



# Kinetic Studies on the Reaction of Hydroxyl Radicals with Aromatic Aldehydes



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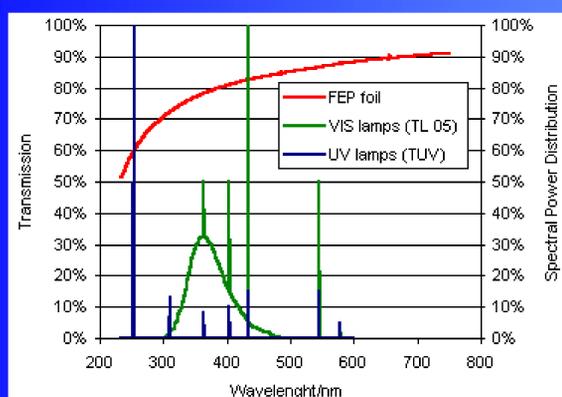
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## Introduction

Aromatic compounds are a major component of anthropogenic hydrocarbon emissions, comprising around 10% globally. Chemicals such as toluene and the xylenes are emitted to the atmosphere from vaporisation 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 oxidants, such as ozone and nitrates, in the troposphere. The hydroxyl (OH) radical initiated oxidation of these simple aromatics also produces a wide range of products including phenols, 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 benzaldehyde and the tolualdehydes are produced from the atmospheric oxidation of toluene and the xylenes respectively. To date no kinetic data has been reported for the reaction of OH radicals with the tolualdehydes. The objective of this work was to carry out kinetic studies on 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 pollution forming ability of aromatic compounds.

## The Teflon Bag Reactor

Reactions were carried out at  $298 \pm 2$  K and atmospheric pressure in a 350 Litre collapsible pillow shaped fluorine-ethene-propene (FEP) Teflon bag reactor, shown right. The FEP foil is highly resistant to chemical attack and shows high transparency even at short wavelengths in the UV region. The reactor is operated using purified air which contains very low levels of non-methane-hydrocarbons ( $< 10$  ppb),  $\text{NO}_x$  ( $< 10$  ppb) and water. The reactor is surrounded by 8 visible lamps (Philips TL05,  $\lambda_{\text{max}} = 350$  nm) and 4 UV lamps (Philips TUV,  $\lambda_{\text{max}} = 254$  nm) arranged on four different circuits which allow variation of light intensity and wavelength.



## 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 compounds studied did not show any significant loss due to photolysis. The tolualdehydes showed less than 2% wall loss over 12 hours. Corrections were made for benzaldehyde wall loss, which was  $6.0 \times 10^{-6} \text{ s}^{-1}$ . Plots in the form of the equation:

$$\ln\left(\frac{[S]_t}{[S]_0}\right) = k_r/k_s \ln\left(\frac{[R]_t}{[R]_0}\right)$$

were found to be linear with near zero intercepts and slopes given by  $(k_r/k_s)$  as shown. Graphs 1-6 show experimentally determined data for the aromatic aldehydes using different reference compounds. Table 1 provides a summary of the slopes derived from the plots and the rate coefficients for the aromatic aldehydes. The reference compounds used in this study and the rate coefficients for their reaction with OH were butyl ether ( $k_{\text{OH}} = 27.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , Mellouki/Tet2 1995) 1,2,4-trimethylbenzene ( $k_{\text{OH}} = 32.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , Atkinson 1989) and propyl ether ( $k_{\text{OH}} = 21.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , Mellouki 1995)

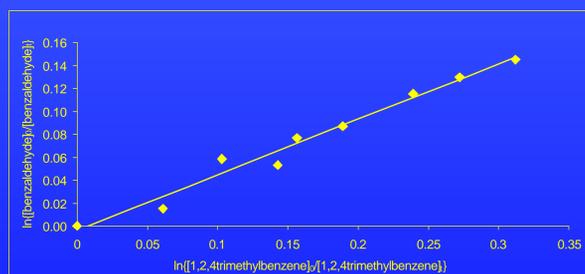
| Substrate              | Reference              | Slope | $k_{\text{OH}}^{\text{sb}}$ |
|------------------------|------------------------|-------|-----------------------------|
| benzaldehyde           | butyl ether            | 0.57  | $15.4 \pm 1.34$             |
|                        | 1,2,4 trimethylbenzene | 0.48  | $15.7 \pm 1.89$             |
| <i>o</i> -tolualdehyde | butyl ether            | 0.89  | $24.7 \pm 2.70$             |
|                        | 1,2,4 trimethylbenzene | 0.74  | $24.1 \pm 4.16$             |
| <i>m</i> -tolualdehyde | propyl ether           | 1.23  | $26.2 \pm 1.30$             |
|                        | 1,2,4 trimethylbenzene | 0.86  | $27.9 \pm 1.34$             |
| <i>p</i> -tolualdehyde | butyl ether            | 0.80  | $22.2 \pm 1.65$             |
|                        | 1,2,4 trimethylbenzene | 0.70  | $22.7 \pm 1.61$             |

a Units of  $10^{12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

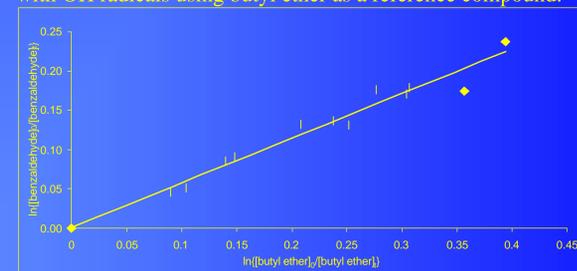
b errors are twice the standard deviation of the linear regression

c Literature value for benzaldehyde (Niki *et al.* 1978)

