

# Atmospheric Oxidation Of Dimethylphenols

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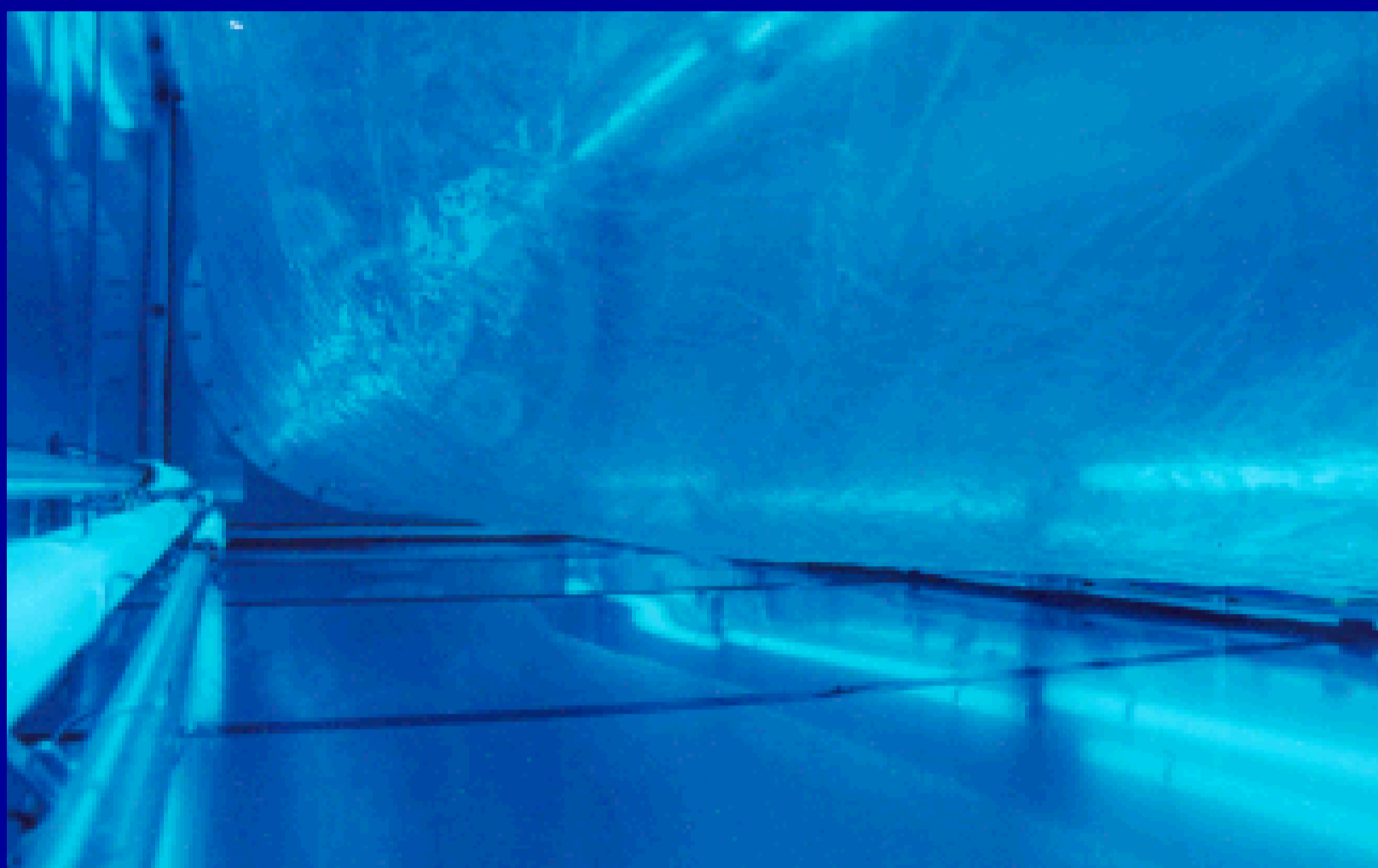
## Introduction

Volatile organic compounds (VOCs) are introduced into the atmosphere from a variety of anthropogenic and biogenic sources. These VOCs undergo a series of chemical and physical transformations which lead to the formation of ozone, nitrates and secondary organic aerosol in urban and rural areas and in the global troposphere (Seinfeld et al., 1998; Seinfeld et al., 1997). Aromatic hydrocarbons are important constituents of gasoline fuels (Hoekman, 1992, Black et al., 1980), vehicle exhaust and ambient air in urban areas. Typically aromatics account for around 20-25% of reformulated gasoline (Kirchstetter et al., 1999) and a significant portion of non-methane organic compounds in ambient urban air.

Aromatic compounds such as benzene, toluene and xylenes (BTX) are highly reactive towards hydroxyl radicals (OH) in the atmosphere and therefore contribute greatly to the formation of these secondary pollutants. The atmospheric oxidation of the xylenes produce dimethylphenols with yields of around 20-25% (Atkinson and Lloyd, 1984, Klotz et al., 1998, Kwok et al., 1997). To date little work has been carried out on the atmospheric chemistry of the dimethylphenols. The rate coefficients for hydroxyl radical reaction have been measured only once before (Atkinson and Aschmann, 1990). Furthermore, there are no product studies reported in the literature. The aim of this work was to measure hydroxyl radical rate coefficients for the dimethylphenols and to identify gas-phase reaction products, in order to develop chemical mechanisms for their atmospheric degradation.

