Kinetic Studies on the Reaction of Hydroxyl Radicals with Aromatic Aldehydes

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Introduction
Aromatic compounds are a major component of anthropogenic hydrocarbon emissions, comprising around 80% globally. Chemicals such as toluene and the xylenes are emitted to the atmosphere from vapourization and incomplete combustion of fuel and also through solvent usage. In addition to being important primary pollutants, these compounds possess high photochemical reactivity and make a major contribution to the formation of photochemical oxidants, such as ozone and peroxyacetyl nitrate, in the troposphere. The hydroxyl (OH) radical initiated oxidation of these simple aromatics also plays a central role in the formation of products including peroxyacetyl nitrates, aromatic aldehydes and unsaturated carbonyl compounds. The secondary atmospheric chemistry of these oxygenated species is largely unknown. In particular very little work has been performed on the aromatic aldehydes even though benzoaldehyde and the tolualdehydes are produced from the atmospheric oxidation of toluene and the xylenes respectively. To date no kinetic data have been reported for the reaction of OH radicals with the tolualdehydes. The objective of this work was to carry out kinetic studies of the OH radical initiated oxidation of o-, m- and p-tolualdehyde and benzaldehyde. Accurate kinetic data will give an improved understanding of this secondary chemistry and allows estimation of the tropospheric lifetimes of these species. In addition, incorporation of this experimental data into photochemical models such as the Master Chemical Mechanism will help us to gain further insight into the photochemical aging ability of aromatic compounds.

The Teflon Bag Reactor
Reactions were carried out at 298 ± 2 K and atmospheric pressure in a 250 Ltr Compete impeller jacketed reactor (FEP) Teflon bag reactor, shown right. The FEP bag is resistant to chemical attack and shows high transparency even at elevated temperatures (< 10 ppb), NO (200 ppm), and water. The reactor is operated using purified air, which contains very low levels of NO, NO2, CO, SO2, and hydrocarbons (< 10 ppb). NO (200 ppm) and water. The reactor is surrounded by 8 visible lamps (Philips TL05, λmax = 350 nm) and 4 UV lamps (Philips TUV, λmax = 254 nm) arranged on four different horizontal planes which allow variation of light intensity and wavelength.

Analysis
Chemical analysis of reaction reactors was achieved using a gas chromatograph (GC) with flame ionisation detector (Varian 3800) connected to the reactor via an automatic gas sampling valve. Changes were taken before photolysis and at selected intervals during the reaction. Chromatographic separation was achieved by means of a CP-SIL 5 column operated at a temperature of 130°C. Relative concentrations of substrate and reference compounds were determined from peak area measurements during analyses.

Results
The relative rate method was used to determine reaction rate coefficients for the tolualdehydes and benzaldehyde. Loss of the substrate (S) was compared to the loss of a reference (R) compound, for which the rate coefficient for reaction with OH is well-known. The compound used as a reference is 1,2,4 trimethylbenzene in this study which is 2.2 hours for o-tolualdehyde butyl ether, 2.1 hours for m-tolualdehyde butyl ether, 1.7 hours for p-tolualdehyde butyl ether, and 2.0 hours for benzaldehyde. Further, the 1,2,4 trimethylbenzene was used as a reference compound.

\[
\ln [S]/[S] = k/T \ln [R]/[R]
\]

where \(k\) is the rate coefficient for the aromatic aldehydes and \(\kappa\) is the rate coefficient for the aromatic aldehydes. The reference compounds used in this study and the correct reaction rates for their reactions with OH were given below. Table 1 provides a summary of the data obtained from the plots and the rate coefficients for the aromatic aldehydes. The reference compounds used in this study and the rate coefficients for their reactions with OH were given below.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Reference</th>
<th>Rate Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzaldehyde</td>
<td>butyl ether</td>
<td>2.8 ± 0.2 s⁻¹</td>
</tr>
<tr>
<td>o-tolualdehyde</td>
<td>1,2,4 trimethylbenzene</td>
<td>2.7 ± 0.2 s⁻¹</td>
</tr>
<tr>
<td>m-tolualdehyde</td>
<td>1,2,4 trimethylbenzene</td>
<td>2.7 ± 0.2 s⁻¹</td>
</tr>
<tr>
<td>p-tolualdehyde</td>
<td>1,2,4 trimethylbenzene</td>
<td>2.7 ± 0.2 s⁻¹</td>
</tr>
</tbody>
</table>

Discussion
This work represents the first reported kinetic study of the reaction of OH radicals with the tolualdehydes. On examining the reaction pathway for the tolualdehydes it can be seen that the tolualdehydes react faster than both o- and p-tolualdehyde, which in turn, are more reactive than benzaldehyde. Furthermore, the OH group is o-, m-, p-directing and thus activates three sites on the ring for the tolualdehydes and two sites for o- and p-tolualdehyde. This explains why m-tolualdehyde is the most reactive of the tolualdehydes because the –OH group also activates the aromatic ring towards electrophilic attack by OH radicals and thus explains why all the tolualdehydes are more reactive than benzaldehyde. Furthermore, the OH group is o-, m-, p-directing and thus activates three sites on the ring for the tolualdehydes and two sites for o- and p-tolualdehyde. This explains why m-tolualdehyde is the most reactive of the tolualdehydes because the –OH group also activates the aromatic ring whilst the –CHO group deactivate.

Summary
Rate coefficients for the reactions of OH with selected aromatic aldehydes have been determined using the relative rate method. Using typical atmospheric concentrations of OH = 1 ± 0.1 molecule cm⁻³, the atmospheric lifetimes of the aldehydes are calculated to be 18.5 hours for benzaldehyde and 11.3, 9.9 and 12.9 hours for o-, m- and p-tolualdehyde respectively. To fully understand the environmental impact of aromatic aldehydes a detailed mechanistic study of their OH-initiated oxidation is required. These experiments are currently in progress in our laboratory and will provide a much improved understanding of this secondary chemistry and its effects on ozone levels.

References

Graph 1: Relative rate plot for the reaction of OH radicals with benzaldehyde using 1,2,4 trimethylbenzene as a reference compound.

Graph 2: Relative Rate plot for the reaction of benzaldehyde with OH radicals using butyl ether as a reference compound.

Graph 3: Relative Rate plot for the reaction of o-tolualdehyde with OH radicals using two reference compounds.

Graph 4: Relative Rate plot for the reaction of m-tolualdehyde with OH radicals using two reference compounds.

Graph 5: Relative Rate plot for the reaction of p-tolualdehyde with OH radicals using two reference compounds.