaction of the bicyclic oxy radical that leads to the formation of ring fragmentation products (Reaction 8):

The only fundamental computational chemistry studies of the subsequent reactions of the bicyclic radicals that have been performed are for the toluene–OH and p-xylene–OH systems [46,47]. These results examined not only the potential for Reactions 6 and 7 to occur with the toluene/OH and p-xylene/OH systems, but the potential for isomerization of the bicyclic radicals to form stable epoxide radicals. In the toluene/OH system, the formation of the epoxide radicals was predicted to be unlikely given that the barriers to formation were relatively high. Computational studies of the p-xylene/OH system predicted the likely formation of the epoxide radicals. Clearly, additional aromatic systems must be studied to ver-
ify other potential pathways for reaction. This is probably one of the single most
needed areas of research required to further elucidate the reactions of aromatic–
OH systems, especially considering that recent chemical mechanism modeling
work by Bloss et al. [12,13] shows poor correlation between predicted results and
experimental data for the ring fragmented unsaturated dicarbonyl products.

2.2.6 Formation of secondary organic aerosol
During the gas-phase reactions of aromatic species, numerous products are
formed that have relatively low vapor pressures so as to lead to the formation
of secondary organic aerosols (SOA) either through nucleation or condensation
processes. As indicated previously, laboratory chamber studies have been con-
ducted in the past to identify the nature of the aerosols formed from the gas-phase
photooxidation of aromatic species, either in the presence or absence of seed
aerosols. Studies have, in general, found that a variety of factors, including the
concentration of NO$_x$, influence the generation of aerosols. However, the chemi-
cal mechanisms of SOA formation are not well understood, in part because of the
highly reactive nature of the first generation products.

It is expected that SOA formation will originate from a variety of pathways,
including cases where:

(I) A gas-phase product of the OH–aromatic reaction simply forms a liquid par-
ticle because of its vapor pressure, in the absence of any “seed” aerosol.
(II) A “seed” aerosol exists and the gas is taken up onto, but not into the aerosol.
(III) The same as condition (ii), but now the gas is taken up into the aerosol, thus
leaving more room for uptake on the surface.
(IV) Multiple gas-phase products from the OH–aromatic reaction interact to form
a critical cluster, and an aerosol is formed.

In general, one might expect the larger ring-retained products that are formed
from the reactions of aromatics to have relatively low vapor pressures, and there-
fore form SOA through mechanism I or IV, whereas the presence of smaller, non-
aromatic ring compounds in the aerosol are likely due to mechanisms II or III.
Experimental studies exist that detect both larger ring-retained compounds (e.g.
benzaldehyde and 2-methyl-4-nitrophenol) and smaller, more volatile non-ring re-
tained compounds (e.g. 3-methyl, 2,5-furanedione, dihydro 2,5-furanedione, and
2,5-furanedione) in the SOA formed from the photooxidation of toluene [18,21].
However, it is important to note that the smaller non-ring retained compounds
were not detected in studies where the overall aerosol mass was lower [24],
thus providing support for mechanism II (or III). In addition, others have pos-
tulated the direct formation of aerosols from aromatic photooxidation that con-
sist of oligomeric forms of polyketone ring-fragmented products [21,24]. These
oligomers are believed to decompose to their monomeric forms during the course
of typical laboratory analyses.
3. SUMMARY: AREAS FOR FUTURE WORK

Although many advances have been made in understanding the tropospheric reactions of anthropogenic aromatic compounds, additional work is clearly needed. Specific areas of foci for future closely coordinated computational and laboratory-based studies are in the areas of:

- the relative importance of aromatic–OH-addition pathways,
- the gas-phase reactions of ring-retained products,
- secondary organic particle formation mechanisms.

As indicated previously, computational studies have indicated the importance of OH addition to multiple positions on a methylbenzene ring. To further characterize the importance of OH addition to each position, computational chemistry studies that further probe the potential products of addition to all positions (including the ipso position) are needed. Specifically, potential pathways that lead to the generation of ring-retained products that may preferentially form low volatility gas-phase products that partition to form aerosols should be probed.

Of critical need are computational chemistry studies that help to explain the formation of secondary organic aerosols in aromatic–OH systems. Two types of computational studies are needed: ones that focus on the generation of ring-retained semi-volatile products, and those that focus on examining the energies of attraction of a gas-phase molecule to a particle surface. Since computational chemistry studies are now being conducted to examine the properties of nanomaterials [48], it seems plausible that these same techniques could be applied to study the potential for secondary organic aerosol formation and atmospheric transformation, considering the interactions of a gas-phase specie with a spherical particle comprised of elemental carbon, organic carbon (such as ones that might be formed according to Cases I or IV), or inorganic composition (such as ammonium sulfate, sodium chloride, or mineral dust i.e. typical aerosols found in the ambient). In each case, computational chemistry calculations could assist in determining the resulting components on the surface, extent of interaction of additional material with the surface, or the extent of surface coverage of gases onto seed aerosols.

REFERENCES