Tropospheric chemistry of aromatic compounds: Evidence for a rate-determining addition of NO$_3$ and OH to substituted toluenes

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Abstract

The OH- and the NO$_3$-initiated oxidation of aromatic hydrocarbons are major sinks for these species, observed in high concentrations in urban areas. This demands a better knowledge of mechanisms and reaction products. The plot of log k (six compounds) for para-substituted toluenes vs Hammett's $\rho$ for the reaction with OH has a $\rho = -2.3 \pm 0.2$; $r^2 = 0.96$. This is in line with the known rate-determining addition of OH involving a polar transition state. The analogous plot with NO$_3$ (nine compounds) gives $\rho = -4.3 \pm 0.6$; $r^2 = 0.87$. This negative value suggests again a polar transition state very similar to that occurring with OH and indicates a rate-determining addition for this reaction. Unrestricted Hartree-Foch (UHF)-Austin Model 1 (AM1) calculations suggest that the isomeric cyclohexadienyl radicals formed in the addition of OH or NO$_3$ to toluene and xylenes have similar stability, with the exception of the "ipso" adduct, which is less stable. The adducts formed by addition of oxygen or NO$_3$ to the cyclohexadienyl radicals are mixtures of substituted cis- and trans 1,2-dihydrobenzenes. AM1 calculations show that these isomers have very similar stability. Hence, the ring cleavage/rearomatization ratio in the reaction of OH with aromatic compounds is probably due to the stereochemical requirements of the E2 reaction leading to rearomatization. This mechanism is in fact possible only for the cis isomer.
Introduction

Alkylbenzenes are important constituents of gasoline. The high concentration of aromatics observed in urban areas demands a better knowledge of mechanisms and reaction products, in particular in regard to the possible formation of noxious compounds (e.g. nitroderivatives). Toluene is present in a polluted urban atmosphere in average concentrations of 97 μg m\(^{-3}\) and monocyclic alkylbenzenes in 284 μg m\(^{-3}\). The removal of these compounds from the troposphere is due to reaction with OH during the day and with NO\(_3\) during the night [1].

The reaction of OH with toluene is suggested to occur 90% via the ADD mechanism (Scheme 1: X = H) and 10% via the H-ABS mechanism [2]:

\[
\text{Ar-CH}_3 + \text{HO} \Rightarrow \text{Ar-CH}_2 + \text{HOH} \quad \text{H-ABS}
\]

Only the ADD mechanism operates with xylenes.

Scheme 1

![Scheme 1](image)

The radical adduct (1: X = H) formed in an equilibrium reaction will react with dioxygen or with NO\(_2\) to give the cis- and trans-dihydrobenzenes (3: X = H) and (4: X = H). The peroxyradical (3: X = H) will then generate ring fission products or phenols (6) [3]. The nitroderivative (4: X = H) will form nitroaromatics (5) [4]. \(k_1\) is rate-limiting and \(k_2\) is said to be much faster than \(k_3\).
Concerning the product-determining steps, ring cleavage predominates over phenol formation [6].

**Results and discussion**

Here we report evidence that the reaction of substituted toluenes with NO₃ (Scheme 1: X = NO₂) proceed with the same ADD mechanism to give in the rate-determining step the equilibrium formation of the cyclohexadienyl radical (1 : X = NO₂). This step will be followed by loss of nitric acid to give the benzyl radical (2) (the EL step) or by reaction with NO₂ to form nitroaromatics (5). k₁ is again rate-limiting. Concerning the product-determining steps, elimination of nitric acid to give the benzyl radical (2) predominates over the formation of nitroaromatics (5) [7].

A hydrogen atom abstraction mechanism is in operation at some extent also in this case [8]:

\[
\text{Ar-CH₃} + \text{NO₃} \Rightarrow \text{Ar-CH₂}^- + \text{HNO₃} \quad \text{H-ABS}
\]

The kinetic isotope effect was found to be 1.5-1.8 with xylenes, thus suggesting the predominance of the rate-determining ADD over a rate-determining H-ABS [9].

A Linear Free Energy Relationship (LFER) study could confirm the similarity of the two mechanisms [10]. Plotting log k vs the electronic parameters at the aromatic nucleus (a Hammett plot) with a group of para-substituted toluenes should give a negative \( \rho \) value for the rate-determining ADD mechanism due to the electrophilic nature of the radicals OX or a nearly 0 \( \rho \) value in the case of the H-ABS mechanism as already known with other H-ABS reactions at the aromatic methyl group [11].

