Correction

Correction for “Reassessing the atmospheric oxidation mechanism of toluene,” by Yuemeng Ji, Jun Zhao, Hajime Terazono, Kentaro Misawa, Nicholas P. Levitt, Yixin Li, Yun Lin, Jianfei Peng, Yuan Wang, Lian Duan, Bowen Pan, Fang Zhang, Xidan Feng, Taicheng An, Wilmarie Marrero-Ortiz, Jeremiah Secrest, Annie L. Zhang, Kazuhiko Shibuya, Mario J. Molina, and Renyi Zhang, which was first published July 17, 2017; 10.1073/pnas.1705463114 (Proc Natl Acad Sci USA 114:8169–8174).

The authors note that, due to a printer’s error, Table 2 appeared incorrectly. The corrected table appears below.

Table 2. Summary of activation energy ($E_a$, kcal·mol$^{-1}$), reaction energy ($\Delta E_r$, kcal·mol$^{-1}$), rate constant ($k$, cm$^3$·molecule$^{-1}$·s$^{-1}$), and branching ratio ($\Gamma$) of the OH–toluene reactions at 298 K

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Quantity</th>
<th>Ortho</th>
<th>Meta</th>
<th>Para</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene + OH → OH-adduct</td>
<td>$E_a$</td>
<td>1.2</td>
<td>2.1</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>$\Delta E_r$</td>
<td>−15.5</td>
<td>−14.6</td>
<td>−14.4</td>
</tr>
<tr>
<td></td>
<td>$k$</td>
<td>$2.7 \times 10^{-12}$</td>
<td>$7.4 \times 10^{-13}$</td>
<td>$1.2 \times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>$\Gamma$ (%)</td>
<td>74, 80.6*, 52†, 59‡</td>
<td>21, 14.3*, 34†, 14‡</td>
<td>3, 5.1*, 11†, 5‡</td>
</tr>
<tr>
<td>OH-adduct + O$_2$ → Cresol</td>
<td>$E_a$</td>
<td>4.4, 3.7§</td>
<td>4.1</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>$\Delta E_r$</td>
<td>−26.3, −28.7§</td>
<td>−26.8</td>
<td>−27.0</td>
</tr>
<tr>
<td></td>
<td>$k$</td>
<td>$1.6 \times 10^{-15}$, $0.9 \times 10^{-15}$, $5.1 \times 10^{-15}$</td>
<td>$2.4 \times 10^{-15}$, $1.7 \times 10^{-15}$</td>
<td>$1.2 \times 10^{-16}$</td>
</tr>
<tr>
<td>OH-adduct + O$_2$ → RO$_2$*</td>
<td>$E_a$</td>
<td>7.5, 7.1§</td>
<td>0.8</td>
<td>−0.4</td>
</tr>
<tr>
<td></td>
<td>$\Delta E_r$</td>
<td>−8.5, −2.9§</td>
<td>−12.2</td>
<td>−9.5</td>
</tr>
<tr>
<td></td>
<td>$k$</td>
<td>$1.5 \times 10^{-16}$, $2.8 \times 10^{-16}$, $1.0 \times 10^{-17}$, $3 \times 10^{-15}$</td>
<td>$2.5 \times 10^{-14}$, $1.5 \times 10^{-14}$</td>
<td>$4.5 \times 10^{-15}$</td>
</tr>
<tr>
<td>α-Cresol + OH → DHMB</td>
<td>$E_a$</td>
<td>−0.4</td>
<td>−15.6</td>
<td>−4.3 $\times 10^{-11}$, $4.3 \times 10^{-11}$</td>
</tr>
<tr>
<td></td>
<td>$\Delta E_r$</td>
<td>−24.3</td>
<td>$4.3 \times 10^{-11}$, $4.3 \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k$</td>
<td>$5.4 \times 10^{-12}$</td>
<td>$4.3 \times 10^{-11}$, $4.3 \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td>DHMD + O$_2$ → 1,2-dihydroxy-3-methylbenzene</td>
<td>$E_a$</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
</tr>
</tbody>
</table>

The value is from the present work, except noted otherwise. $\Gamma$ is calculated by excluding those from the OH ipso addition and the H-abstraction pathways.

