

**Final Technical Report**

**Laboratory Investigation of Organic Aerosol Formation from  
Aromatic Hydrocarbons**

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Our work for this DOE funded project includes: (1) measurements of the kinetics and mechanism of the gas-phase oxidation reactions of the aromatic hydrocarbons initiated by OH; (2) measurements of aerosol formation from the aromatic hydrocarbons; and (3) theoretical studies to elucidate the OH-toluene reaction mechanism using quantum-chemical and rate theories.

**(1) Measurements of Gas-Phase Kinetics and Mechanism**

Work has been accomplished to develop laboratory instrumentation to conduct kinetic and mechanistic measurements of the aromatic hydrocarbon reactions initiated by OH, using chemical ionization (CIMS) and proton transfer reaction mass spectrometry (PTRMS) and tandem mass spectrometry (MS/MS). Experiments have been carried to detect intermediate radicals for the OH-aromatic hydrocarbon reactions using a high-pressure flow reactor coupled to CIMS detection at MIT. A PTR-MS has been developed at Texas A&M for the subcontract of the project. The PTRMS has been used to quantify product yields for compounds such oxygenated and nitrated organic compounds.

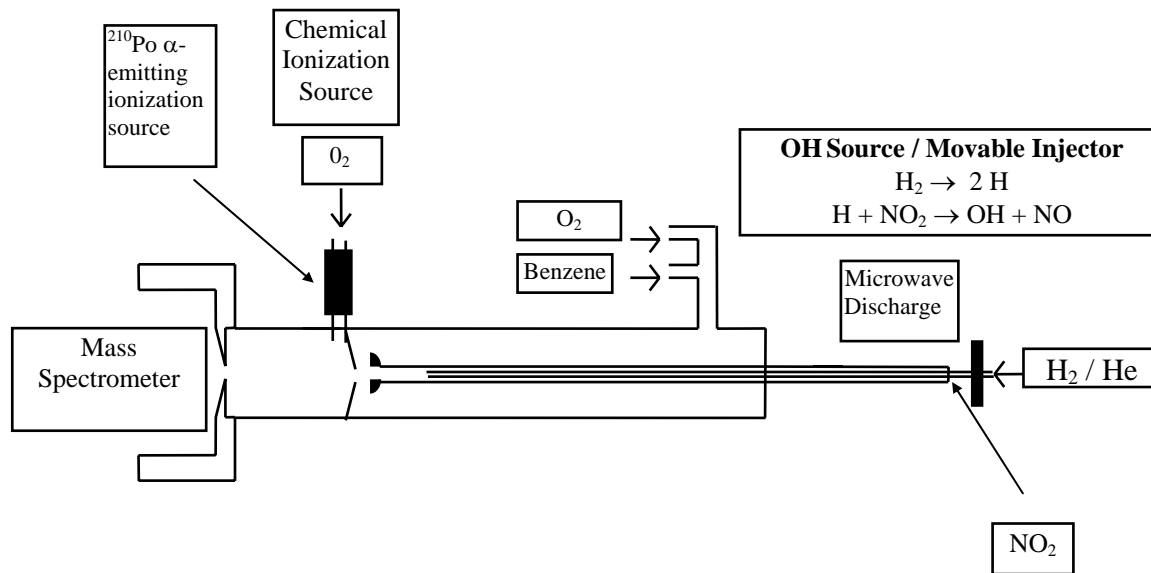
A primary effort was focused on the quantification of the phenol yield from the benzene + OH reaction over a broad range of experimental conditions using CIMS coupled to a turbulent flow-tube. The benzene system, a proxy also for other aromatic systems, was extensively studied with the following objectives: (1) to elucidate the cause of existing differences between flow-tubes compared to simulation chamber work (2) to determine the time scale of phenol formation.

**Parameter space probed for phenol formation from the benzene + OH reaction**

Phenol formation from the OH-radical initiated oxidation of benzene was investigated using a 1.2m long flow-tube of 1" inner diameter, equipped with a movable injector, as shown in Figure 1. OH-radicals were generated from microwave discharge of trace amounts of purified H<sub>2</sub> in 3 SLPM He (UHP) at 154 ±4 Torr to produce H-atoms that were subsequently titrated from addition of NO<sub>2</sub> inside the movable injector. The amount of OH-radicals that reacted in a given experiment was quantified from the relative decrease of an OH-tracer substance, such as 2,5-dimethylphenol, which was added in trace amounts.