The kinetics of the reaction between HO or NO₃ and substituted toluenes in the gas phase at 298 K was studied. Table 1 shows the rate constants obtained.

One problem for the Hammett plot was constituted by the fact that the attack of OX to a para-substituted toluene generates four isomeric adducts (Scheme 2). Hence the \( k_{exp} \) was a combination of four reaction rate constants. A Hammett plot could be found only in the case in which the same combination of these rate constants holds for the whole set of compounds studied.

Some reaction rates were already been measured [12]. The reaction rate of 4-isopropyltoluene with OH was measured independently, and that with 4-t-butylltoluene was measured for the first time. These data were necessary in order to have enough variability for the electronic parameter of the substituent (\( \sigma \)).
The plot of log k (six compounds) for para-substituted toluenes vs Hammett’s σ for the reaction with OH has a \( r = -2.3 \pm 0.2; r^2 = 0.96 \). This is in line with a rate-determining addition of OH involving a polar transition state (Figure 1).

**Table 1**

Rate constants of the reaction of substituted toluenes with NO₃ and OH at 298 K (\( k = \text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1} \)).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( k ) (NO₃)</th>
<th>Reference</th>
<th>( k ) (OH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-chlorotoluene</td>
<td>( &gt; 5 \times 10^{-17} ) (upper limit)</td>
<td>toluene</td>
<td>4-methoxybenzene</td>
</tr>
<tr>
<td>4-fluorotoluene</td>
<td>( &gt; 5 \times 10^{-17} ) (upper limit)</td>
<td>toluene</td>
<td>1,3,5-trimethylbenzene</td>
</tr>
<tr>
<td>3-chlorotoluene</td>
<td>( &gt; 5 \times 10^{-17} ) (upper limit)</td>
<td>toluene</td>
<td>1,3,5-trimethylbenzene</td>
</tr>
<tr>
<td>4-ethyltoluene</td>
<td>( 4.57 \pm 0.73 \times 10^{-16} )</td>
<td>4-methoxybenzene</td>
<td>4-methoxybenzene</td>
</tr>
<tr>
<td></td>
<td>( 7.71 \pm 1.10 \times 10^{-16} )</td>
<td>1,3,5-</td>
<td>ethylene</td>
</tr>
<tr>
<td></td>
<td></td>
<td>trimethylbenzene</td>
<td>15.94 ± 1.30 \times 10^{-12}</td>
</tr>
<tr>
<td>3-ethyltoluene</td>
<td>( 4.4 \times 10^{-16} )</td>
<td>1,3,5-</td>
<td>13.96 ± 0.89 \times 10^{-12}</td>
</tr>
<tr>
<td>4-isopropyltoluene</td>
<td>( 9.98 \pm 0.15 \times 10^{-16} )</td>
<td>trimethylbenzene</td>
<td>4-methyltoluene</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4-methoxybenzene</td>
<td>ethylene</td>
</tr>
<tr>
<td>4-t-butyltoluene</td>
<td>( 5.99 \pm 0.45 \times 10^{-16} )</td>
<td>1,3,5-</td>
<td>4-methyltoluene</td>
</tr>
<tr>
<td></td>
<td>( 7.15 \pm 0.45 \times 10^{-16} )</td>
<td>trimethylbenzene</td>
<td>13.96 ± 0.89 \times 10^{-12}</td>
</tr>
<tr>
<td>4-methoxytoluene</td>
<td>( 3.12 \pm 0.54 \times 10^{-15} )</td>
<td>4-methyltoluene</td>
<td>1,3,5-trimethylbenzene</td>
</tr>
<tr>
<td>3-methoxytoluene</td>
<td>( 2.16 \pm 0.40 \times 10^{-15} )</td>
<td>1,3,5-</td>
<td>1,3,5-trimethylbenzene</td>
</tr>
<tr>
<td></td>
<td>( 2.3 \times 10^{-15} )</td>
<td>trimethylbenzene</td>
<td>1,3,5-trimethylbenzene</td>
</tr>
<tr>
<td>4-ethoxytoluene</td>
<td>( 2.67 \pm 0.53 \times 10^{-15} )</td>
<td>4-methyltoluene</td>
<td>1,3,5-trimethylbenzene</td>
</tr>
<tr>
<td></td>
<td>( 2.00 \pm 0.34 \times 10^{-15} )</td>
<td>4-methyltoluene</td>
<td>1,3,5-trimethylbenzene</td>
</tr>
</tbody>
</table>
Figure 1: Hammett plot for the reaction of para-substituted toluenes with OH.