*From ref. 30.
†From ref. 22, including a branching ratio of 3% for OH ipso addition.
‡From ref. 23, including a branching ratio of 15% for ipso position.
§From ref. 26.
¶From ref. 10.
#From ref. 41.
Reassessing the atmospheric oxidation mechanism of toluene

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Contributed by Mario J. Molina, June 8, 2017 (sent for review April 3, 2017; reviewed by Sasha Madronich and Fanggun Yu)

Photochemical oxidation of aromatic hydrocarbons leads to tropospheric ozone and secondary organic aerosol (SOA) formation, with profound implications for air quality, human health, and climate. Toluene is the most abundant aromatic compound under urban environments, but its detailed chemical oxidation mechanism remains uncertain. From combined laboratory experiments and quantum chemical calculations, we show a toluene oxidation mechanism that is different from the one adopted in current atmospheric models. Our experimental work indicates a larger-than-expected branching ratio for cresols, but a negligible formation of ring-opening products (e.g., methylglyoxal). Quantum chemical calculations also demonstrate that cresols are much more stable than their corresponding peroxy radicals, and, for the most favorable OH (ortho) addition, the pathway of H extraction by O₂ to form the cresol proceeds with a smaller barrier than O₂ addition, to form the peroxy radical. Our results reveal that phenolic (rather than peroxy radical) formation represents the dominant pathway for toluene oxidation, highlighting the necessity to reassess its role in ozone and SOA formation in the atmosphere.

Toluene is the most abundant aromatic hydrocarbon in the atmosphere and is emitted primarily from anthropogenic sources, i.e., from automobiles and industrial activities. Photochemical oxidation of toluene plays an important role in tropospheric ozone and secondary organic aerosol (SOA) formation, profoundly impacting air quality, human health, and climate (1–8). However, the detailed chemical mechanism of toluene oxidation in the atmosphere remains uncertain (4, 5). Oxidation of toluene is initiated by the hydroxyl radical (OH): the initial OH–toluene reaction results in minor H abstraction (about 10%) and major OH addition (about 90%) (9–20). The H-abstraction pathway leads to the formation of benzaldehyde, whose oxidative pathway is well established (4, 5). The OH addition pathway results in the formation of methylhydroxydehydro-adienyl radicals (the OH–toluene adducts), which subsequently react with O₂ via three plausible pathways (Fig. 1). I.e., H abstraction to yield phenolic compounds and hydroperoxy radicals (HO₂⋯) (pathway I), O₂ addition to form primary peroxy radicals or RO₂ (pathway II), and H abstraction and subsequent O-bridge formation to aromatic oxide/oxepin (pathway III). Previous theoretical studies have suggested that the primary RO₂ cyclizes to form bicyclic radicals, rather than reacting with NO to form alkyl radicals under atmospheric conditions (16). The bicyclic radicals then undergo unimolecular rearrangement, followed by H abstraction, to form epoxide intermediates or react with O₂ to form secondary RO₂, followed by ring cleavage to produce small α-carbonyl compounds such as glyoxal and methylglyoxal (16, 21). The toluene–oxide/methyloxepin channel remains speculative, and several previous quantum chemical calculations have shown a high barrier for this pathway (22–26). Numerous experimental studies have been performed to investigate the products from the OH–toluene reactions (2–5, 18, 27). For example, previous studies have reported a highly variable yield of cresols (11, 12, 15, 18, 19, 27), ranging from 9.0 to 52.9%. In addition, the yields of glyoxal and methylglyoxal determined from the previous studies are also conflicting, ranging from <4% to about 39% for glyoxal and <4 to 17% for methylglyoxal (12, 13, 18). From an atmospheric modeling perspective (2–5), ozone aromatics | oxidation | ozone | secondary organic aerosol | air pollution


Reviewers: S.M., National Center for Atmospheric Research; and F.Y., State University of New York at Albany.

The authors declare no conflict of interest.

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www.pnas.org/cgi/doi/10.1073/pnas.1705463114
formation from toluene oxidation is conventionally assumed with a large (65%) contribution from the production of RO₂ (pathway II) and a minor (18%) contribution from HO₂ formed with cresols (pathway I). Both RO₂ and HO₂ generated react with nitric oxide (NO) to yield nitrogen dioxide (NO₂), which subsequently undergoes photodissociation to lead to ozone formation. In addition, aromatic ring cleavage from the primary RO₂ and cresol pathways (pathways I and II) results in several products, including glyoxal, methylglyoxal, and low-volatility compounds that likely contribute to SOA formation (1-3, 8, 28-33).

In this study, we evaluated the detailed oxidation mechanism of the OH–toluene reactions by combining direct experimental measurements and quantum chemical and kinetic rate calculations, to improve the understanding of the pathways leading to ozone and SOA formation in the atmosphere.

