Atmospheric Impact of Xylene Oxidation Products

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Introduction

Over the last century, the development of global technology has enhanced trace gas emissions causing local, regional and global pollution of our atmosphere. One of the most important groups of trace gases are the Volatile Organic Compounds (VOCs) which are released into the atmosphere from a variety of anthropogenic and biogenic sources. The major anthropogenic sources are incomplete combustion and other evaporative emissions from solvents and fuels. Biogenic VOCs include isoprene and the terpenes, which are emitted from trees and shrubs.

VOCs are primary pollutants. However photochemical degradation in the presence of nitrogen oxides (NO_x) can give rise to secondary pollutants such as ozone and nitrates which are the major components of photochemical smog.
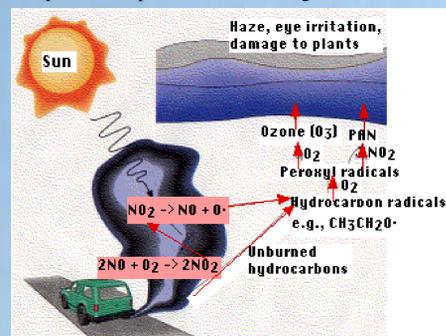

**Figure 1:** Photochemical smog formation

The key reactive species which initiates photochemical smog formation is the hydroxyl radical (OH), which is formed from the photolysis of ozone in the presence of water vapour.

$$O_3 + h\nu \, (\lambda > 290 \text{ nm}) \rightarrow O^* + O_2^*$$

$$O^* + H_2O \rightarrow OH + OH$$

The hydroxyl radical reacts with VOCs to form oxidised products such as aldehydes and ketones and also convert NO to NO_2. The products that have sufficiently low vapour pressure can exist primarily in the condensed phase i.e. in the form of secondary organic aerosol.. In particular the oxidation of the larger cyclic alkenes, aromatic hydrocarbons and the larger cycloalkanes lead to condensed phase multifunctional organic products.

Tropospheric Ozone

Ozone is formed in the troposphere from the photolysis of NO_2 at $\lambda > 315$ nm.

$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M \quad (M = N_2 \text{ or } O_2)$$
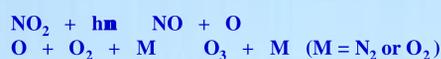
The production of ozone is enhanced in the presence of VOCs as the degradation reactions lead to the conversion of NO to NO_2 and thus lead to further ozone formation. This has important implications since ozone is a known irritant to humans and also affects vegetation .

Aromatic Compounds

Aromatic compounds are a major component of anthropogenic VOC emissions, comprising around 10 % globally. Chemicals such as xylene and toluene are emitted to the atmosphere from fuel and solvent usage. These compounds are highly reactive towards OH radicals and make a major contribution to the formation of oxidants such as ozone and nitrates in the troposphere. The hydroxyl radical initiated oxidation of these compounds produces a wide range of products such as **phenols**, **aromatic aldehydes** and unsaturated carbonyl compounds. However, the atmospheric reactivity of these products is largely unknown. The reaction of OH with xylenes proceeds by two different pathways as shown below for p-xylene.
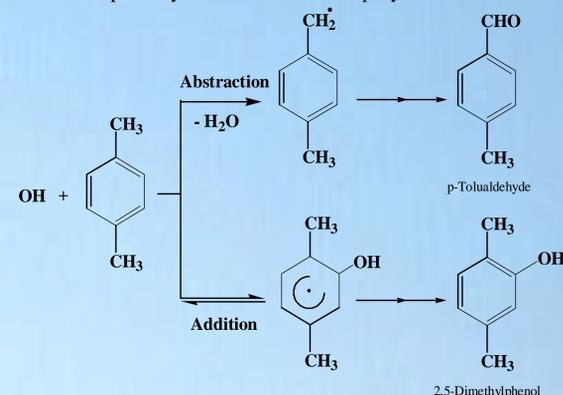

Figure 2: Xylene oxidation mechanism

Laboratory Studies

Due to differences in reactivity and structure, the relative contribution of VOCs to ozone formation can vary significantly from one compound to another. In order to understand the effect of a particular VOC on ozone formation, both the **rate coefficient** for its reaction with OH radicals and its **atmospheric degradation mechanism** must be known. Kinetic information on VOCs allows estimation of tropospheric lifetimes. Mechanistic studies allow identification of oxidation products and the key steps to oxidant formation. In order to study the photoxidation processes of VOCs the CRAC lab has designed and built two environmental smog chambers. A large volume chamber for carrying out product studies and a smaller chamber for kinetic studies
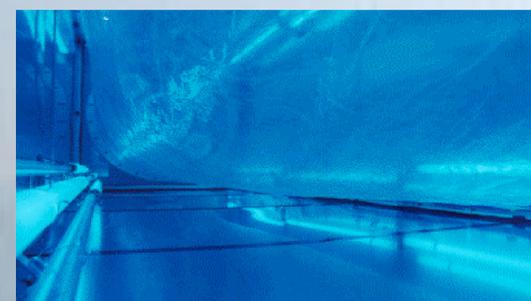

