The photocatalytic degradation of phenolic compounds

Thesis

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The Photocatalytic Degradation of Phenolic Compounds

A thesis submitted for the degree of
Doctor of Philosophy in Chemistry

to
The Open University

by
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January 1998

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ABSTRACT

Semiconductor photocatalysis degrades phenolic pollutants to carbon dioxide and water, but the mechanisms of this potentially attractive method of environmental remediation remain unclear. This study aimed to elucidate the primary molecular events by HPLC analysis of the initial products of degradation in water or aqueous acetonitrile.

The position of substituents relative to the hydroxyl group were found to influence the reaction rate and also primary oxidation steps, and hence the intermediate profile. 2,6-Dialkylated phenols reacted fastest and showed high conversion to dehydrodimeric products as a prelude to degradation. In contrast, 3,5-dialkylated phenols and 4-tert-butylphenol reacted more slowly and appeared to degrade directly to small polar compounds with little accumulation of primary carbocyclic intermediates.

The rate of photocatalytic degradation of two isomeric dibromohydroxybenzonitriles was also influenced by substitution pattern. 3,5-Dibromo-2-hydroxybenzonitrile, however, is itself photolabile in daylight giving 3-bromo-2,5-dihydroxybenzonitrile in aqueous solution. The analogous reaction does not occur for 3,5-dibromo-4-hydroxybenzonitrile, the difference in behaviour being attributed to differences in the electronic spectra of the two compounds.

The mechanism of photocatalysis appears to be influenced by the orientation of the substrate on the catalyst surface. For the alkyl phenols, particularly those with tert-butyl substitution, minimisation of disturbance to the polar network of the solvent directs the more hydrophobic parts of the molecule towards the oxidising surface of the catalyst. In addition, this effect encourages clustering of molecules with the subsequent formation of aggregated products.

While part of the behaviour observed may be attributable to the presence of acetonitrile in the solvent, the hydrophobic profile of a substrate undergoing heterogeneous photocatalytic oxidation in water would seem to be a significant determinant of the molecular pathway selected in the first phase of its degradation.
STATEMENT

The work included in this thesis was carried out by the author between October 1994 and August 1997 in the laboratories of the Department of Chemistry at the Open University, Milton Keynes under the supervision of Dr Roger R. Hill and Dr David R. Roberts.

I declare that the work presented is the result of my own investigations apart from the following which is fully acknowledged:

Mr Pravin Patel – preparation of 2,6-di-tert-butyl-4-hydroperoxy-4-methyl-2,5-cyclohexadien-1-one and 2,6-di-tert-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one and attempted preparation of bis(4-oxy-4-methyl-2,6-di-tert-butylcyclohexa-2,5-dien-1-one) (one page of Experimental).

Mr Graham Jeffs – preparative photolysis and purification of bis(4-oxy-4-methyl-2,6-di-tert-butylcyclohexa-2,5-dien-1-one) (half a page of Experimental).

Use was made of Departmental NMR spectroscopy and mass spectrometry services operated by Mr Gordon Howell and Mr Brandon Cook, respectively. Data were also supplied by Pfizer Central Research, Sandwich, Kent, UK (LC-MS) and SERC Mass Spectrometry Service Centre, University College of Swansea (HRMS).

The material embodied in this thesis has not been submitted, nor is currently being submitted for any other degree.

Parts of the work have been presented or published as listed below:


RSC Young Environmental Chemists Meeting, De Montfort University, Leicester, March 1997 (talk).


RSC 7th Annual Young Chemists Symposium, SmithKline Beecham Pharmaceuticals, Harlow, June 1997 (talk).

The Third International Conference on TiO₂ Photocatalytic Purification and Treatment of Water and Air, Radisson Twin Towers Hotel, Orlando, Florida, USA, September 1997 (talk and poster).


Jill Clarke
January 1998
ACKNOWLEDGEMENTS

I would like to thank my supervisors, Dr Roger Hill and Dr David Roberts, for their patient
and steadfast support during this project. Their heterogeneous but complementary
perspectives have, I believe, provided me with excellent training in chemistry research. It
has been a pleasure and a privilege to work with them.

I would also like to thank the other staff of the Chemistry Department at Walton Hall for
their help, particularly Gordon Howell for running NMR spectra, Brandon Cook for mass
spectra and Pravin Patel for preparing two important compounds. A large proportion of
this project required the use of HPLC and I would like to express special thanks to Graham
Jeffs for his invaluable help and guidance in this technique.

I am most grateful for external assistance from: Dr Steven Robinson of Pfizer Central
Research for LC-MS data, Dr Malcolm Rose for help with mass spectra interpretation and
derivatisation of dihydroxybenzenes by phenyl boronic acid and Dr Kevin McCullough for
data from ZINDO calculations.

I gratefully acknowledge the award of an Open University Research Development Fund
postgraduate studentship and a Karanikis Travel Scholarship.

Finally, I would like to thank my family and friends for their love and support throughout
my studies.
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SYMBOLS AND ABBREVIATIONS

abs.
ACN
conc.
δ
ε
GLC
h
HPLC
HRMS
IR
λ
LC-MS
Lit.
m/z
min
MS
ν
nm
NMR
pH
ppm
PuP
r.t.
T
t
TLC
UV
UVA

absorbance
acetonitrile
concentration
chemical shift
molar absorptivity
gas-liquid chromatography
hour
high-performance liquid chromatography
high-resolution mass spectrometry
infra-red
wavelength
HPLC coupled to MS
literature
mass-to-charge ratio
minutes
mass spectrometry
wavenumber
nanometre
nuclear magnetic resonance
- log [H+]
parts per million
purity parameter / nm
retention time
temperature
time
thin layer chromatography
ultraviolet
ultraviolet light, λ 320-400 nm
CHAPTER 1
INTRODUCTION

1.1 Preamble

The project described in this thesis examines the degradation of possible and model phenolic aquatic pollutants by the technique of semiconductor photocatalysis. It addresses an area where understanding of the process is unclear, namely the molecular mechanism of the initial steps in the reaction. This introduction gives some background information on the problem of water pollution, how it has been dealt with in the past and why new methods of remediation are required. After describing the fundamentals and scope of catalytic photooxidation, the mechanism, as currently perceived, is reviewed to enable the objectives of this project given in the final section to be seen in the context of existing knowledge.