**Results**

Fig. 24 depicts a mass spectrum (m/z = 95 to 135) of the OH–toluene reactions in the presence of O₃ and NO under our typical experimental conditions (SI Appendix, Fig. S1 and Table S1). The peaks at m/z = 107 and 109 correspond to protonated benzaldehyde (C₆H₅CHO⁺) and cresols (C₅H₆O⁺), respectively. The peak at m/z = 125 is attributed to dihydroxymethylbenzenes (C₆H₄O₂⁻), corresponding to the secondary products from the subsequent oxidation of cresols initiated by OH (33), to be discussed below. Although the oxymethyloxepin intermediates correspond to the same molecular weight (MW) as cresols, their formation is excluded because of a large activation barrier for this pathway (16). Fig. 2B displays single-ion monitoring of the three products, i.e., benzaldehyde, cresols, and dihydroxymethylbenzenes, versus consumed toluene. The ion–molecule reaction rate constants calculated using the average dipole orientation (ADO) theory (34-36) are 4.1 × 10⁻³⁹ cm⁻³ molecule⁻¹ s⁻¹, 2.5 × 10⁻³⁹ cm⁻³ molecule⁻¹ s⁻¹, 3.6 × 10⁻³⁹ cm⁻³ molecule⁻¹ s⁻¹, and 2.1 × 10⁻³⁹ cm⁻³ molecule⁻¹ s⁻¹ for benzaldehyde, cresols (averaged over α-, β-, and m-cresol), dihydroxymethylbenzenes (averaged over 1,2-dihydroxy-3-methylbenzene and 1,2-dihydroxy-4-methylbenzene), and toluene, respectively. The yields of those products are quantified to be (11.3 ± 2.0)% for benzaldehyde, (39.0 ± 5.0)% for cresols, and (8.9 ± 1.3)% for dihydroxymethylbenzenes. Table 1 summarizes our measured product yields, along with comparison with the previous studies.

The yield of 11.3% for benzaldehyde determined in our present work is in agreement with the previous studies reporting a range of 5 to 12% (9, 11, 12, 18). We determined a lower limit of 41.9% for the total branching ratio of the cresol pathway (pathway I), including those from the combined formation of cresols and dihydroxymethylbenzenes. Our estimated cresol yield is much higher than that from most of the previous studies (12, 15, 18, 19, 27). For example, another experimental investigation using a flow reactor in conjunction with chemical ionization mass spectrometry (CIMS) detection reported yields of 28.1% at m/z = 109 and 23.5% at m/z = 125 (18). Although the sum of the two peaks from that work is comparable to our present value, the authors attributed the peak m/z = 125 to dienedial, which was speculated to form from O₂ addition to the OH–toluene adduct followed by breaking of the OH group (18). In addition, it was commented on by Jenkin et al. (37) that the experimental work by Baltaretu et al. (18) might be complicated by possible interferences, because both radicals and the reactants were premixed with high concentrations in the side arm of the flow reactor. Also noticeably, we measured a negligible yield of methylglyoxal (less than 2%), in contrast to the fact that the previous environmental chambers studies consistently observed large amounts of small α-carbonyl compounds (glyoxal and methylglyoxal) as the ring-opening products (12). The negligible formation of methylglyoxal in our current work is also distinct from our previous study of the OH–m-xylene reactions, in which larger amounts of methylglyoxal and the coproducts of glyoxal and methylglyoxal were detected and quantified (35). Baltaretu et al. (18) also reported a small methylglyoxal yield, i.e., less than 4%, consistent with our present work. We did not detect any compound with an MW similar to that of epoxides and estimated the epoxide yield to be less than 1%. Bartolotti and Edney (38) suggested the formation of epoxide intermediates based on the large stability for epoxides, which was further corroborated by Yu and Jeffries (39), who found...
Table 1. Product yields from OH-initiated oxidation of toluene in the presence of O₂ and NO

<table>
<thead>
<tr>
<th>Product</th>
<th>Previous work</th>
<th>This work*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic acid</td>
<td>11³, 5.3⁴, 6.0⁵</td>
<td>11.3 ± 2.0</td>
</tr>
<tr>
<td>(MW = 106)</td>
<td>4.9⁶, 5.8⁶, 6.5⁶</td>
<td></td>
</tr>
<tr>
<td>Cresols</td>
<td>52.9², 15.3⁶, 28.1⁶</td>
<td>39.0 ± 5.0</td>
</tr>
<tr>
<td>(MW = 108)</td>
<td>17.9⁴, 17.2², 25.2²</td>
<td></td>
</tr>
<tr>
<td>Dihyroxyxymethylbenzenes</td>
<td></td>
<td>8.9 ± 1.3</td>
</tr>
<tr>
<td>(MW = 124)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW = 96</td>
<td>(unidentified)</td>
<td>-5</td>
</tr>
<tr>
<td>Glyoxal (MW = 58)</td>
<td>9.8², 4.1², 23.8³</td>
<td>39.0⁶††</td>
</tr>
<tr>
<td>Methylglyoxal (MW = 72)</td>
<td>10.6², 5.5², 16.7³, &lt; 4%⁴</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Epoxides (MW = 140)</td>
<td>7.2³</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