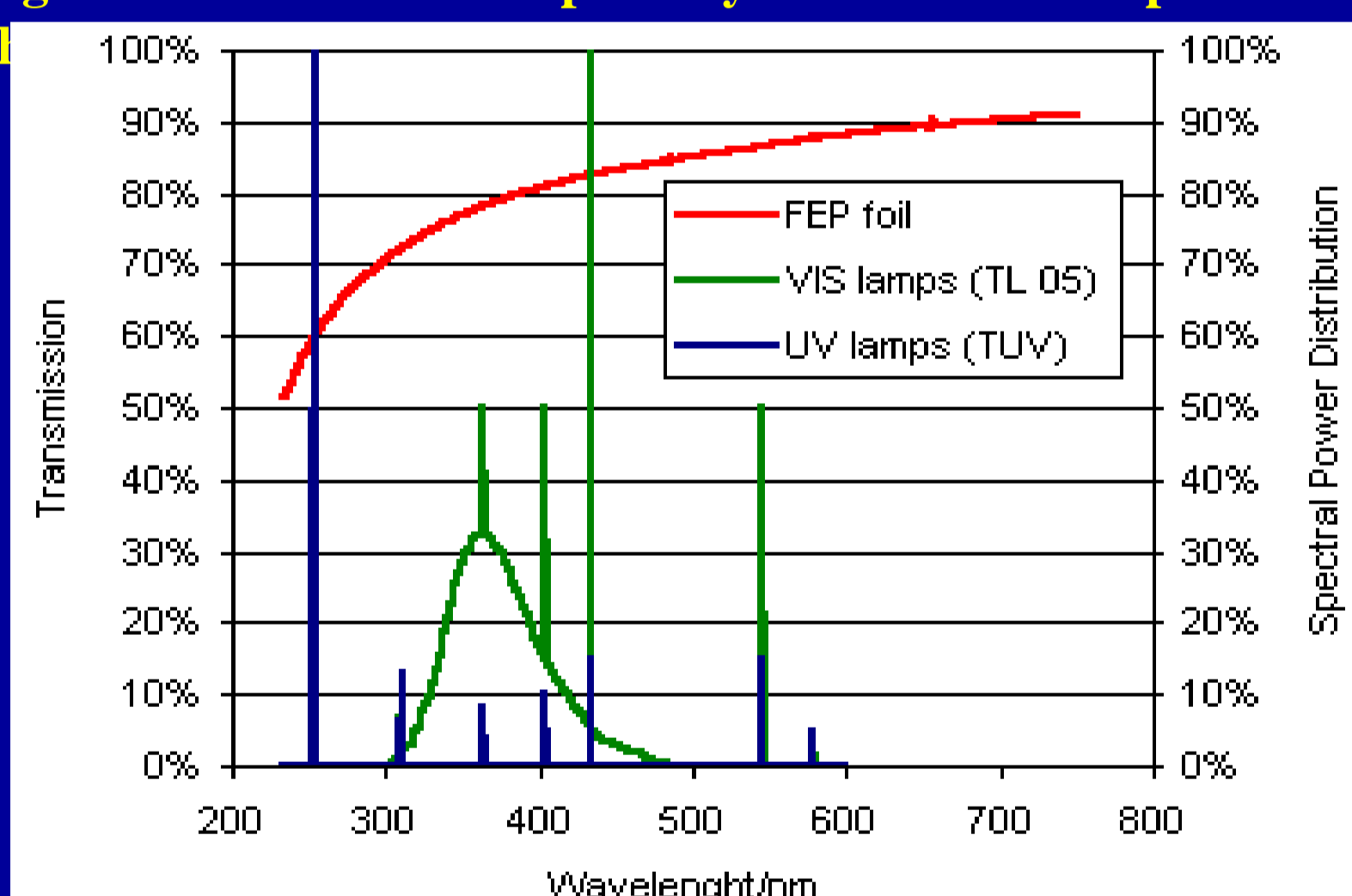
## The CRAC Large Volume Reaction Chamber

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 low volatile organic compounds and their gas-particle conversion processes at low ppmV and ppbV concentrations.



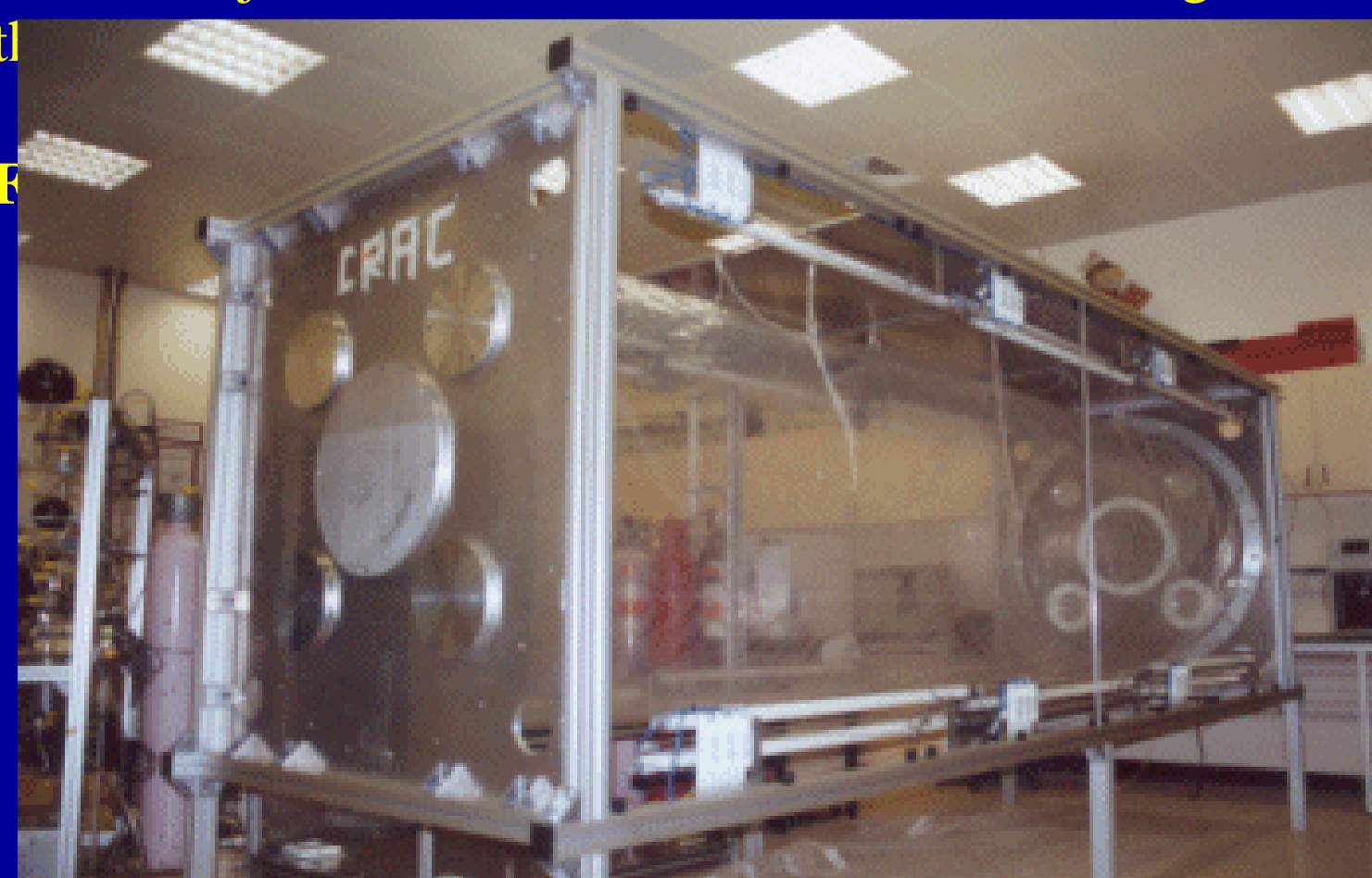
The chamber has a cylindrical shape with a length of 4.2 m and a diameter of 1.2 m, resulting in a volume of approximately 4750 l and a high volume to surface area ratio of > 0.25m. This high volume to surface area ratio minimises interactions at the surfaces such as wall losses and wall reactions. The 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.