1.2 Water pollution

The issue of environmental pollution has come to the fore over the past thirty years. Government bodies and the public have become increasingly aware of the effect that growing population and industrialisation are having on the health of both humans and natural habitats. All life on earth is dependent on water and the maintenance of clean aquatic environments should be a top priority. Water pollution is not, however, just a late 20th century phenomenon. The earliest recorded British legislation prohibiting the pollution of water dates from 1388 with an Act forbidding the dumping of animal remains, dung and garbage into rivers, ditches and streams because of the "great annoyance damage and peril of the inhabitants" (Murley, 1991a).

There are commonly considered to be seven types of water pollution: (i) bacterial and viral, (ii) organic, (iii) radioactive, (iv) toxic and trace chemical, (v) eutrophication, (vi) thermal, and (vii) oil (ReVelle and ReVelle, 1974a). Each of these categories provides its
own challenge to those responsible for their remediation, but it is organic pollutants that will be discussed here.

There are two ways in which organic pollutants can be detrimental in aqueous environments. Firstly, some organic wastes discharged either by industry or from domestic outflows can be utilised by bacteria and protozoa as food. In the process of decomposition, energy is released and oxygen, from the surrounding water, consumed. In cases of severe pollution, eutrophication of the water may ensue. The quantity of organic matter in water is measured by the biological oxygen demand (BOD), that is the amount of oxygen needed to oxidise fully, by biological means, reducing material in a water sample. It is also taken as an indication of the overall level of water pollution. A high BOD in a water course leads to a low dissolved oxygen concentration; this in turn, gives rise to severe ecological changes i.e. the death of fish and other forms of animal and plant life (ReVelle and ReVelle, 1974b).

Secondly, organic chemicals can be directly toxic to living organisms. Some of the exotic organic compounds that can now be found in natural water include surfactants from detergents, pesticides, various industrial products, and the decomposition residues of other organic compounds (Hodges, 1973). One group of toxic organic compounds which can be present in the aqueous environment are phenols, which will now be considered.

1.3 The significance of phenols as pollutants

Phenolic compounds are known to be significant aquatic pollutants, and enter the environment either as manufactured chemicals or as waste products from industry (Table 1-1).

Phenols are also a significant component of creosote, which is a complex mixture of organic compounds obtained from the distillation of coal tar. It consists of about 85% polynuclear aromatic hydrocarbons (PAH) and 10% phenols, the majority of these being alkyl phenols i.e. the cresols and xylenols. Creosote and pentachlorophenol are probably the most widely used pesticides in the wood-preserving industry, accounting for an annual
consumption of approximately 45 000 tonnes per annum in the USA. The industry, in turn, generates between 840 and 1 530 dry tonnes of hazardous waste sludge (Serpone, et al., 1994). The phenols can have solubilities of up to 80 g dm$^{-3}$ and may find their way into the environment by rainwater leaching from treated wood or contaminated soil. The highest environmental concentrations are found in the vicinity of wood treatment facilities.

<table>
<thead>
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<th>pollutant</th>
<th>source</th>
<th>form</th>
<th>reference</th>
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<td>pentachlorophenol</td>
<td>timber industry</td>
<td>antisapstain agent, wood preserver, antifungal agent</td>
<td>Wild, et al., 1992</td>
</tr>
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<td>phenols, including ortho &amp; meta-diphenols</td>
<td>oil-mill wastewater</td>
<td>waste product</td>
<td>Duran, et al., 1991</td>
</tr>
<tr>
<td>creosote (phenol, 2,4-dimethylphenol, 2-methylphenol, 4-methylphenol)</td>
<td>wood treatment facilities</td>
<td>wood preserver</td>
<td>Rosenfeld &amp; Plumb, 1991</td>
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<tr>
<td>chlorophenols, polyhydroxybenzenes</td>
<td>pulp and paper mill waste waters</td>
<td>waste product</td>
<td>Masten &amp; Davies, 1994; Garcia, 1994</td>
</tr>
<tr>
<td>nitrophenols</td>
<td>dye industry</td>
<td>waste product</td>
<td>Garcia, 1994</td>
</tr>
<tr>
<td>chlorophenols</td>
<td>pesticide industry</td>
<td>waste product</td>
<td>Garcia, 1994</td>
</tr>
<tr>
<td>alkylphenols, polynuclear phenols</td>
<td>oil refineries and petrochemical plants</td>
<td>waste product</td>
<td>Garcia, 1994</td>
</tr>
</tbody>
</table>

Investigation of disused sites in the USA (Goerlitz, et al., 1985) found contamination of surrounding aquifers from unlined surface ponds, formerly used for storing and recirculating creosote, which were in direct hydraulic contact with the ground water. Occasions when the ponds had been overfilled led to further contamination of local ground water. The total concentration of 2,4- and 3,5-dimethylphenol in ground water taken from a borehole adjacent to a typical surface pond was about 10 mg dm$^{-3}$ and 3 mg dm$^{-3}$ at a distance of 300 metres from the pond.

Extraction of oil from shales is a process that may well increase in volume as energy reserves decline. Phenols are present in oil-shale waste waters co-produced with shale oil.
during distillation. The nature of the waste water is variable, but research has been focused on its chemistry as it must be treated before disposal (Leenheer, et al., 1982). Its composition usually includes compounds such as carboxylic acids, amines and pyridines but about 20% of the dissolved organic carbon (DOC) is made up of phenols. These include phenol itself (~7%), o-cresol (~3%), m- and p-cresol (~5%) and dimethylphenols (~8%).

Even when present in concentrations as low as parts per billion, phenolic compounds are toxic to aquatic life and can impart taste and odours to drinking water. In higher concentrations, phenols are toxic to most life forms and there is concern about increased human exposure (Garcia, 1994). Indeed, pentachlorophenol appears on the European Union (EU) "Black List" of substances so toxic, persistent or bio-accumulative in the environment that pollution by them is to be eliminated (Murley, 1991b).

Ever increasing environmental legislation, such as The Water Act 1989 and numerous EU Directives (Murley, 1991c), has prompted attempts to minimise the discharge of these pollutants and also to develop procedures for removing them from waste streams before they enter the aqueous environment.