*The yield represents the sum of all isomers, if applicable. Each value represents an average of more than 15 measurements at various experimental conditions (SI Appendix, Table S1). The uncertainty reflects both random error due to data scattering and systematic error related to the ion–molecule rate constants and possible fragmentation of the proton transfer reactions. Experimental conditions: [toluene] = (0.2 to 2) × 10⁻¹² molecules cm⁻³, [NO] = (0.5 to 2) × 10⁻¹⁰ molecules cm⁻³, [O₂] = (0.7 to 1.5) × 10⁻¹⁰ molecules cm⁻³, and [OH] = (0.8 to 8) × 10⁻¹⁰ molecules cm⁻³.

1From ref. 9.
2From ref. 11.
3From ref. 12.
4From ref. 18.
5From ref. 19.
6From ref. 27.
7From ref. 15.
8From ref. 13.

Experimental evidence for epoxides by detecting compounds with MW matching a series of epoxides resulting from the OH–toluene system. However, isomerization of bicyclic radicals to the more stable epoxide radical has been shown to possess significantly higher barriers than those of O₂ addition to form bicyclic peroxy radicals (16, 26).

To further elucidate the toluene oxidation mechanism and corroborate our experimental results, we performed quantum chemical calculation for OH addition to the ortho, meta, and para positions of toluene and the subsequent reactions with O₂. The potential energy surface diagrams of the toluene reactions are displayed in Fig. 3. OH addition at the ortho position occurs with the lowest activation energy (E_a) of 1.2 kcal mol⁻¹ and the largest reaction energy (ΔE_r) of −15.5 kcal mol⁻¹ among the three pathways (Fig. 3A and Table 2). The kinetics calculations presented in Table 2 show a rate constant of 2.7 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ for OH ortho addition at 298 K, which is an order of magnitude higher than those of OH addition to the meta and para positions. The branching ratio (Γ) of OH ortho addition is estimated to be 76%. The energetics, rate constants, and branching ratios of the OH–toluene reactions are summarized in Table 2, along with comparisons with previously published experimental and theoretical results.

We further evaluated the competing reactions of the OH–toluene adducts with O₂ lead to cresols (pathway I), organic peroxy radicals (RO₂⁻) (pathway II), and toluene oxide (pathway III). SI Appendix, Fig. S2 shows that the reaction of the ortho OH adduct with O₂ to form 1,2-toluene oxide occurs with an E_a value of 33.6 kcal mol⁻¹ and a ΔE_r value of 16.2 kcal mol⁻¹. Hence, the large activation energy and instability of the toluene oxide imply that its formation is thermodynamically and kinetically inhibited, in agreement with the previous studies (26). Our previous theoretical study indicated that, at each OH addition site, only one isomeric pathway via the peroxy radical is accessible for ring cleavage (16). On the basis of that study (16), the preferred peroxy radical corresponds to O₂ additions at the C₃ position (o-RO₂⁻ and p-RO₂⁻) for the ortho and para OH–toluene adducts, respectively, and at the C₆ position (m-RO₂⁻) for the meta OH–toluene adduct. As illustrated in Fig. 3A and Table 2, the E_a for form cresol is 4.4 kcal mol⁻¹, which is lower by 3.1 kcal mol⁻¹ than that to form o-RO₂⁻ and 0.5 kcal mol⁻¹ than m-RO₂⁻. The rate constant calculated is 1.6 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ for cresol formation (Table 2). In contrast, the E_a values to form p- and m-cresol are larger than those to form p- and m-RO₂⁻, although both p- and m-cresols are more stable (by about 15 kcal mol⁻¹) than p- and m-RO₂⁻, and the Γ values calculated are 9% and 3%, respectively, to form p- and m-cresol. The fate of the primary RO₂⁻ is governed by the competition between decomposition back to the OH–toluene adducts and O₂ cyclization to form bridged bicyclic radicals. SI Appendix, Fig. S3 shows that the E_a values for RO₂⁻ decomposition are smaller than those of cyclization for p- and m-RO₂⁻. Considering the large differences in the relative stability between cresols and primary RO₂⁻ and the high E_a values for p- and m-RO₂⁻ cyclization, the majority of RO₂⁻ formed from the two channels shifts reversibly to cresols by equilibrium. Hence, we conclude that cresol formation represents the nearly exclusive pathway for the OH-addition reactions.