Figure 1: FEP foil transparency and emission spectra of lamps



## Analytical Instruments

The reaction chamber is equipped with a number of analytical instruments to monitor concentration-time profiles of reactants and products during the experiments. A GC-MS (Varian Saturn 2000) and GC-FID (Varian 3800) are directly connected to the reaction system via automated gas sampling valves. The MS can be operated in chemical ionisation mode and in conjunction with the MS-MS function is a great tool for



## References

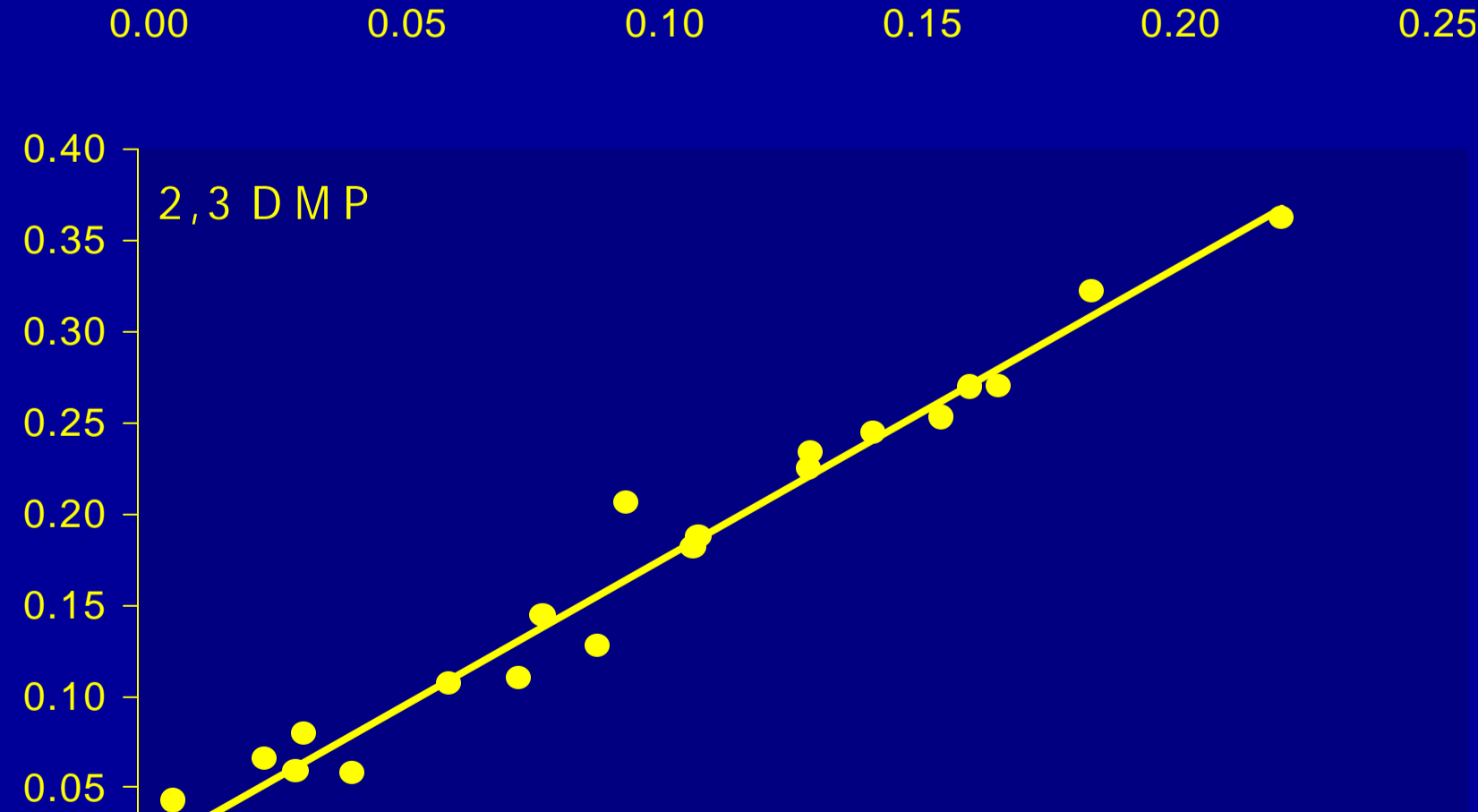
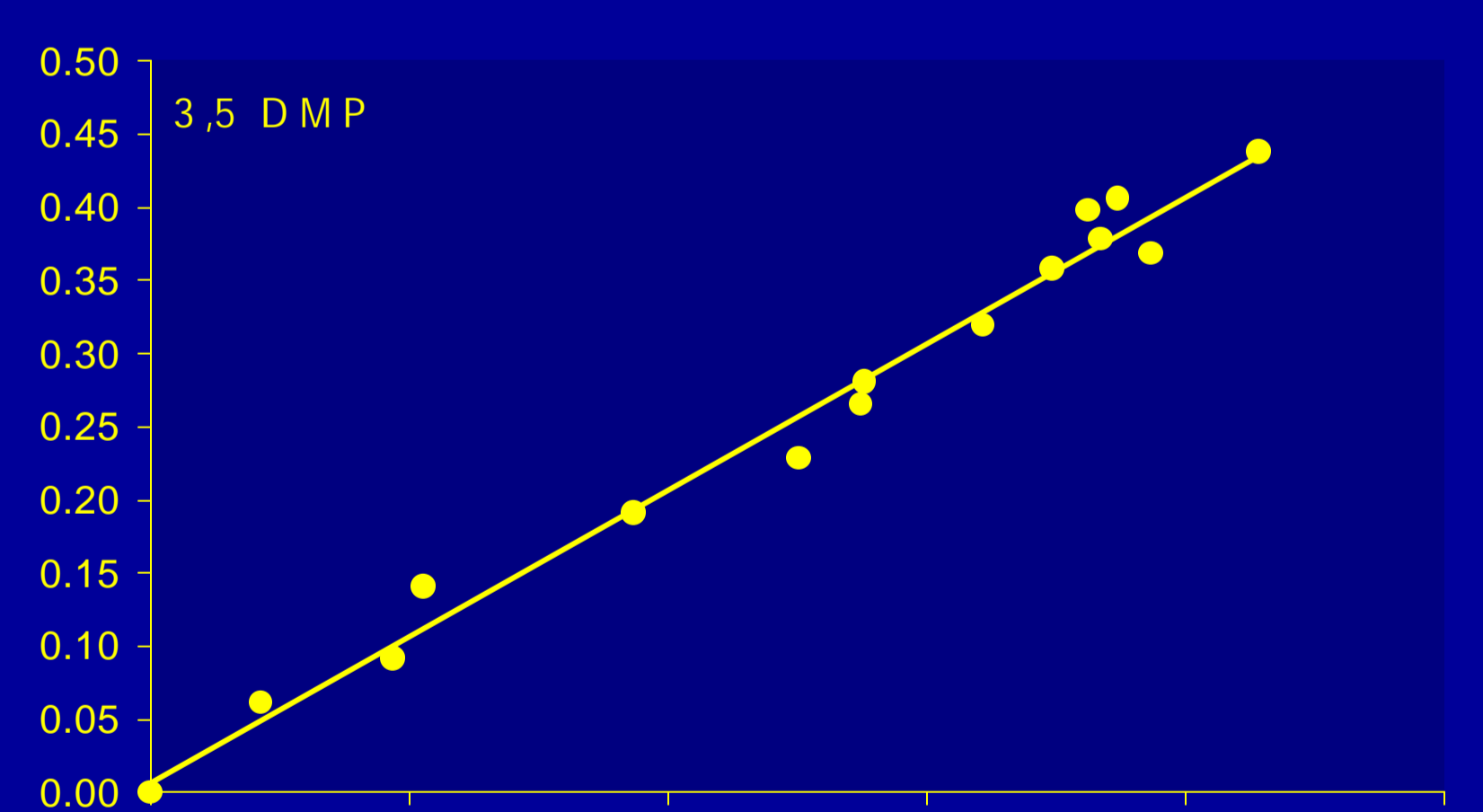
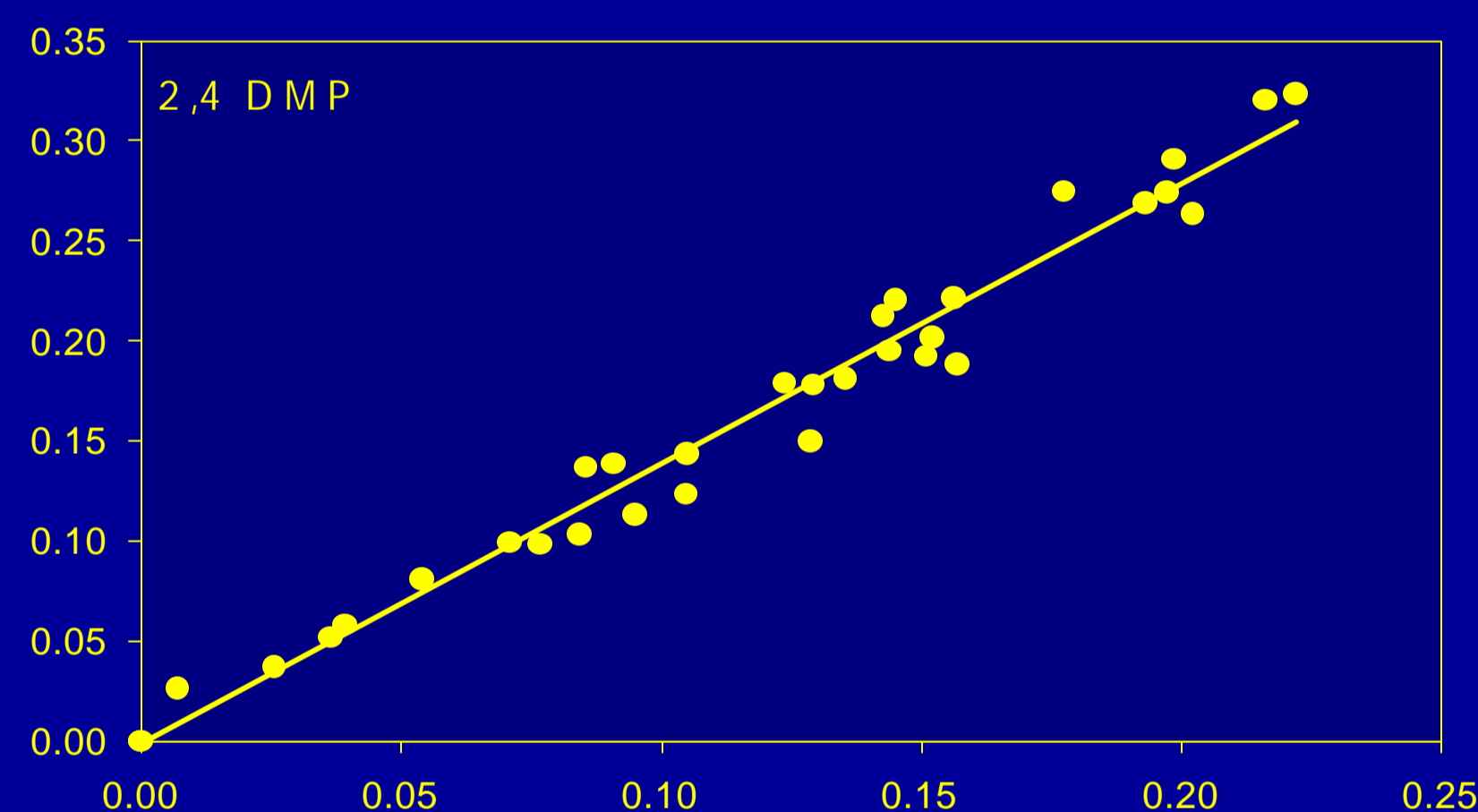
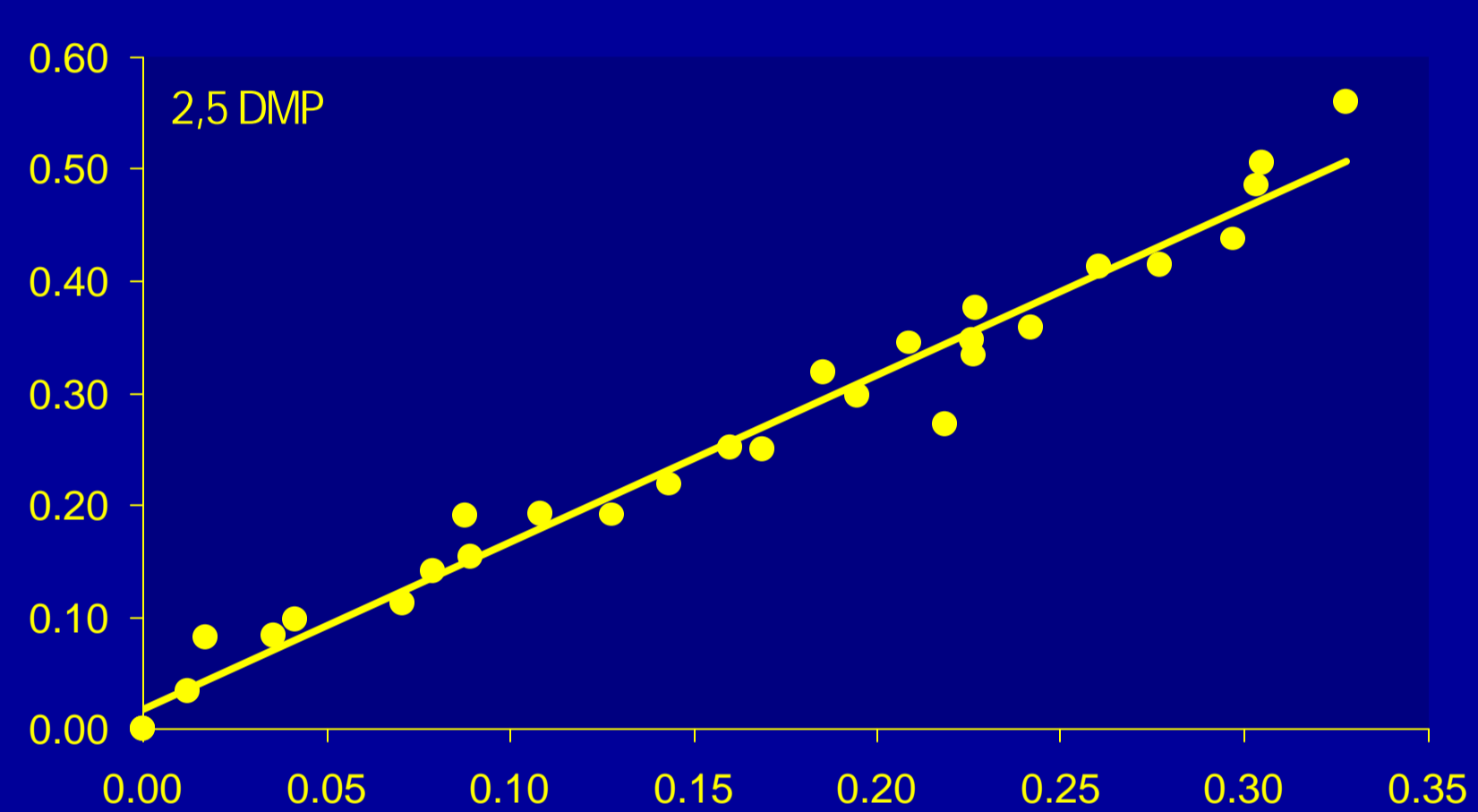
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## Relative Rate Kinetics