### 1.4 Current methods of environmental remediation

There are a number of methods currently in use for removing pollutants from waste streams and from the atmosphere, some of which have environmental disadvantages. Air-stripping and absorption by carbon are merely a form of pollution conversion in which the original polluting materials are transformed into gaseous and solid pollutants, respectively. Destructive technologies such as chlorination and ozonation use strong oxidants, which are themselves more or less hazardous. Moreover, while ozonation is effective for the degradation of many organic compounds, the process requires considerable capital investment and high electrical consumption. Disposal is also required for unused ozone to prevent the escape of this toxic gas into the atmosphere. The technique is also ineffective in the destruction of halomethanes and triazine herbicides, such as atrazine (43) (Halmann, 1996c).
Biodegradation by activated sludge is effectively used for the remediation of "normal" organic pollutants, such as those from domestic waste or food industries, and many industrial waste streams. The sludge consists of bacteria and protozoa which feed on organic material, as they do on organic pollutants in natural waterways, but in treatment processes aeration maintains oxygen levels to ensure complete degradation. When this is achieved, part of the sludge is recycled to seed the raw waste, whilst the remaining effluent is subjected to further treatment (Porteous, 1992). Many xenobiotic compounds, such as chlorophenols, herbicides, textile dyes and surfactants are, however, resistant to such treatment. Pentachlorophenol and 2,4-dichlorophenol, for example, inhibit the respiratory activity of micro-organisms in the sludge. It is sometimes possible to acclimatise the organisms to such compounds and the degradation of recalcitrant chemicals may be facilitated by the use of mixed populations of bacteria (Halmann, 1996e).

1.5 Environmental purification and treatment by TiO\textsubscript{2} photocatalysis

In recent years, there has been considerable interest in the use of photochemical processes to provide alternative routes of water and air purification, and several methods have been developed which are collectively referred to as Advanced Oxidation Technologies (AOTs). The three AOTs which lead to relatively rapid and complete destruction of most organics are UV-ozonation, UV-peroxidation and heterogeneous photocatalysis. Although all three techniques have their merits, the latter process is a particularly attractive method for water decontamination as it uses neither O\textsubscript{3} nor H\textsubscript{2}O\textsubscript{2}. Moreover, the process can be carried out at ambient temperatures and can lead to the total mineralisation of organic carbon to CO\textsubscript{2}, usually without the formation of significant intermediate products (Serpone, 1995). Complete mineralisation is essential as partial degradation could produce compounds which are more hazardous than the original pollutant.
The most widely studied photocatalyst is titanium dioxide, TiO₂, which has a number of properties to recommend it. It is cheap, readily available, insoluble under most conditions, photostable, non-toxic and the most active of the commercially available photocatalysts (Al Sayyed, 1991). Unfortunately it is essentially a UV absorber having an intrinsic threshold limit (λₜₜʰ), above which it does not absorb, of 390 nm (Mills et al., 1993a). The ideal photocatalyst would be active at visible light wavelengths, utilising the main part of terrestrial sunlight thereby significantly reducing the cost of the technology.

The overall process of heterogeneous photocatalytic oxidation can be summarised as follows:

\[
\text{organic pollutant + O}_2 \xrightarrow{\text{semiconductor}} \text{CO}_2 + \text{H}_2\text{O} (+ \text{mineral acid})
\]

Many different aspects of semiconductor photocatalysis have been studied and, indeed the topic is now a major research front. The kinetics of the reaction, both under experimental conditions and by modelling is an active field (Ollis, 1997) as are the removal of inorganic ions from wastewater (Korgel and Monbouquette, 1997), removal of organics from the vapour phase (Datye, et al., 1997; Hall, et al., 1997), the development of self-cleaning TiO₂-coated glass (Pichat, et al., 1997) and paving blocks (Murata, et al., 1997), and improvement of reactor design for solar water detoxification (Bahnemann, et al., 1997).

Whilst the ultimate aim of all the strands of research is the complete and rapid mineralisation of hazardous pollutants, detailed knowledge of the molecular pathways involved will enable the efficiency of systems to be improved.

1.6 Mechanistic aspects of semiconductor photocatalysis

1.6.1 Introduction

Nearly all organic compounds can be degraded by semiconductor photocatalysis but, despite considerable research efforts over recent years, important details of the mechanism of this process are still unclear. The often reported rapid degradation of substrates has frustrated attempts to elucidate the intermediate steps in the reaction.
The following sections attempt to give an overview of the underlying mechanistic principles of semiconductor photocatalysis as proposed in the current literature. They begin by examining the surface chemistry of the catalyst with relation to the initial events on absorption of light, the effect of the catalyst’s crystal structure and the chemical nature of the surface. The second two points relate to adsorption of organic molecules at the surface which is also affected by the spatial and chemical structure of the substrate. An adsorbed molecule will be in close proximity to oxidising species. The nature and formation of these species are explored, along with their mode of attack. Oxidation of organic compounds in photocatalysis leads to the formation of intermediate products, which, for substituted benzene derivatives, are often aromatic in nature. Finally the breakdown of aromatic to aliphatic compounds is reviewed.

1.6.2 Influence of TiO₂ crystal structure and surface chemistry

The photocatalytic process is initiated by the absorption of light by a semiconductor photocatalyst, e.g. TiO₂, leading in the excitation process to the formation of charge carriers (Figure 1-1).

![Figure 1-1 Formation of charge carriers in semiconductor photocatalysis.](image)
The following general mechanism is proposed from the results, obtained by laser flash photolysis measurements, of studies of the primary processes. (Hoffmann, et al., 1995):

**Primary process**

charge-carrier generation

\[
\text{TiO}_2 + h\nu \longrightarrow h\nu^+ + e_{cb}^-
\]

charge-carrier trapping

\[
h\nu^+ + \text{Ti}^{IV} \text{OH} \longrightarrow \{\text{Ti}^{IV} \text{OH}^*\}^+ \\
e_{cb}^- + \text{Ti}^{IV} \text{OH} \rightleftharpoons \{\text{Ti}^{III} \text{OH}\}
\]

\[
e_{cb}^- + \text{Ti}^{IV} \longrightarrow \text{Ti}^{III}
\]

charge-carrier recombination

\[
e_{cb}^- + \{\text{Ti}^{IV} \text{OH}^*\}^+ \longrightarrow \text{Ti}^{IV} \text{OH} \\
h\nu^+ + \{\text{Ti}^{III} \text{OH}\} \longrightarrow \text{Ti}^{IV} \text{OH}
\]

**Characteristic times**

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<thead>
<tr>
<th>Reaction</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>(h\nu^+ + \text{Ti}^{IV} \text{OH}) (\longrightarrow) ({\text{Ti}^{IV} \text{OH}^*}^+)</td>
<td>fast (10 ns)</td>
</tr>
<tr>
<td>(e_{cb}^- + \text{Ti}^{IV} \text{OH}) (\rightleftharpoons) ({\text{Ti}^{III} \text{OH}})</td>
<td>shallow trap (100 ps)</td>
</tr>
<tr>
<td>(e_{cb}^- + \text{Ti}^{IV}) (\longrightarrow) (\text{Ti}^{III})</td>
<td>deep trap (10 ns)</td>
</tr>
<tr>
<td>(h\nu^+ + {\text{Ti}^{III} \text{OH}}) (\longrightarrow) (\text{Ti}^{IV} \text{OH})</td>
<td>fast (10 ns)</td>
</tr>
</tbody>
</table>