We performed additional calculations of the subsequent reactions of p-cresol with OH and O₂ (Fig. 3B). OH addition at C₃ position of p-cresol occurs with an E_a value of −0.4 kcal mol⁻¹ and a ΔE_r value of −15.5 kcal mol⁻¹, corresponding to a rate coefficient of 4.3 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹ to form the dihydroxy-3-methylbenzene (DHMB) radical. Subsequently, the C₃ DHMB radical undergoes readily H abstraction by O₂, with an E_a value of 2.2 kcal mol⁻¹ and a ΔE_r value of −26.5 kcal mol⁻¹, corresponding to a rate coefficient of 5.4 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ to form 1,2-dihydroxy-3-methylbenzene (MW = 124). In contrast, the formation of aromatic ketones (also MW = 124) is both thermodynamically and kinetically hindered (SI Appendix, Fig. S4). Hence, our theoretical calculations support the formation of dihydroxy-3-methylbenzenes as the observed mass peak at m/z = 125. Our theoretical predictions agree with two previous experimental results, showing that the major oxidation products from the reactions of cresols with OH are dihydroxy-3-methylbenzenes with a molar yield of 65 to 73% (33, 40). Furthermore, a fast rate constant of (1.6 to 2.1) × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ for the reaction of dihydroxy-3-methylbenzenes with OH has been reported (40, 41).
indicating that the secondary products in the OH–toluene reactions undergo additional reactions with OH to form ring-opening products, including small α-carbonyl compounds (glyoxal and methylglyoxal), organic acids, and other low-volatility products (33). As is evident from Table 2, our calculations of the energetics, rate constants, and branching ratios for the OH–toluene reactions compare favorably with the previously available experimental and theoretical results, considering the respective uncertainties. For example, our calculated rate coefficient of \(4.3 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}\) for OH addition to o-cresol to form the DHMB radical is in agreement with the experimental value of \((4.3 \pm 0.5) \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}\) by Courtois et al. (41). Additional structural parameters for the reactants, key intermediates, transition states, and products involved in the OH–toluene reaction system are shown in SI Appendix, Fig. S5.

Hence, our combined experimental and theoretical methods (42–60) provide kinetic and mechanistic insights into the OH–toluene reactions. In particular, the agreement between our experimental and theoretical results provides compelling evidence for the dominant cresol yield but a negligible formation of methyloxyl from the initial steps of the OH–toluene reactions. In our work, we quantified only the most abundant peaks detected by our ion drift (ID)-CIMS scheme (using \(\text{H}_3\text{O}^+\)), accounting for about 64% of the tolune consumed. Another recent experimental study showed that OH addition to the aromatic ring of o-cresol leads to hydroxy, dihydroxy, and trihydroxy methyl benzoquinones and dihydroxy, trihydroxy, tetrahydroxy, and penta hydroxy toluenes, detected in the gas phase by CIMS (using \(\text{CF}_3\text{O}^-\) and \(\text{H}^+\text{OH}_2\)) where \(n = 1, 2, \ldots\) ) and in the particle phase using offline direct analysis with real-time mass spectrometry (33).

The differences in the measured product yields between our present experimental work and the previous laboratory experiments are explainable by the distinct conditions among the various experimental studies. Although the environmental chamber method has been applied extensively in development of parameterizations of formation of ozone and SOA for atmospheric modeling purposes (5), there were several intricate difficulties for the chamber approach, which made it rather unsuitable for detailed kinetic and mechanistic investigations of atmospheric hydrocarbon chemistry. Specifically, the limitations in the earlier chamber studies included longer reaction times (minutes to hours), higher reactant concentrations, wall loss, and the lack of online detection and quantification of reactive reactants and products by advanced analytical instruments. For example, an earlier experimental study reported a yield of 25.2% for the cresols from the OH–toluene reactions (27). The concentrations of the reactants used in that study were about \(4 \times 10^{13}\) and \(1 \times 10^{13}\) molecules cm\(^{-3}\) for toluene and NO\(_2\), respectively, and the OH concentration was not measured but was estimated from the decay in the tolune concentration. The concentrations of the reactants and products were measured by using offline gas chromatography with flame ionization detection. For the irradiation time of about 10 min during their chamber experiments, a lifetime of cresols was estimated to be about 250 s, using the rate coefficient of \(4.3 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}\) for the reaction between cresols and OH from this work and another experimental study (40). Hence, there likely existed significant secondary reactions of cresols with OH in the earlier chamber investigations, responsible for the measured lower cresol yields in the majority of those studies (12, 19, 27).