Hydroxyl radical reaction rate coefficients were determined using a relative rate method in which the decay of reactants were measured relative to a reference organic compound in the presence of hydroxyl radicals. The photolysis of methyl nitrite was used as the source of hydroxyl radicals. Typical starting concentrations were 10-15 ppmV of reactant and reference compounds. Reactant and reference concentrations were monitored using GC-FID and linear relative rate plots were obtained. Typical examples are shown below.

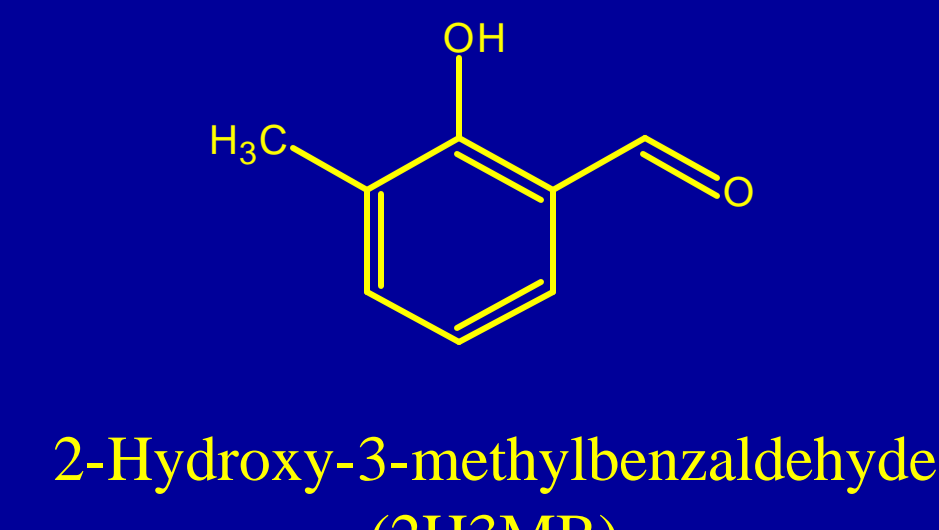
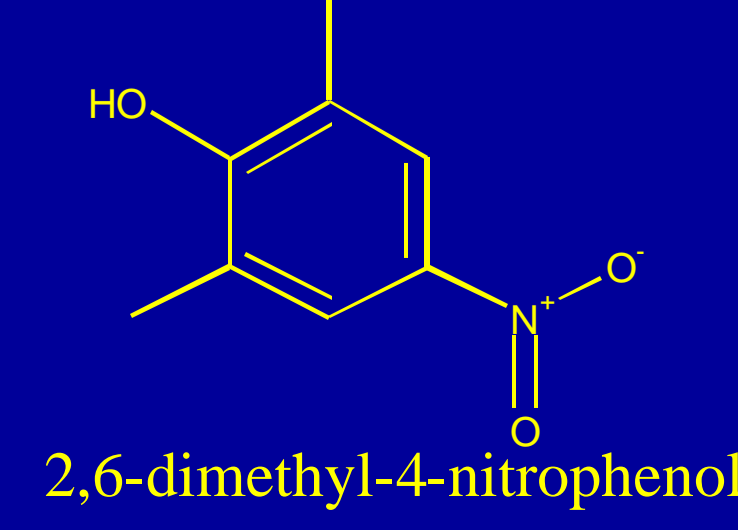
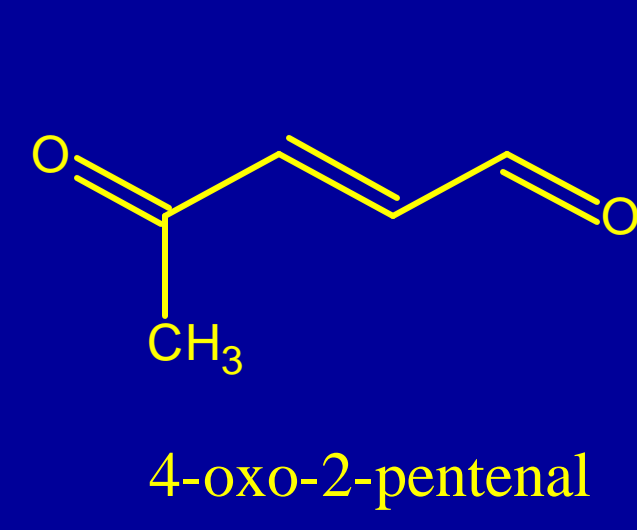
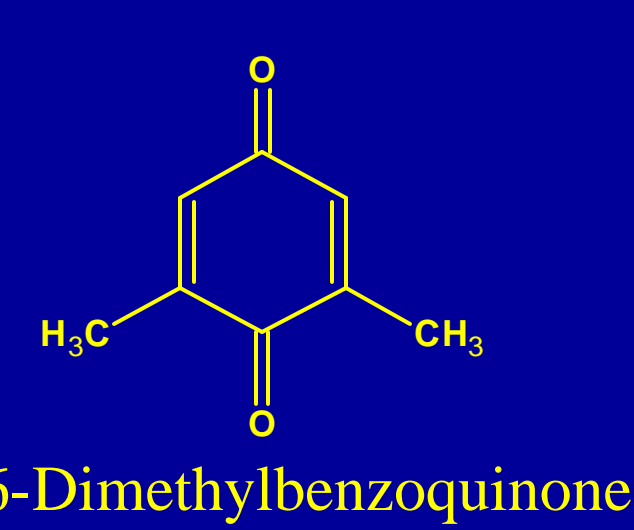
	$k_1/k_2$ relative to p-cresol	$k_{OH} \times 10^{11} (\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1})$	
2,3-Dimethylphenol	1.38±0.1	<b>7.22±0.48</b>	literature 8.02±2.03
2,4-Dimethylphenol	1.40±0.08	<b>7.32±0.42</b>	7.15±1.84
2,5-Dimethylphenol	1.49±0.1	<b>7.80±0.51</b>	8.00±2.29
2,6-Dimethylphenol	1.43±0.16	<b>7.50±0.86</b>	6.59±1.73
3,4-Dimethylphenol	1.41±0.13	<b>7.39±0.67</b>	8.14±2.12
3,5-Dimethylphenol	2.00±0.14	<b>10.44±0.73</b>	11.3±3.0

Rate coefficients were determined using  $k_{OH}(\text{p-cresol}) = 5.20 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . (Atkinson, R. et. al. 1978)



The dimethylphenols react significantly faster than phenol and the cresols. The additional methyl substituents activate the ring towards hydroxyl radical attack at the ortho and para sites.

3,5-dimethylphenol reacts quicker than the other dimethylphenols as each position available for OH radical attack is doubly activated due to the substituent positions.



## Product Identification

Identification of reaction products was performed by three different methods; (i) direct GC-MS analysis of gaseous reaction mixtures, (ii) PFBHA derivatisation of carbonyls and subsequent GC-MS analysis, (iii) bubbling the reaction mixtures through an organic solvent followed by GC-MS analysis.