**Key**

>\text{TiOH} primary hydrated surface functionality of \(\text{TiO}_2\)

e_{cb}^- conduction-band electron

\(h\nu^+\) valence-band hole

\{\text{Ti}^{IV} \text{OH}^*\}^+ surface-trapped VB hole (i.e. surface-bound hydroxyl radical)

\{\text{Ti}^{III} \text{OH}\} surface-trapped CB electron

Titanium dioxide (\(\text{TiO}_2\)) exists in three crystalline polymorphs (anatase, rutile and brookite) and in an amorphous phase. Only anatase and rutile phases have relevance to heterogeneous photocatalysis. The surface of titania, in aqueous suspensions, is assumed to be completely hydroxylated. The anatase structure shows much higher photocatalytic activity than the rutile form. It has been proposed that, for rutile, faster recombination of charge carriers and lower adsorption of reactants is responsible for this disparity. The latter effect can be rationalised by a lower number of surface hydroxyl groups present on rutile (Bahnemann, et al., 1994). Other workers (Shaw, et al., 1996) support the view that surface hydroxylation plays an important role in the enhanced activity of anatase. They also suggest that it is due to the greater extent of adsorption of \(\text{O}_2\) on the surface which
allows efficient trapping of conduction band electrons, and hence prevents charge carrier recombination. Both forms have the same band gap, but the anatase surface is reported to be highly heterogeneous with three kinds of Lewis acid sites (differently co-ordinated Ti$^{4+}$ ions) and at least two kinds of hydroxyl groups present on the surface. This is due to the exposure of different planes on the crystallites (Hadjiivanov and Klissurski, 1996).

Comparison of the photooxidation of a number of substrates using commercial samples of TiO$_2$ with different anatase/rutile ratios and crystallite sizes shows that larger crystallites are more efficient photocatalysts because of the longer migration distances available for photoproduced electrons and holes, which probably reduces the rate of electron-hole recombination. However, annealing TiO$_2$ above 600°C decreases the photocatalytic activity towards 4-chlorophenol, a trend mirrored by the decrease in surface area of TiO$_2$ particles (Halmann, 1996a).

One commercially produced form of TiO$_2$, Degussa P25, has been widely used in photocatalytic studies. It is a non-porous 70: 30% anatase : rutile mixture with a surface area of 55 ± 15 m$^2$ g$^{-1}$ and crystallite sizes of 30 nm in 0.1 μm diameter aggregates. P25 owes its high photoreactivity to slow recombination, possibly due to the anatase/rutile structure which promotes charge-pair separation, as well as the small particle size and hence high surface area. The efficiency of a photocatalyst depends, amongst other factors, on the recombination lifetime of charge carriers and also the interfacial electron-transfer rate constant. An increase in either of these variables will lead to higher quantum efficiencies (Hoffmann, et al., 1995). P25 is one of the most efficient photocatalysts for the degradation of a wide range of substrates, but modified TiO$_2$ catalysts with higher efficiencies are being developed (Rajh, et al., 1997; San Román, et al., 1997).

The interactions of electron donors and acceptors with a semiconductor photocatalyst are determined, in part, by surface chemistry. Metal oxide particles suspended in water are known to be amphoteric. In the case of TiO$_2$, the principal amphoteric surface functionality is the “titanol” moiety, >TiOH (Hoffmann, et al., 1995). In aqueous TiO$_2$ suspensions, the pH of the medium determines the form of the titanol. The potential
difference at the interface between two phases, i.e. the catalyst surface and the substrate solution, is measured in terms of electrokinetic potential, also called $\zeta$ (zeta) potential. The point at which there is no potential difference is termed the zero $\zeta$ potential, isoelectric point (pI), or zero point of charge (pH$_{zpc}$). For Degussa P-25 the zero $\zeta$ potential occurs at pH = 5.6. At more acidic pH (1) the semiconductor particle surface is positively charged, while at pH > 5.6 (2) the surface is negatively charged (Terzian, et al., 1991):

$$\text{Ti}^{IV}-\text{OH} + H^+ \Leftrightarrow \text{Ti}^{IV}-\text{OH}_2^+ \quad (1)$$

$$\text{Ti}^{IV}-\text{OH} + \text{OH}^- \Leftrightarrow \text{Ti}^{IV}-\text{O}^- + H_2O \quad (2)$$

Other values quoted for the neutral point include pH$_{zpc}$ 6.25 (Hoffmann, et al., 1995) and pI 6.8 (Halmann, 1996a). At this point, the immersed solid oxide would have zero net charge and electrically equivalent concentrations of positive and negative complexes.

This implies that, for TiO$_2$, interactions with cationic electron donors and acceptors will be favoured for heterogeneous photocatalytic activity when pH > pH$_{zpc}$, while anionic electron donors and acceptors will be favoured at low pH under conditions when pH < pH$_{zpc}$. The redox potential of the valence-band hole or trapped hole, however, decreases by 59 mV for each increasing unit of pH. If shifting the redox potential is dominating the reactivity of the TiO$_2$ particles, then lower rates of substrate oxidation should be observed at high pH. But, at alkaline pH, surface adsorption of the electron donors appears to play a more important role in determining the photoreactivity than the shift in nominal redox potential (Hoffmann, et al., 1995).

To summarise, the rate of energetically wasteful recombination of the charge carriers, formed by the absorption of light, appears to be dependent on the crystalline structure of the titanium dioxide catalyst and on the availability of sinks for the charge carriers. Overall reactivity of the catalyst is also determined by the nature of the surface, which can also be affected by the pH of the aqueous suspension. P25 TiO$_2$, among commercially available catalysts, appears to have the most efficient combination of crystal structure and surface area yet achieved.
1.6.3 Adsorption on and desorption from the catalyst surface

As will be seen later, photocatalytic degradation can only occur when either or both substrates and potential oxidising or reducing intermediaries are in close proximity to the photoinduced charge carriers on the catalyst particles. Therefore, adsorption on the catalyst surface plays an important part in the process. There is a strong correlation between degradation rates and the concentration of organic pollutant adsorbed on the surface, implying that oxidising species, i.e. hydroxyl radicals or holes, are directly available at the surface (Hoffmann, et al., 1995).