On the other hand, the technique of high-pressure turbulent flow reactors in conjunction with CIMS detection has been developed for accurate kinetic measurements of atmospheric gas-phase reactions (35, 36). The main advantage of the fast-flow reactor system lies in the ability to isolate the individual reaction steps and intermediates (35, 36, 42–44, 48, 61). Specifically, the CIMS technique allows for online detection of many reactants, intermediates, and products with high sensitivity and selectivity (35, 36). In addition, the ID-CIMS method provides quantification of the gas-phase concentrations of the intermediates and products without the necessity of calibration, which is advantageous because of the general difficulty in obtaining the authentic standards for products of hydrocarbon reactions (34–36). Furthermore, a turbulent flow condition effectively minimizes the wall loss (35, 36). In our experiments, the reactant concentrations were \(0.4 \times 10^{12}\) and \(5.4 \times 10^{12}\) molecules cm\(^{-3}\) for toluene and NO\(_2\), respectively, about one to two orders of magnitude lower than those of the environmental chamber studies (12, 19, 27). In addition, the OH concentration was directly quantified in our experiments, in a range of \(0.8 \text{ to } 8.0 \times 10^{10}\) molecules cm\(^{-3}\). Secondary reactions were
effectively suppressed in our experiments because of the short reaction time in the flow reactor (on the order of about 50 ms). The lifetime of cresols was estimated to be about 2 s in our experiments, responsible for our measured high yield of cresols. Under our experimental conditions, the self-reaction of the OH–toluene adducts was unimportant on the basis of this rate constant reported previously (10); this reaction was estimated to be about one to two orders of magnitude lower than that of the OH–toluene adduct with O₂. Furthermore, the absolute O₂ concentration had no effect for the competing reactions between the cresol and primary RO₂ pathways (i.e., pathway I vs. pathway II in Fig. 1), and the previous experimental results did not show a pressure dependence of the OH–toluene reaction system (61).

Also, our theoretical calculations indicate that formation of glyoxal and methylglyoxal via primary RO₂ is minimal, consistent with the absence in the ring-opening α-carbonyl products detected in our experiments. It is anticipated that those species are formed as the multigeneration products from the cresol pathway (33), likely similar to the cases with their high yields in the previous chamber experiments (12, 13).

**Conclusion**

Photochemical oxidation of toluene contributes importantly to ozone and SOA formation in urban environments, with key implications for air quality and human health (1–3, 62). In addition, by directly scattering and absorbing solar radiation and indirectly serving as cloud condensation nuclei or ice nuclei, SOA represents the major component in global radiative forcing on climate (1–3). For toluene oxidation, ozone formation in current atmospheric models is represented mainly via primary RO₂, with a minor contribution from cresols (5). In contrast, our experimental and theoretical results reveal the exclusive prompt productions of cresols and related peroxynitrates. 

The experiments were performed using a fast-flow reactor in conjunction with ID-CIMS. Detailed description of the ID-CIMS technique can be found in our previous publications (42–44).

Quantum chemical calculations were performed with the Gaussian 09 suite of programs (45). Geometry optimization of the relevant species were executed at the M06-2X level with the standard 6-311G(d,p) basis set [M06-2X/6-311G(d,p)]. This level of theory has been successfully applied to atmospheric reactions (46, 47). The vibrational analysis was made at the same level of theory to characterize the nature of each critical point along the potential energy surface (PES) with a local minimum or a transition state (exactly one imaginary frequency) and to make zero-point-energy corrections. The minimum-energy path was constructed with the intrinsic reaction coordinate theory to confirm that the transition state connected with the minima along the reaction path. Because kinetic calculations of the organic reaction systems were highly sensitive to the predicted energetics (48–51), single-point energy calculations were performed to refine the PES using the QCISD(T)/6-311+G(2d,p) level. The dual-level potential profile along the reaction path was further refined with the interpolated single-point energy method (52), in which extra single-point calculations were performed to correct the lower-energy reaction path. The dual-level dynamics approach was denoted as X/Y, where a single-point energy calculation at level X was used to correct the lower-level reaction path. The dual-level dynamics approach was denoted as X/Y, where a single-point energy calculation at level X was used to correct the lower-level reaction path.
ACKNOWLEDGMENTS. This work was supported by National Natural Science Foundation of China (41575122, 41375102, 21577177, and 41425015), Science and Technology Program of Guangzhou City (Grant 2017070010188), the Robert A. Welch Foundation (Grant A-1417), the Ministry of Science and Technology of China (Grant 2013CB955800), and a collaborative research program between Texas A&M University and the National Natural Science Foundation of China. B.P. was supported by a NASA Earth and Space Science Fellowship Program, and W.M.-O. was supported by the National Research Foundation Graduate Research Fellowship Program. Additional support for this research was provided by the Texas A&M University Supercomputing Facilities. The authors acknowledge the use of the Laboratory for Molecular Simulations at Texas A&M.