The analogous plot with NO₃ (nine compounds) gives \( \rho = -4.3 \pm 0.6; r^2 = 0.87 \). (Figure 2). This negative value suggests again a polar transition state very similar to that occurring with OH and indicates a rate-determining ADD for this reaction.

Figure 2: Hammett plot for the reaction of para-substituted toluenes with NO₃.

The fact that the rate constants for meta-substituted toluenes did not fit the Hammett plot was probably due to the fact that they give six (and not four) isomeric radical adducts (Scheme 3).
A negative $p$ value of -1.82 ± 0.27; $r^2 = 0.84$ was obtained in the reaction of substituted benzenes (nine compounds) with OH (Figure 3).

The reasons of the branching occurring in the evolution of adducts (3: $X = H$) and (4: $X = H$) (ring fission vs rearomatization) and in the position of the phenolic group in the rearomatized compound has not yet been explained. In order to study in detail the composition of the equilibrium mixture of radical adducts (2), some preliminary semiempirical full geometry optimizations and energy calculation was made using the Unrestricted Hartree-Fock (UHF) [13]-Austin Model 1 (AM1) [14-15] method on the radical adducts of toluene and the three xylenes. Table 2 shows the $\Delta H^\circ$ of the reactions forming the radical adduct. These adducts are equilibrium mixtures of various isomers, where one of the two stereogenic carbons is still present.

At this low level of theory and with these small energy differences among the isomers, only the "ipso" isomer may be considered to be less stable than the others. Hence it will be present in lower amount in the equilibrium mixture.

Figure 3: Hammett plot for the reaction of substituted benzenes with OH.
Table 2
Unrestricted Hartree-Fock-AM1 method on the radical adducts of toluene and the three xylenes ($\Delta H^\circ = \text{Kcal mole}^{-1}$.)

<table>
<thead>
<tr>
<th></th>
<th>From toluene</th>
<th>From o-xylene</th>
<th>From m-xylene</th>
<th>From p-xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = OH</td>
<td>-27.87</td>
<td>-28.53</td>
<td>-27.96</td>
<td>-28.71</td>
</tr>
<tr>
<td>X = O$_2$N$_2$</td>
<td>-20.45</td>
<td>-21.41</td>
<td>-19.95</td>
<td>-21.56</td>
</tr>
<tr>
<td>$\Delta H^\circ$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-33.28</td>
<td>-33.44</td>
<td>-36.63</td>
<td>-35.73</td>
</tr>
<tr>
<td></td>
<td>-33.36</td>
<td>-27.52</td>
<td>-37.32</td>
<td>-22.78</td>
</tr>
<tr>
<td></td>
<td>-34.19</td>
<td>-27.45</td>
<td>-35.73</td>
<td>-26.87</td>
</tr>
</tbody>
</table>

Similar energy calculations of the isomeric cis- and trans-1,2-dihydrobenzene adducts formed by addition of X (OH, NO$_2$) followed by addition of Y (O$_2$, NO$_2$) (Scheme 4) showed that they have very similar stability, and are then likely to be present in nearly equimolecular amounts. For example, the AM1 calculated energy for cis-and trans-1,4-dimethyl-6-hydroxy-5-nitro-1,3-cyclohexanediene is shown in scheme 4.
Concerning their evolution, it can be noted that only the cis adduct can give a E2 elimination of HX, which is the only possibility in gas phase (E1 occurs via a carbocation which is not easily formed in gas phase) and the stereochemical requirement of this reaction is that H* and the leaving group X must be in anti-trans position (Scheme 5). Figure 4 and 5 show the calculated shapes of a cis- and trans adduct for X = O₂ and Y = OH. Hence, rearomatization results only from the cis adduct, whereas both the cis- and the trans adduct may give ring fission. This could be the reason of the high ring fission-rearomatization ratio in the reactions with OH.

In conclusion, the application of Structure-Reactivity Relationships to kinetic measurements for gas phase reactions may give informations about the reaction mechanism. This approach could also be used as chemical information for atmospheric modelling. In fact, using the appropriate Hammett equation in a deterministic model has a higher value than giving the individual rate constants. Furthermore, semiempirical calculations may be used for predicting conformations of reaction intermediates and reaction enthalpies.

Further, the study has contributed to a basic understanding of the mechanisms of NO₃ reactions with aromatics, which includes also the very fast reactions with phenol and cresols, important products of the reactions of aromatic hydrocarbons with the OH radical.
Acknowledgements

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Keywords

Tropospheric chemistry; Aromatic compounds, Hammett correlation, Linear Free Energy Relationships, Semiempirical calculations.

References