Most studies suggest that adsorption of organic substrates on TiO$_2$ surfaces can be described in terms of Langmuirian adsorption isotherms. Originally developed for gaseous systems, an adsorption isotherm is generally described in terms of the relationship between the amount of gas adsorbed on a surface at constant temperature and the equilibrium pressure.

**Langmuir isotherm for single-site adsorption**

\[
\theta = \frac{bp_A}{1 + bp_A}
\]  

where \( b \) = adsorption coefficient which is the ratio \( k_a/k_d \) (rate constants for adsorption and desorption); \( p_A \) is the pressure of the gas being adsorbed and \( \theta \) is the fractional surface coverage (for gas adsorbed on solid) (Mortimer, 1996). In terms of an organic reactant in a TiO$_2$/aqueous suspension the isotherm takes the following form:

\[
\theta_r = \frac{K_{ads}C_{eq}}{(1 + K_{ads}C_{eq})}
\]  

where \( \theta_r \) is the fractional surface coverage of the reactant, \( K_{ads} \) is the fast adsorption/desorption equilibrium constant and \( C_{eq} \) is the equilibrium concentration of the reactant in the bulk solution (Cunningham and Sedlak, 1993).

A study of 22 organic solutes showed the dependence of the photooxidation rate on concentration obeys the Langmuir expression (4) for each substrate (Matthews, 1988), the
limiting decomposition rate at higher substrate concentrations being related to the extent of adsorption of the substrate molecule on the TiO$_2$ surface. In physical terms, the Langmuir model from which the isotherm is derived implies that adsorbed species are attached to the surface of a substrate at definite localised sites with each site only accommodating one adsorbed species. At maximum adsorption this would correspond to the formation of a monolayer. It also suggests that there is the same probability of adsorption at all sites, independent of whether adjacent sites are occupied or not, implying that the surface is completely uniform. If this is a correct assumption, the differential heat of adsorption is independent of the fractional surface coverage and the forces of attraction and repulsion between adjacent adsorbed species are negligible.

As for the adsorbing function of the catalyst, most minerals expose a surface to the exterior which consists of hydroxyls protruding into the medium. These surface hydroxyls prefer to form hydrogen bonds with molecules adjacent to the mineral surface. Associations of organic molecules with the surface include van der Waals, dipole-dipole and H-bonding interactions (Schwarzenbach, et al., 1993a). Several studies indicate that adsorption of phenols and alcohols on TiO$_2$ surfaces occurs via the phenolic OH group. FTIR studies of the adsorption of 4-chlorophenol on the surface of Degussa P25 show that it forms approximately one monolayer and is chemisorbed by a phenolic link. A downward shift in the wavenumber of the C=C peak also suggests a weakening of the aromatic ring (Gray and Stafford, 1994). Other work with 4-chlorophenol provides evidence that the formation of several different surface structures by an adsorbate may be expected to yield several concurrent reaction pathways (Schwarzenbach, et al., 1993a).

Despite strong evidence for Langmuirian behaviour, as previously stated the anatase surface is highly heterogeneous with different roles proposed for individual titanium sites. It is postulated that the adsorption or photoadsorption of molecular oxygen occurs on Ti(III) sites (surface-trapped conduction band electron), while organic substrates such as cresols adsorb on surface hydroxyl Ti(IV)-OH sites (Halmann, 1996b). This view is supported by other workers (Sclafani, et al., 1994; Matthews, 1988). Sclafani and co-workers found that the maximum photoactivity for the decomposition of phenol in a TiO$_2$
heterogeneous system occurs when both H\textsubscript{2}O\textsubscript{2} and O\textsubscript{2} are present. Their mechanism involves at least two sites on the surface of TiO\textsubscript{2}: one type adsorbs the organic species and the other adsorbs H\textsubscript{2}O\textsubscript{2} and O\textsubscript{2} in competition. When the three species are simultaneously present, charge separation occurs involving adsorbed oxygen species as electron traps and adsorbed H\textsubscript{2}O\textsubscript{2} species both as hole and electron traps. This results in powerfully oxidising radical species being formed. They therefore envisaged the oxidation process in these cases as occurring via two parallel pathways: one involving the reduced oxygen radical species and the other by the radical species produced by H\textsubscript{2}O\textsubscript{2} photodecomposition. The role of hydrogen peroxide in the mechanism of semiconductor photocatalysis is considered further in section 1.6.4.

Due to the rapid nature of electron-hole recombination, interfacial electron transfer is only kinetically significant when a relevant donor or acceptor is preadsorbed. Indeed, it has been suggested that preliminary adsorption is a prerequisite for efficient degradation. In aqueous metal oxide suspensions, hydroxyl substituents or water molecules can serve the role of surface-bound traps for photogenerated holes, forming surface-adsorbed hydroxyl radicals. Many organic substrates can themselves act as adsorbed traps for the photogenerated hole, either directly or via a surface hydroxyl radical. (Fox and Dulay, 1993).

In contrast, surface hydroxylation has also been found to have a retarding effect on the photodegradation of phenol. It is reported that hydroxylated anatase restricts the adsorption of phenol by steric hindrance and competes in the hole capture process. Hydroxyl radicals do not appear to act as charge transfer intermediates, and, indeed, are not detected. On completely dehydroxylated TiO\textsubscript{2}, annealed above 600 °C, phenol can be adsorbed, possibly through the hydroxyl, forming phenoxy-like species. Oxidation by direct hole transfer is then possible, with products such as quinones and polyhydroxyl aromatics being formed, which in turn are mineralised at the surface (Kutty and Ahuja, 1995).

The nature of the substrate molecule also affects adsorption. Association of organic solutes, especially hydrophobic ones, with mineral surfaces may be significant. The
hydrophobic effect minimises the disruption of hydrogen bonds between H2O molecules by non-polar molecules. This serves to drive hydrophobic organic compounds out of the bulk aqueous phase and onto surfaces, its influence increasing with the size of the non-polar part of the molecule. Substrates and their products present in the photolysate are degraded according to their relative oxidisabilities and also their concentration on the photocatalyst surface, which depends partly on their hydrophobicities. Studies with long chain alkyl compounds show that adsorption increases proportionally with increasing chain length, almost certainly due to increasing hydrophobicity of longer chains (Schwarzenbach, et al., 1993).