The amount of phenol formed per benzene reacted is denoted the phenol-yield. The phenol-yield was measured as a function of the following parameters: (1) variable injector position; (2) variable amounts of H<sub>2</sub> in the generation of OH-radicals; (3) addition of ppm-levels of oxygen in the OH-source (via MWD); (4) efficiency of H-atom titration to OH-radicals by adding variable

amount of NO<sub>2</sub>; (5) addition of trace amounts of NO to the OH-source region; (6) oxygen mixing ratio of the carrier gas was varied from 10% to 98%; (7) benzene concentration was varied from 8x10<sup>11</sup> to 4x10<sup>13</sup> molecule cm<sup>-3</sup>; (8) NO levels in the flow-tube were varied up to about 10<sup>13</sup> molecule cm<sup>-3</sup>; (9) OH-radical lifetime was varied from 20 to 1000 msec; (10) the fraction of OH-radicals to react with the OH-tracer substance was varied from 10 to 80%. For all experiments the operating temperature and pressure were held constant at 298±3 K and 154±4 Torr, respectively.



**Figure 1. Schematic Diagram of the CIMS Experimental Setup**

The phenol yield decreased when (a) high concentrations of HO<sub>2</sub> radicals were present; and (b) at lower OH-lifetimes. It was found insensitive to (c) ppm-levels of oxygen that were being added to the He-carrier gas of the MWD used to generate OH-radicals, (d) in the presence of low but variable NO<sub>x</sub> levels. Phenol yields increased with (e) experiments that used longer lifetimes of OH-radicals, and (f) trace amounts of NO being added in the generation of OH-radicals. The highest phenol-yield (i.e., 53.8±8%) was observed at an OH-lifetime of 650ms, or about 7x10<sup>11</sup> and 10<sup>10</sup> molecule cm<sup>-3</sup> of benzene and 2,5-dimethylphenol, respectively. Systematically lower phenol-yields were measured at shorter OH-lifetimes, with values below 30% were typical for OH-lifetimes below 30 ms. The observed differences were highly significant within the overall experimental error, which was about 15%.

Our experimental results demonstrate that the oxidation mechanism of benzene, the simplest of aromatic hydrocarbons, is sensitive to the conditions under which experiments are performed. Previous findings had shown that high concentrations of NO<sub>x</sub> (above 5x10<sup>12</sup> molecule cm<sup>-3</sup>, i.e., typically above those observed even in the polluted atmosphere) deviate the pathways of benzene oxidation [Volkamer *et al.*, 2002; Klotz *et al.*, 2002]. Further, high radical concentrations had been suggested at the core of apparent contradictory findings with regard to the presence of hexadienedials among first-generation oxidation products from the benzene + OH reaction in the presence of moderately low concentrations of NO<sub>x</sub>, which are observed in flow systems [Berndt *et al.*, 1999], but are not observed in simulation chambers [Volkamer *et al.*, 2001; Klotz *et al.*,

2002]. The possible role of high radical concentrations to deviate oxidation pathways is compatible with our results. Particularly, activation energies of radical-type intermediates (i.e., OH-adducts and subsequent peroxy radicals) carry excess energies of 10 to 40 kcal/mol [Lay *et al.*, 1996; Suh *et al.*, 2003].

As chamber data is derived at much lower (atmospherically relevant) radical levels, results obtained from chambers may be more atmospherically relevant. Our results demonstrate that it is possible to find experimental conditions in flow tubes that approximate phenol-yields from chamber-type setups, enabling experiments at much shorter time-scales which are more economic and less time-intensive to carry out. Our results help to set first boundaries on how this can be accomplished, i.e., for OH-lifetimes above 250 ms. A comparison of the phenol-yields from this work to literature values is presented in Table 1.

**Table I. Comparison of phenol-type yields with literature data.**

Experiment	Yield% (Product)	Time scale of the Experiment	Experimental Setup
<u><i>OH + Benzene</i></u>	(phenol)		
This work	48.7 ±5.6	50 ms	Flow-tube
[Berndt and Boge, 2006]	60 ±10	10 min	Flow chamber (no NOx)
[Volkamer <i>et al.</i> , 2002]	53.1 ±6.6	5 min to 2 hours	Chamber (low NOx)
[Berndt and Boge, 2001]	32	50 ms	Flow-tube
[Berndt <i>et al.</i> , 1999]	23 ±7	50 ms	Flow-tube
[Bjergbakke <i>et al.</i> , 1996]	25 ±5	few min	Chamber / Pulse radiolysis
<u><i>OH + Toluene</i></u>	(cresols)*		
This work	18.8 ±2.1	50 ms	Flow-tube
[Klotz <i>et al.</i> , 1998]	17.9 ±2.7	5 min to 2 hours	Chamber (low NOx)
[Smith <i>et al.</i> , 1998]	17.9 ±1.3	2 min	Flow chamber (low NOx)

\*combined o-, m-, p-cresol

### **Time scale of phenol formation**

The mixing time of Benzene and OH-radicals in the flow-tube is few ms, and considerably shorter than the reaction time which was varied between 35 and 75 ms, depending on the injector position. We find that the phenol yield does not depend on the injector position. An upper limit for the time-scale of phenol formation is thus derived as 35ms.