Figure 3: Inside the CRAC Chamber

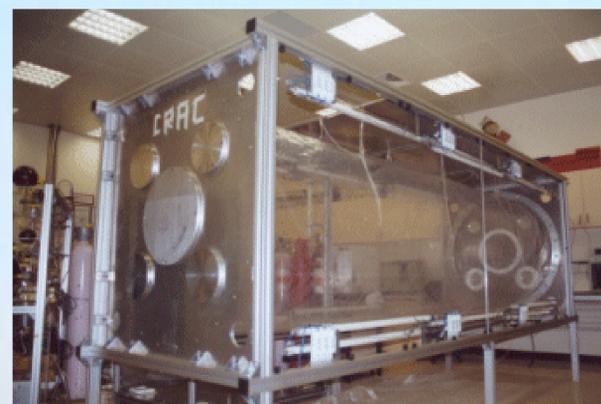## The CRAC Large Volume Reaction Chamber

Figure 4: The large volume reaction chamber

The large volume reaction chamber at the Centre for Research into Atmospheric Chemistry is designed and custom built for research into the gas-phase reactions of volatile organic compounds and their gas-particle conversion processes. The chamber has a cylindrical shape with a length of 4.2 m and a diameter of 1.2 m, resulting in a volume of approximately 4750 l and a high volume to surface area ratio of > 0.25m. This high volume to surface area ratio minimises interactions at the surfaces such as wall loses and wall reactions.

The cylinder is made of fluorine-ethene-propene (FEP) foil with a thickness of 0.127 mm. It is closed at both ends by FEP foil-covered aluminium end plates of 15 mm thickness.

The FEP foil is highly resistant to chemical attack and shows high transparency even at short wavelengths in the UV region. The cylinder is surrounded by 18 UV lamps (Philips TUV, 40 W) and 18 visible lamps (Philips TL05, 40 W) which can be used to provide light of varying wavelengths and intensities. Reactions are performed using low concentrations (ppm / ppb range) of VOCs in purified air at atmospheric pressure.
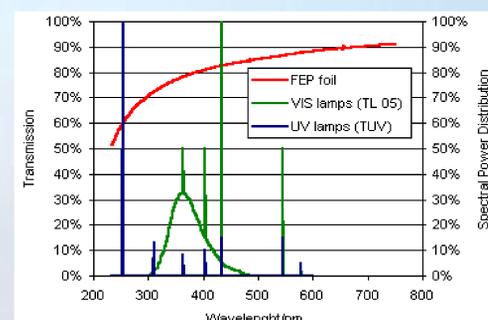

Figure 5: FEP foil transparency and emission spectra of chamber lamps

Kinetic Studies

Rate coefficients for the reaction of OH with **dimethylphenols** and **tolualdehydes** were determined using the Relative Rate Method. This involved monitoring the loss of aromatic compound relative to the loss of a reference compound for which the rate coefficient for reaction with OH is known. Kinetic information allows the estimation of tropospheric lifetimes. The lifetimes (τ) are calculated from the bimolecular rate constant k_{OH}. Table 1 provides a summary of the rate coefficients and the subsequent lifetimes obtained for the tolualdehydes and dimethylphenols. The short lifetimes indicate that degradation will occur in the boundary layer and free troposphere. The **dimethylphenols** and **tolualdehydes** will therefore contribute to local and regional O_3 formation. The dimethylphenols are at least three times more reactive than the tolualdehydes and will have a relatively greater environmental impact.

Table 1

Reactant	$k_{OH}{}^{ab}$	t_{OH} [hours]
2,3-Dimethylphenol	7.22±0.48	3.9
2,4-Dimethylphenol	7.32±0.42	3.8
2,5-Dimethylphenol	7.80±0.51	3.6
2,6-Dimethylphenol	7.50±0.86	3.7
3,4-Dimethylphenol	7.39±0.67	3.8
3,5-Dimethylphenol	10.44±0.73	2.7
Benzaldehyde	1.57±1.66	17.5
o-tolualdehyde	2.34±0.90	11.6
m-tolualdehyde	2.18±1.73	12.7
p-tolualdehyde	2.15±0.70	12.9

[a] Units of $10^{-11} cm^{-3} molecules^{-1} s^{-1}$
[b] Errors are twice the standard deviation of the linear regression

Product Identification

Experiments to determine the gas-phase oxidation products from the OH radical initiated oxidation of dimethylphenol and tolualdehyde isomers were preformed in the large volume reaction chamber at atmospheric pressure in clean non-methane hydrocarbon free air. Analysis of the reactant/product mixtures were performed using direct gas sampling to a GC-MS (Varian Saturn 2000). Table 2 shows a number of products identified from the photoxidation of 2,6-dimethylphenol and m-tolualdehyde.

Table 2

Reactant	Abstraction product	Addition product
2,6-Dimethylphenol	2-Hydroxy-3-methylbenzaldehyde	2,6-Dimethylbenzoquinone
m-Tolualdehyde	Isophthalaldehyde	2-Hydroxy-3-methylbenzaldehyde

Secondary Organic Aerosol Formation

Aromatic hydrocarbons have been shown to be efficient precursors of Secondary Organic Aerosol (SOA) formation in the troposphere. Experiments to investigate the potential of dimethylphenols to produce SOA during atmospheric photoxidation were carried out at the EUPHORE facility.

Figure 6: Chamber B of the EUPHORE facility Valencia, Spain

A rapid formation of particles was observed for dimethylphenol photoxidation as shown below in Figure 7.

Figure 7: Particle size distribution during dimethylphenol oxidation

Future Work

The two major goals during the next year of this project are the quantification of reaction products using *in situ* FTIR spectroscopy and the determination of SOA yields. The kinetic and mechanistic data obtained in this work can be included in photochemical models (e.g the Master Chemical Mechanism) which are used to predict secondary pollutant formation. It is envisaged that the inclusion of this kinetic and mechanistic data will improve the accuracy of the models.

Background: Photochemical haze over the San Juan Mountains outside L.A.