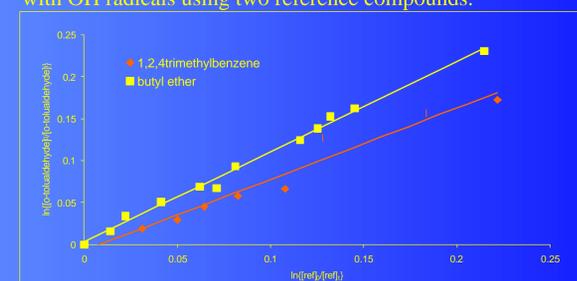
Graph 1: Relative rate plot for the reaction of OH radicals with benzaldehyde using 1,2,4 trimethylbenzene as a reference compound.



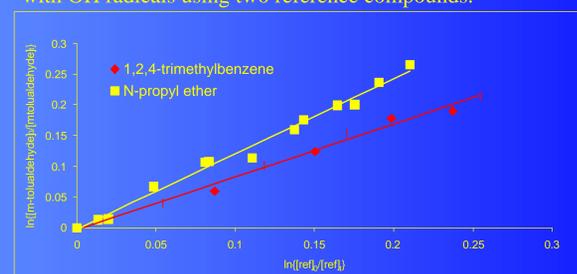
Graph 2: Relative Rate plot for the reaction of benzaldehyde with OH radicals using butyl ether as a reference compound.



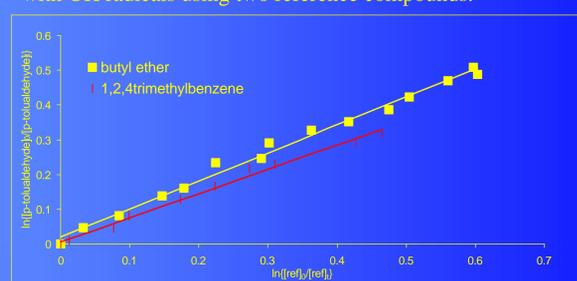
Graph 3: Relative Rate plot for the reaction of *o*-tolualdehyde with OH radicals using two reference compounds.



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.



The reactor is coupled to a Pyrex vacuum line which is used to handle gaseous and liquid samples. Measured volumes of aromatic aldehydes and reference compounds were introduced to the chamber by injecting them into a glass impinger and flushing the compounds through with purified air. Hydroxyl radical generation was carried out by the photolysis of methyl nitrite ( $\text{CH}_3\text{ONO}$ ) in air as follows.



Experiments were performed using 5-25 ppm of substrate and reference compounds and about 100 ppm of  $\text{CH}_3\text{ONO}$ .

## Analysis

Chemical analysis of reaction mixtures was achieved using a gas chromatograph (GC) with flame ionisation detection (Varian 3800) connected to the reactor via an automatic gas sampling valve. Samples were taken before photolysis and at regular intervals during the reactions. Chromatographic separation was achieved by means of a CP-SIL8 column operated at a temperature of  $140^\circ\text{C}$ . Relative concentrations of substrate and reference compounds were determined from peak area measurements during analyses.

## References

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## Discussion

This work represents the first reported kinetic study of the reaction of OH radicals with the tolualdehydes. On examining the reactivity pattern for the tolualdehydes it can be seen that *m*-tolualdehyde reacts faster than both *o*- and *p*-tolualdehyde, which, in turn, are more reactive than benzaldehyde. The  $-\text{CH}_3$  group activates the aromatic ring towards electrophilic attack by OH radicals and thus explains why all the tolualdehydes are more reactive than benzaldehyde. Furthermore, the  $-\text{CH}_3$  group is *o*-, *p*-directing and thus activates three sites on the ring for *m*-tolualdehyde and two sites for *o*- and *p*-tolualdehyde. This explains why *m*-tolualdehyde is the most reactive of the tolualdehydes. A similar pattern is observed for the reactivity of the cresols with *m*-cresol being more reactive than both *o*- and *p*-cresol. However, the cresols are much more reactive than the tolualdehydes because the  $-\text{OH}$  group also activates the aromatic ring whilst the  $-\text{CHO}$  group deactivates.

## Summary

Rate coefficients for the reactions of OH with selected aromatic aldehydes have been determined using the relative rate method. Using a typical tropospheric concentration of  $[\text{OH}] = 1 \times 10^6 \text{ molecule cm}^{-3}$ , the atmospheric lifetimes of the aldehydes are calculated to be 18.5 hours for benzaldehyde and 11.3, 9.9 and 12.2 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.