Figure 3: GC-MS data showing the formation of 2,6-Dimethyl-4-nitrophenol during the reaction of 2,6-Dimethylphenol with NO<sub>x</sub>

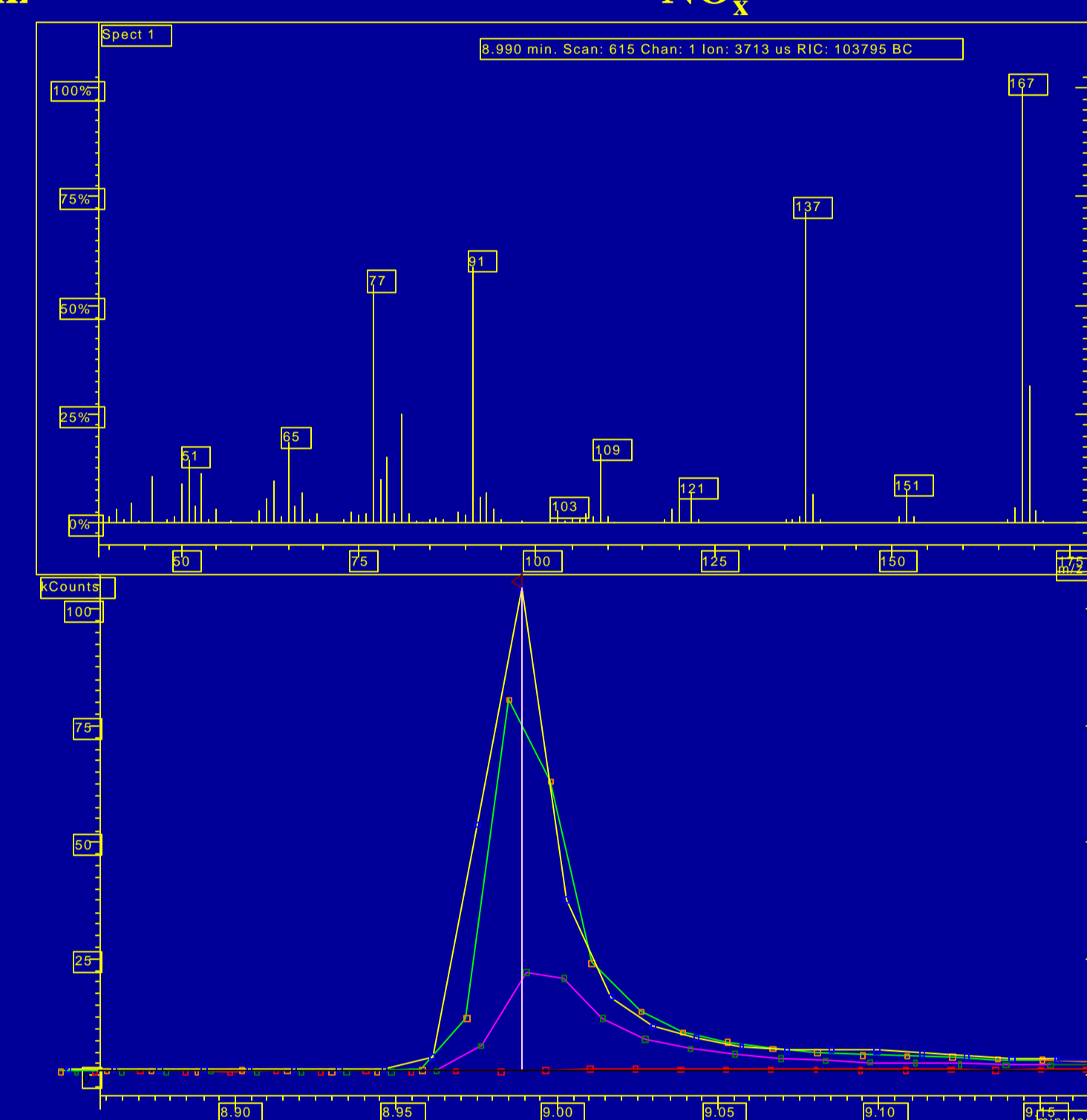


Figure 4: RICs showing the formation of reaction products, using H<sub>2</sub>O<sub>2</sub> as OH radical precursor without NO<sub>x</sub>