Other workers have attempted to correlate photocatalytic degradability with molecular structure for substituted aromatic compounds. For para-substituted phenols the change in the apparent reactivity constant, $k'$, is relatively small over a variety of substituents for non-halophenols, but there was a direct relationship between the $k'$ and Hammett constant, $\sigma$, for para-substituted monohalogenated phenols (O'Shea and Cardona, 1994). The Hammett constant is a representation of the effect different substituents have on the electronic character of a given aromatic system, and hence the compound's reactivity. The authors proposed that the relationship between Hammett constants and kinetic parameters indicates that a number of different pathways are involved in the TiO2-catalysed photooxidation of para-substituted phenols, and that the mechanism is dependent on the electronic nature of the substituent. Another study (Amalric, et al., 1996), of meta- and para-substituted benzenes, formulated an equation for the correlation:

$$\log k_{app} = 0.20 \log K_{ow} - 0.20 \sigma^+ - 0.033 MR - 0.43$$

Equation 5 replaces the Hammett constant, $\sigma$, with the Brown constant, $\sigma^+$, which takes into account the resonance effect for para-anisoles. It also introduces the octanol-water partition coefficient, $K_{ow}$, which reflects the hydrophobicity of the molecule; this is considered to be related to the extent of adsorption on TiO2. The other parameters are $k_{app}$ (in min$^{-1}$) the pseudo-first order rate constant of the pollutant disappearance in TiO2 aqueous suspensions, and MR the molar refractivity of the substrate. The latter parameter
relates to the dispersion of the substrate on the catalyst surface, whether the molecules are isolated or form some kind of clusters. The study concluded that the photocatalytic degradation of aromatic compounds, such as substituted anisoles, is faster for substrates that are better electron-donors and are more evenly dispersed at the TiO₂ surface. This conclusion is supported by a study of benzenesulfonates (Sangchakr, et al., 1995). Although not thought to affect adsorption, para-substitution changes the degradation rate as follows: CH₃ > H > OH > Cl > NO₂. This order indicates that the rate is accelerated by electron-donating substituents and retarded by electron-withdrawing substituents, a correlation that confirms the electrophilic nature of the photocatalytic reaction.

These studies also suggest that increased hydrophobicity would lead to a highly adsorbed substrate, in aqueous suspensions of TiO₂, and may cause clustering of molecules on the surface. Such non-Langmuirian behaviour could result in dimerisation due to the close proximity of oxidised radicals but, so far, there is little published evidence to support this hypothesis.

Substitution patterns also affect adsorption and thereby the rate of degradation. Laser photolysis experiments show that the surface complexation by benzene derivatives significantly accelerates electron transfer from the conduction band of the colloidal oxide to acceptors in solution e.g. methylviologen, the rate of enhancement being strongly dependant on the structure and chemical nature of the adsorbate, i.e. on the degree of adsorption. Mono- and bidentate benzene derivatives, e.g. benzoic acid, phthalic acid [1,2-C₆H₄(COOH)₂], isophthalic acid [1,3-C₆H₄(COOH)₂], terephthalic acid [1,4-C₆H₄(COOH)₂], salicylic acid [o-HOC₆H₄COOH], and catechol bind to the surface of TiO₂ colloids. At monolayer coverage, isophthalate enhances the rate of interfacial electron transfer to methylviologen 1700 times while terephthalate increase the rate by a factor of 133 indicating more efficient adsorption by isophthalate (Hoffmann, et. al., 1995).

To sum up, adsorption on the catalyst surface has an important role in the degradation process as it is the means by which the organic substrate is brought into contact with the oxidising species that will bring about its degradation. It is widely believed to obey a
Langmuir adsorption isotherm with a monolayer resulting at maximum adsorption, but this opinion is not universally supported. The Langmuirian model also states that interactions between adjacent adsorbed species are negligible. The molecular structure of the adsorbate, particularly the electron donating/withdrawing and hydrophobic nature of substituents will affect the way in which the molecule is held on the surface. Orientation will also be directed by hydroxylation of the catalyst surface.

1.6.4 The formation of oxidising species

This section begins by presenting the evidence for the proposal that hydroxyl radicals are the principal oxidising species in an aqueous TiO₂ photocatalytic system. It then considers whether they attack substrate molecules on the catalyst surface or in solution. Next, the possibility of substrate oxidation directly by a valence band hole is explored. Recombination of valence band holes and conduction band electrons is prevented if there is an electron acceptor available. The role of oxygen as an electron sink is then considered. Finally, some novel mechanisms which propose oxygen as an oxidising agent are described.

Absorption of light by a semiconductor particle leads to charge carrier formation which in turn, if there is no recombination, forms oxidising species. These are generally considered to be hydroxyl radicals (·OH), valence band holes (hvb⁺) and superoxide radicals (O₂⁻⁻).

Free hydroxyl radicals are very reactive (E⁰ = 1.55 V) and non-specific and react with most compounds at close to diffusion-controlled rates (Pichat, 1994). Oxidation by hydroxyl radicals as the principal reactive species is supported by the presence of hydroxylated degradation intermediates. These products are consistent with those found when similar aromatics react with a known source of hydroxyl radicals. The existence of hydroxyl and hydroperoxyl radicals in TiO₂ catalysed photolysates has been confirmed by ESR studies. However, evidence has also been found for the direct hole oxidation of tightly bound electron donors (Hoffmann, et al., 1995). Hydroxylated products could be formed, in principle, either by homolytic attack by a hydroxyl radical on a π system or by combination with a singly oxidised intermediate. Both electron-spin resonance and indirect
kinetic evidence point to the formation of the hydroxyl radical on TiO₂ in contact with water. On irradiated TiO₂ powders with strongly adsorbed substrates time-resolved diffuse reflectance spectroscopy shows the presence of single-electron oxidised intermediates which could be interpreted as direct hole-trapping by the substrate although this may be indistinguishable from the participation of surface-bound hydroxyl radicals in their formation. In other words, it seems likely that the principal charge trapping event is formation of a surface-bound *OH radical, which can initiate primary oxidation chemistry of substrates bound at the surface rather than diffusing into bulk solution (Fox and Dulay, 1993). Figure 1-2 suggests ways in which a valence band hole could be trapped and illustrates that a surface trapped hole could be conceptually equivalent to a surface-bound hydroxyl.

Figure 1-2 Proposed mechanism for the formation of surface trapped holes and surface bound hydroxyl.