### **Formation of phenol-type compounds from other aromatic hydrocarbons**

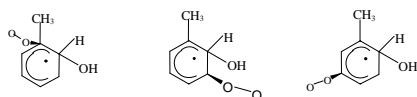
Using a similar approach described above, the yield of phenol-type compounds was investigated from the OH-radical initiation of toluene, and first experiments on further aromatics have been started. The results obtained for the toluene system are shown in Table 1; they are in excellent agreement with previous findings on much longer timescale. For toluene, no dependence of the cresol-yields was found for OH-lifetimes ranging between 50 and 850 ms. Just as benzene, the formation of cresols from toluene occurs on the time-scale of ms (upper limit).

## (2) Experimental Studies for SOA Formation

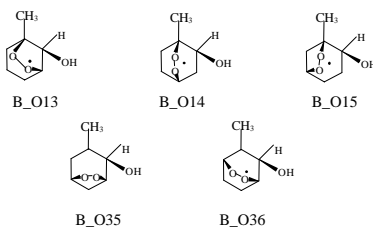
An experimental setup for investigation of secondary organic aerosol formation has been developed. This system includes a differential mobility analyzer (DMA), a condensation particle count (CPC), a diffusive aerosol chamber (DAC). We have performed experimental studies to investigate new particle formation involving low-volatility organic compounds. Atmospheric aerosols often contain a substantial fraction of organic matter, but the role of organic compounds in new nanometer-sized particle formation is highly uncertain. Our laboratory experiments show that nucleation of sulfuric acid is considerably enhanced in the presence of aromatic acids. Theoretical calculations identify the formation of an unusually stable aromatic acid–sulfuric acid complex, which likely leads to a reduced nucleation barrier. The results imply that the interaction between organic and sulfuric acids promotes efficient formation of organic and sulfate aerosols in the polluted atmosphere because of emissions from burning of fossil fuels, which strongly affect human health and global climate.

## (3) Theoretical Studies Using Quantum-Chemical and Rate Theories

Atmospheric photochemical oxidation of toluene is mainly initiated by attack from hydroxyl radical OH. The toluene-OH reaction results in minor H-atom abstraction from the methyl group and major OH addition to the aromatic ring (about 90%). The OH-toluene adducts react with O<sub>2</sub> either by O<sub>2</sub> addition to form (primary) peroxy radicals or by H-abstraction to yield phenolic compounds. The later channel accounts for about 16% of the total products. The fate of the peroxy radicals is governed by competition between reaction with NO to form alkoxy radicals and cyclization to form bicyclic radicals. The bicyclic radicals undergo unimolecular rearrangement to form epoxide radicals or bimolecular reaction with O<sub>2</sub> to form (secondary) bicyclic peroxy radicals. The mechanistic complexity of the toluene oxidation further arises from multiple isomeric pathways at each reaction stage. For example, O<sub>2</sub> addition to the ortho adduct occurs at 1, 3, or 5 on the ring,



The next step involves formation of bicyclic radicals with an O-O bridge across the benzene ring, forming five possible isomers.



The bicyclic radicals may isomerize to form eight possible epoxide radicals. The detailed mechanism of toluene oxidation, however, remains highly speculative. In previous experimental

product studies, the carbon balance is less than 50%, and interpretation of the identified reaction products is hindered due to the existence of multiple reaction pathways and steps.

We have performed theoretical studies of the aromatic peroxy, bicyclic, epoxide, and bicyclic peroxy radicals from the OH-toluene reactions. The quantum chemical computations were carried out similarly to those in our previous work. Briefly, geometry optimization and vibrational frequency calculations were executed using the DFT method at the B3LYP/6-31G(d,p) level of theory. The DFT geometries were then employed in single-point energy calculations using CCSD(T)/6-31G(d). A basis set correction factor was applied to the CCSD(T) energetics, corresponding to the CCSD(T)/6-31G(d) + CF method. Additional calculations were conducted using CASSCF to confirm the energetics of the OH-toluene reaction.