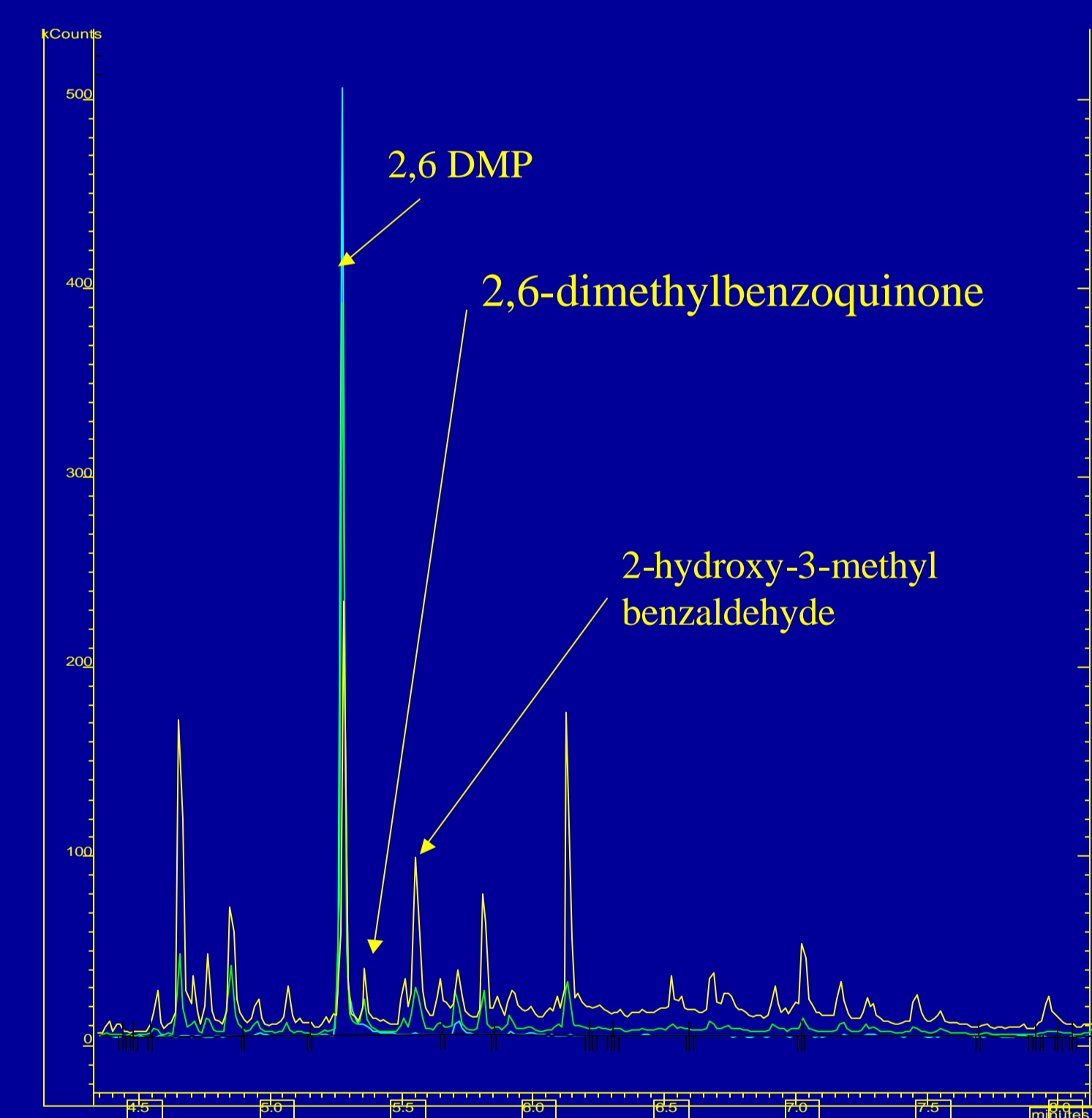
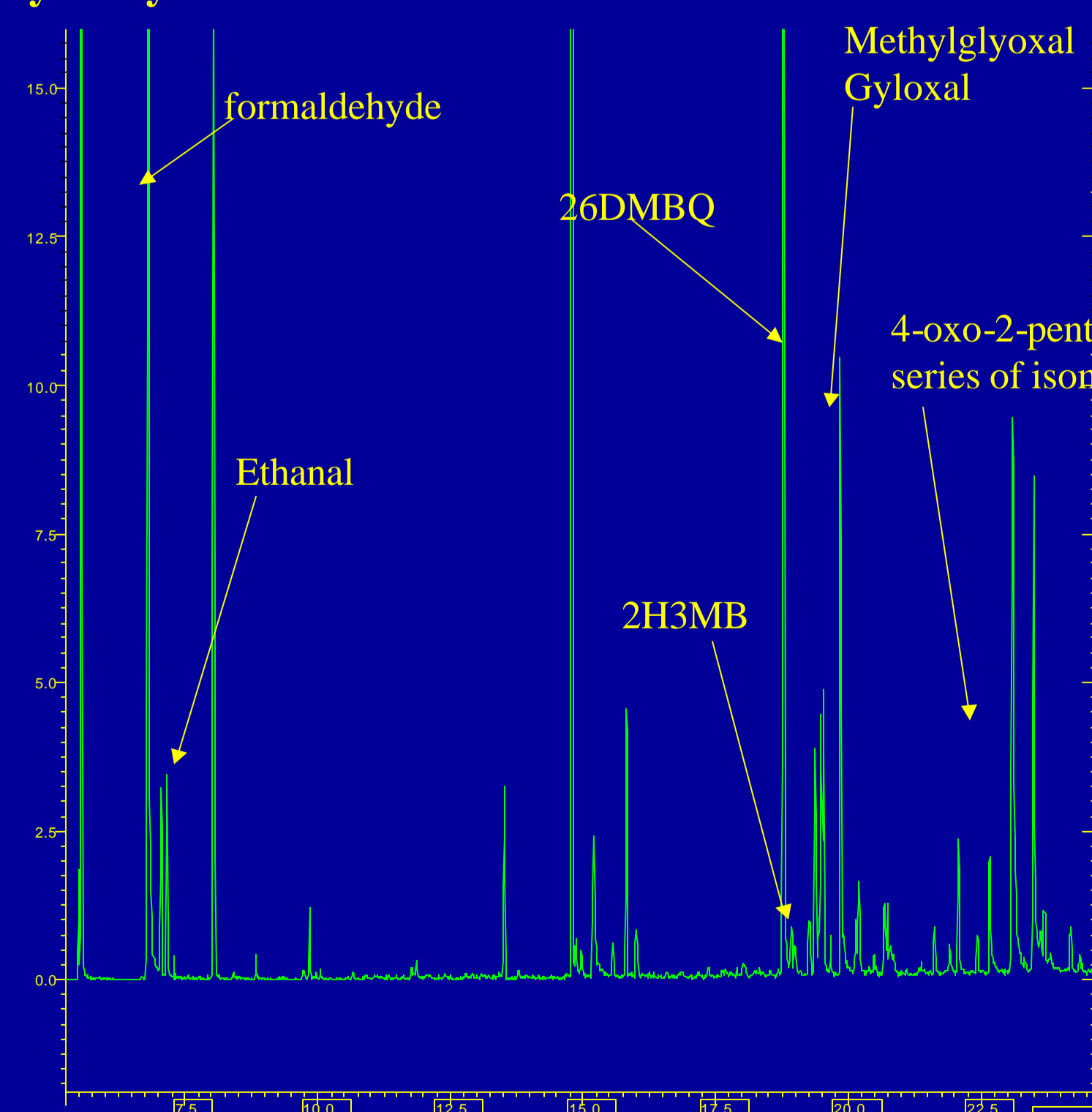


Figure 5: 181 RIC showing PFBHA-Carbonyl derivatives formed during the reaction of 2,6-Dimethylphenol with hydroxyl radicals.



Labeled peaks have been identified by matching retention times and mass spectra to commercially available or synthesized standards.