Further support for the argument that hydroxyl radicals react at the catalyst surface comes from a study of the TiO₂ degradation of 3-chlorophenol at varying pH in the presence of inorganic ions. At pH 8, the presence of concentrations as large as 0.1 M NaCl, Na₂SO₄, NaNO₃, or NaHCO₃ had no effect on the initial rate. At pH > 6.3 the catalyst surface is negatively charged and will repel negative ions preventing interference in the action of *OH. At pH < 6.3, however, chloride, sulphate, and phosphate ions adsorb on the surface,
interfering with hydroxylation of organic substrates and inhibiting photodegradation. The insensitivity of TiO2-promoted photodegradation, at basic pH, to common inorganic ions is an important advantage over some other advanced oxidation processes. The homogeneous systems H2O2-O3, H2O2-UV light and O3-UV light are all inhibited by the presence of bicarbonate ions which scavenge hydroxyl radicals in solution. This suggests that the reaction between 3-chlorophenol and •OH in photocatalysed reactions takes place on the catalyst surface and not in solution (Halmann, 1996a).

There is, however, other conflicting evidence as to whether reactions of hydroxyl radicals occur on the catalyst surface or in solution or both. As noted above, HCO3−, a known hydroxyl radical scavenger, does not affect the rate of photocatalytic degradation of 3-chlorophenol, implying that any reaction mediated by hydroxyl radicals must occur on the catalyst surface and not in solution. It was also found that, if the surface OH groups are chemically blocked by attachment of silicon oxides, the photocatalytic activity of Pt-loaded TiO2 declines. Conversely, the inhibitory effect of 2-propanol on the oxidation of furfuryl alcohol on ZnO has been interpreted as evidence for homogeneous phase trapping of the hydroxyl. Kinetic arguments suggest that at low substrate coverages by phenol, photogenerated hydroxyl radicals diffuse into solution where they effect photooxidation, while they react at the surface when the substrate is present at high coverages (Fox and Dulay, 1993).

If freely diffusing hydroxyl radicals were the sole oxidant in photocatalysis, one might expect that the addition of a potential source of hydroxyl radicals, e.g., hydrogen peroxide, to a photolysate would increase the photocatalytic efficiency of a given degradation (hydrogen peroxide could scavenge a conduction band electron to form a hydroxyl radical and a hydroxide ion (6)). Indeed, if this were the case, since hydrogen peroxide is formed in the photocatalytic process, as a reaction proceeds and its concentration rises, there would be a subsequent rise in the concentration of hydroxyl radicals and the rate of loss of substrate would be expected be enhanced. In fact, adding quantities of hydrogen peroxide to the photolysate in the photocatalysed oxidation of chloroethylenes and chloral hydrates by TiO2 does not enhance the reaction at concentrations below 10−4 or above 10−1 M and
has a negative (or no) effect on the photocatalysis in the degradation of chloroacetic acids, atrazine, and chlorinated solvents. It is possible that hydrogen peroxide, or the hydroperoxy radical, may in fact function as a hydroxyl radical scavenger. In contrast, enhanced oxidative degradation was observed with phenol, organophosphorus derivatives, and dioxins (Fox and Dulay, 1993). Other studies (Halmann, 1996a) indicate that the presence of low concentrations of hydrogen peroxide, i.e. $10^{-4}$ to $10^{-2}$ mol dm$^{-3}$, enhances the photocatalytic oxidation of organic compounds in aqueous TiO$_2$ dispersions. This favourable effect is ascribed to the ability of H$_2$O$_2$ to accept conduction band electrons, thus assisting charge separation, while forming hydroxyl radicals (Equation 6).

$$H_2O_2 + e^- \rightarrow \cdot OH + OH^- \quad (6)$$

It is considered, however, that excess hydrogen peroxide promotes the formation of peroxo compounds on the surface of the TiO$_2$ particles, such as Ti(O)$_2$(OH)$_2$ and Ti(OOH)(OH)$_3$, which inhibit photocatalysis.

So oxidative electron transfer may occur indirectly through ($\text{>{TiIVOH}^+}$), the surface-trapped valence-band hole (i.e. surface-bound hydroxyl radical), directly via the valence-band hole, $h_{\text{vb}}^+$ (Hoffmann, et al., 1995) or by $^*\text{OH}$ generated from water bound to the surface. Evidence for the latter process is provided by the photocatalytic degradation of 4-hydroxybenzyl alcohol (HBA) on TiO$_2$ or ZnO in aqueous solution (Richard, 1993). Three photoproducts were identified: 4-hydroxybenzaldehyde (HBZ), 3,4-dihydroxybenzyl alcohol (DHBA) and hydroquinone (HQ). In the presence of an $^*\text{OH}$ quencher (isopropanol) the formation of DHBA was completely inhibited and the formation of HBZ partly reduced, but production of HQ was unaffected. However, the oxidation of HBA by $^*\text{OH}$, produced in the Fenton reaction, leads to HBZ and DHBA, with HQ being virtually absent. The author suggests that this is evidence that positive holes and hydroxyl radicals have different regioselectivities in the photocatalytic transformation of HBA. HQ results from oxidation by $h_{\text{vb}}^+$, DHBA from the reaction with $^*\text{OH}$ and HBZ is produced by both species (Scheme 1-1).
Although it is known that isopropanol quenches $^\cdot$OH in homogeneous media, there are no grounds for assuming that it will affect the reaction of surface-bound $^\cdot$OH radicals. If this is the case, then DHBA is formed by the action of aqueous phase $^\cdot$OH, HQ by either a surface bound hydroxyl radical, {>Ti$^{IV}$OH$^*$}+, or a valence band hole, $h_{vb}^+$, and HBZ, possibly, by all three species. That is to say, it is not possible to differentiate between the reactions of surface-bound hydroxyl radicals and direct hole oxidation on the basis of this evidence.

![Scheme 1-1 Proposed mechanism of photocatalytic degradation of 4-hydroxybenzyl alcohol.](image)

**Scheme 1-1** Proposed mechanism of photocatalytic degradation of 4-hydroxybenzyl alcohol.

From surface coverage measurements for 3-chloro-4-hydroxybenzoic acid (CHBzA) it was found that the solute molecules occupy only a minor fraction of the surface solution monolayer, the rest being occupied, presumably, by water molecules. Therefore the nature of the predominant initial interfacial reaction of holes ($h_{vb}^+$) photogenerated in the valence band of TiO$_2$ and migrating to the TiO$_2$/aqueous solution microinterface is statistically more likely to be of the type $h_{vb}^+ + H_2O \rightarrow H_2O^+$ (which dissociates to give {>Ti$^{IV}$OH$^*$})
than \( h_{vb}^+ \) is unlikely. However, adsorbed substrate molecules could be in close proximity to \( \{Ti^{IV}OH^+\}^+ \) leading to charge transfer along the surface solution monolayer to yield CHBzA\(^+\) (Cunningham and Sedlak, 1993).