Our results resolve several controversial issues and refine our understanding of the mechanism of toluene oxidation in the atmosphere. Initial OH addition occurs primarily at the ortho and para positions and represents the major isomeric branching step. The reaction of the adduct with O<sub>2</sub> to form primary peroxy radicals is characterized by a reversible process, with all peroxy radical isomers being likely to form. The relative stability and activation barriers of the peroxy radicals, however, have little effect on isomeric branching, since propagation of the toluene oxidation is largely determined by the exit channel of the peroxy radicals. Ozone production from the primary peroxy radicals is unimportant, since the peroxy radicals mainly cyclize to produce the bicyclic radicals rather than react with NO. Rearrangement of bicyclic radicals to more stable epoxides is too slow to matter because of the higher activation barriers, and we conclude that there is negligible formation of epoxide carbonyls from the epoxide intermediates. At each OH addition site, only one isomeric pathway *via* a bicyclic peroxy radical is accessible. The consecutive reactions of bicyclic peroxy radicals facilitate conversion of NO to NO<sub>2</sub> (and hence O<sub>3</sub> formation), and subsequent ring cleavage leads to formation of several unsaturated anhydrides (dihydro-2,5-furandione, 2,5-furandione, and 3-methyl-2,5-furandione) which have been detected as the primary SOA components. Our thermochemical and kinetic data allow for a quantitative assessment of the formation potential of ozone, epoxide carbonyls, and SOA. The results also explain previous product observations and provide guidance for future experimental and field studies to identify intermediates, stable products, and SOA components from the oxidation of toluene in the atmosphere.

### **Publications related to this project**

- (1) Suh, I., D. Zhang, R. Zhang, L.T. Molina, and M.J. Molina, Theoretical study of OH addition to toluene, *Chem. Phys. Lett.* **364**, 454-462 (2002).
- (2) Lei, Wenfang, R. Zhang, L.T. Molina, and M.J. Molina, Theoretical study of chloroalkenylperoxy radicals, *J. Phys. Chem.*, **106**, 6415-6420 (2002).
- (3) Lei, W., D. Zhang, R. Zhang, L. T. Molina, and M. J. Molina, Rate constants and isomeric branching of the Cl-isoprene reaction, *Chem. Phys. Lett.*, **357**, 45-50 (2002).

- (4) Zhang, R., I. Suh, J. Zhao, D. Zhang, E.C. Fortner, X. Tie, L.T. Molina, and M.J. Molina, Atmospheric new particle formation enhanced by organic acids, *Science* **304**, 1487-1490 (2004).

### References:

- Berndt, T. and O. Boge, *Physical Chemistry Chemical Physics*, 3, 4946, 2001.
- Berndt, T. and O. Boge, *Physical Chemistry Chemical Physics*, 8, 1205-1214, 2006.
- Berndt, T., O. Boge, and H. Herrmann, *Chemical Physics Letters*, 314, 435, 1999.
- Bjergbakke, E., Sillesen, A., Pagsberg, P., *J. Phys. Chem.* **100** (14), 5729-5736, 1996..
- Klotz, B., S. Sorensen, I. Barnes, K. H. Becker, T. Etzkorn, R. Volkamer, U. Platt, K. Wirtz, and M. Martin-Reviejo, *Journal of Physical Chemistry A*, 102, 10289-10299, 1998.
- Klotz, B., R. Volkamer, M. D. Hurley, M. P. S. Andersen, O. J. Nielsen, I. Barnes, T. Imamura, K. Wirtz, K. H. Becker, U. Platt, T. J. Wallington, and N. Washida, *Physical Chemistry Chemical Physics*, 4, 4399-4411, 2002.
- Lay, T. H., J. W. Bozzelli, and J. H. Seinfeld, *Journal of Physical Chemistry*, 100, 6543-6554, 1996.
- Smith, D. F., C. D. Mciver, and T. E. Kleindienst, *Journal of Atmospheric Chemistry*, 30, 209-228, 1998.
- Suh, I., R. Y. Zhang, L. T. Molina, and M. J. Molina, *Journal of the American Chemical Society*, 125, 12655-12665, 2003.
- Volkamer, R., B. Klotz, I. Barnes, T. Imamura, K. Wirtz, N. Washida, K. H. Becker, and U. Platt, *Physical Chemistry Chemical Physics*, 4, 1598-1610, 2002.
- Volkamer, R., U. Platt, and K. Wirtz, *Journal of Physical Chemistry A*, 105, 7865-7874, 2001.