Experimental Method

The flow reactor was constructed from precision-bore Pyrex tubing of 2.0 cm i.d. and 75 cm in length. All surfaces exposed to the radicals were coated with halocarbon wax to reduce wall loss. A flow of nitrogen carrier gas (~30 l min\(^{-1}\)) was introduced into the flow reactor through an entrance port in the sidearm of the flow reactor (Fig. S1). A high-capacity (700 L min\(^{-1}\)) oil-free dry scroll pump was used to evacuate the flow reactor through an exit port in the downstream end of the reactor and the majority of the flow was directed through this port. Only a small fraction (about 1%) of the flow was extracted into the drift tube through a small orifice (1 mm). The pressure in the flow reactor was monitored by a capacitance manometer (1000 Torr full scale) in the downstream end of the flow reactor and was regulated at about 100 Torr under the turbulent flow condition (S1). All experiments were performed at 298 ± 2 K. Typical flow velocity in the flow reactor ranged from 800 to 1500 cm s\(^{-1}\). All the gas flows were monitored with calibrated mass flow meters (Millipore Tylan 260 Series). A quadropole mass detector was employed to filter and analyze the mass of the reactants, intermediates and products under the counting mode operation.

The hydroxyl radical OH was generated by the following reaction (S2),

\[ \text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO} \]  

OH radicals were produced by introducing a small amount of 3% H\(_2\)/He mixture through a microwave discharge followed by adding an excess of a 1% NO\(_2\)/He mixture downstream. OH radicals were detected using the negative reagent ion SF\(_6^-\). A negative voltage (-5 kv) was applied to the electrode of a corona discharge, by which the molecules of SF\(_6\) were ionized. SF\(_6^-\) and OH\(^-\) were then guided by a weak negative electric field (about 2.0 Volt cm\(^{-1}\)) through the drift tube. The OH concentration was estimated using the procedures similar to those in our previous studies (S2).

The products from the OH-toluene reactions were monitored and quantified using hydronium ion (H\(_3\)O\(^+\)) as the reagent ion. H\(_3\)O\(^+\) ions were generated by leaking a small amount of water vapor from a bubbler containing deionized water into the nitrogen flow, which then passed through the corona discharge. For the proton transfer reaction,

\[ \text{R} + \text{H}_3\text{O}^+ \rightarrow \text{H}_2\text{O} + \text{RH}^+ \]  

only a small fraction of reagent ions H\(_3\)O\(^+\) were converted into product the ion RH\(^+\), which was then detected by ID-CIMS. Calibration showed an excellent agreement between the toluene concentrations estimated from the known volumetric mixing ratio of the gas standard in the flow reactor and that measured by the ID-CIMS method (within 10%).

The experimental procedures for product measurements of the OH-initiated oxidation of toluene in the presence of O\(_2\) and NO were similar to those in our previous studies (S1, S3). The unique feature of the flow reactor/ID-CIMS technique lies in its capability of quantifying the product yields without the necessity of calibration with authentic samples, as we have previously...
demonstrated the application to quantify product yields from OH-isoprene and OH-m-xylene reactions (S1,S3). The product yield of the OH-toluene reactions is derived from,

\[ Y(\%) = \frac{k_{\text{prod}}}{k_{\text{tol}}} \times \frac{\Delta S_{\text{prod}}}{\Delta S_{\text{tol}}} \quad (3) \]

where \( k_{\text{prod}} \) and \( k_{\text{tol}} \) are the ion-molecule rate constants of the product and toluene with \( \text{H}_3\text{O}^+ \), respectively. \( \Delta S_{\text{prod}}/\Delta S_{\text{tol}} \) is the ratio of the protonated product formed to the protonated toluene consumed. The ion-molecule reaction constants were calculated from the ADO theory, which has been validated for accurate determination of the reaction rates between \( \text{H}_3\text{O}^+ \) and a series of hydrocarbons and oxygenated organic species (S1).

Commercially available toluene (Sigma-Aldrich, 99.5%) was used as received without further purification. The following gases were purchased from Matheson-Trigas: \( \text{H}_2 \) (99.999%), \( \text{O}_2 \) (99.98%), \( \text{NO}_2 \) (99.5%), \( \text{SF}_6 \) (99.996%) and from Aldrich Chemical: NO (98.5%). Deionized water (18M\( \Omega \cdot \text{cm} \)) was generated from Barnstead E-Pure Water System. Mixture of 0.5% toluene/He was prepared volumetrically in a 2 L glass bulb. The toluene mixture, along with a small carrier flow of \( \text{N}_2 \), was introduced into the flow reactor using a 10 sccm flow meter. NO was introduced through an activated carbon trap to remove impurities (e.g., \( \text{NO}_2 \)) before being added to the reactor.

References


### Table S1

Summary of the experimental conditions, i.e., the total flow, Reynolds number (\( Re \)), flow velocity (\( u \)), and concentrations of toluene, NO, \( \text{O}_2 \), and OH (in molecules cm\(^{-3} \)). Pressure in the drift tube \( P_{\text{dt}} = 1.7 \text{ Torr} \), pressure in the flow tube \( P_{\text{ft}} = 100 \text{ Torr} \), electric field gradient \( E = 58.8 \text{ V cm}^{-1} \), and \( E/N \) ratio = 104.4 Td.

<table>
<thead>
<tr>
<th>No.</th>
<th>Total Flow (l min(^{-1} ))</th>
<th>( Re )</th>
<th>( u ) (m s(^{-1} ))</th>
<th>[toluene] (10(^{12} ))</th>
<th>[NO] (10(^{11} ))</th>
<th>[( \text{O}_2 )] (10(^{14} ))</th>
<th>[OH] (10(^{10} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28.0</td>
<td>2361</td>
<td>15.6</td>
<td>0.4–1.6</td>
<td>5.4</td>
<td>7.0</td>
<td>7.6</td>
</tr>
<tr>
<td>2</td>
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<td>2319</td>
<td>15.3</td>
<td>0.4–1.7</td>
<td>5.4</td>
<td>7.1</td>
<td>1.5</td>
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<td>2354</td>
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<td>0.3–1.6</td>
<td>6.6</td>
<td>12</td>
<td>1.2</td>
</tr>
<tr>
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<td>0.2–1.7</td>
<td>6.2</td>
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<tr>
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<td>14</td>
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<td>27.5</td>
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<td>0.5–1.9</td>
<td>19</td>
<td>14</td>
<td>1.3</td>
</tr>
</tbody>
</table>
**Fig. S1.** Schematic diagram of the fast flow reactor coupled to an ion-drift chemical ionization mass spectrometry (ID-CIMS).

![Schematic diagram of the fast flow reactor coupled to an ion-drift chemical ionization mass spectrometry (ID-CIMS).](image)

**Fig. S2.** Potential energy surface of the competing abstraction and addition reactions of the OH-toluene adduct with $O_2$.

![Potential energy surface of the competing abstraction and addition reactions of the OH-toluene adduct with $O_2$.](image)
**Fig. S3.** Potential energy surface of the competing decomposition and cyclization for (A) o-RO₂, (B) p-RO₂, and (C) m-RO₂ (in kcal mol⁻¹).
Fig. S4. Potential energy surface of the subsequent reactions of o-cresol with OH radical and O₂.
**Fig. S5.** Key structural parameters for the reactants, intermediates, transition states, and products involved in the OH-toluene reaction system (in Å).

**A**

Toluene + OH → o-OH-adduct

![TS1](image1)

o-OH-adduct + O\(_2\) → o-cresol/o-RO\(_2\)

![TS2\(_{o-cresol}\)](image2) ![TS3\(_{o-RO2}\)](image3) ![o-Cresol](image4) ![o-RO\(_2\)](image5)

**B**

Toluene + OH → m-OH-adduct

![TS1](image6)

m-OH-adduct + O\(_2\) → m-cresol/m-RO\(_2\)

![TS2\(_{m-cresol}\)](image7) ![TS3\(_{m-RO2}\)](image8) ![m-Cresol](image9) ![m-RO\(_2\)](image10)