Recombination of the conduction band electron with the valence band hole is reduced when there is an efficient sink for the excited electron. The redox potential of the conduction band of TiO\(_2\) is lower than that for the reduction of oxygen in inert solvents. Accordingly, adsorbed oxygen serves as a trap for the photogenerated conduction band electron resulting in the formation of superoxide \( O_2^{•−} \), a highly active species which can attack either organic molecules or adsorbed intermediates or, after protonation and further reduction, can form hydrogen peroxide and, hence, act as another source of hydroxyl radicals (Fox and Dulay, 1993).

\[
O_2 + 2H^+ + 2e^- \rightarrow H_2O_2
\]  

A two-electron reduction of oxygen would lead to the formation of \( H_2O_2 \) (7) which could also be formed by direct oxidation of two molecules of water by two valence-band holes. It has been shown by isotopic labelling experiments, however, that all the oxygen in photochemically produced hydrogen peroxide arises from dioxygen. Indeed, it has been suggested that electron transfer to oxygen may be the rate-limiting step in semiconductor photocatalysis (Hoffmann, et al., 1995).

The role of activated oxygen species was investigated on TiO\(_2\) particulate film electrodes. It was demonstrated that the presence or absence of oxygen can influence the reaction pathway, and therefore the product profile. This result illustrates that the role of oxygen in photocatalysis is more than simply reacting with conduction band electrons and preventing charge recombination (Gray and Stafford, 1994).

One group of workers went further and suggested that, in one case, all oxidation steps rely on the direct participation of oxygen. Photooxidation of trichloroethylene vapour on dehydroxylated TiO\(_2\) gives the products dichloroacetyl chloride (DCAC), CO, phosgene (Cl\(_2\)CO), CO\(_2\), HCl and a small amount of trichloroethane. When the experiment was
repeated with $^{18}$O$_2$ and H$_2$O$^{16}$O(g) all product oxygen was found to originate from $^{18}$O$_2$ and it was concluded that surface hydroxyl groups were not involved in the photooxidation. They proposed that oxidation of trichloroethylene on TiO$_2$ is by "electronically activated chemisorbed O$_2". A reaction scheme is suggested, but details of the mechanism are unclear (Fan and Yates, 1996).

Another alternative mechanism involving oxygen as the principal oxidising agent was proposed by Heller (Heller, 1995). The photooxidation of films of aliphatic hydrocarbons, alcohols, ketones, carboxylic acids, and aldehydes on TiO$_2$-coated buoyant glass microbubbles was studied in water. His results led him to propose that the initial reactions of the photogenerated hole-electron pair in humid air are:

\begin{align*}
\text{hv}^+ + \text{H}_2\text{O} & \rightarrow \cdot\text{OH} + \text{H}^+ \quad (8) \\
\text{e}^- + \text{O}_2 + \text{H}^+ & \rightarrow \cdot\text{OOH} \quad (9) \\
\cdot\text{OH} + \text{RH} & \rightarrow \text{R}^* + \text{H}_2\text{O} \quad (10) \\
\text{R}^* + \text{O}_2 & \rightarrow \text{ROO}^* \quad (11) \\
\text{ROO}^* + \cdot\text{OOH} & \rightarrow \text{ROOOOH} \rightarrow \text{products} \quad (12)
\end{align*}

were $\text{hv}^+$ is a valence band hole and RH is the substrate (8-12). The decomposition of the tetraoxide is postulated to occur so rapidly that no detectable intermediates are formed. For example, with benzene, any volatile intermediates, if formed, reacted so rapidly that they were not detected. However, the infrared spectrum of a non-volatile intermediate found on the TiO$_2$ photocatalyst showed the presence of polymerised conjugated aldehyde functions and their oxidation products, carboxylic acids. The mechanism proposed for the degradation of benzene is shown in Scheme 1-2.

Photolysis studies of substrates which, under identical conditions in the presence of oxygen, lead to degradation showed no significant photooxidation in its absence despite the presence of electron capturing Fe$^{3+}$. Neither the holes nor the hydroxyl radicals generated by reaction of holes with water molecules are adequate for the oxidation when the photogenerated electrons are captured by Fe$^{3+}$. It is proposed that equations 9 and 11, hole trapping by O$_2$ in acid media to form the hydroperoxy radical, and formation of the
organoperoxy radical, respectively, are essential steps in the reaction. These two species react to give a hydrotetraoxide which decomposes to products. The absence of oxygen, therefore, drastically reduces the rate of oxidation. Moreover, oxidation of the hydroperoxy radical or the superoxide radical anion by Fe$^{3+}$ present in the photolysate prevents the formation of the labile hydrotetraoxide and also inhibits the reaction.

![Scheme 1-2 Proposed mechanism of degradation of benzene via a tetraoxide intermediate.](image)

There are similarities and differences between tetraoxide-involving radiolytic processes and those on TiO$_2$ nanocrystallites. Both involve electrons: hydrated electrons in radiolysis and conduction band electrons in photocatalysis. Furthermore, both involve *OH radicals. The important difference is that in radiolysis there can be a higher transient density of hydrated electrons and *OH and more radical combination. As radical concentrations are low on TiO$_2$ surfaces, the dominant intermediate is organohydrotetraoxide formed upon combination of two dissimilar radicals in the same reaction zone near the site of absorption of a photon. It was concluded that oxidation is mostly by oxygen, not by photogenerated holes (h$_{vb}^+$), nor by their initial reaction product with water, *OH radicals. Although
valence band holes of anatase phase TiO₂ nanocrystallites are required for the oxidation to be initiated, according to Heller the actual oxidiser is molecular oxygen. It is also found that not only holes but photogenerated electrons are essential in the oxidation of reactants other than aldehydes. Interpretation of the crucial experiments with Fe³⁺ have recently been queried largely on the grounds of the presumed identity of the iron species involved (Mills and Le Hunte, 1997).

To summarise, most studies indicate that adsorbed *OH radicals (surface trapped holes) are the major oxidising species, while free hydroxyl radicals play a minor role, if any. Formation of the observed hydroxylated intermediates can all be explained via surface reaction of this species (Serpone, 1994).

\[
\begin{align*}
\text{OH} + \text{TiO} &= \text{•OH} \\
\text{TiO}_2 &\xrightarrow{hv} \text{TiO} \\
\end{align*}
\]

Direct hole oxidation can occur with tightly bound substrates, but this is thought to be a minor process. Oxygen plays an important role in the photodegradation reaction, acting as a trap for conduction band electrons and, in turn going on to take part in a number of possible oxidation mechanisms. The proposition that oxygen controls the whole oxidation process, leading eventually to the formation of an organohydratetraoxide which rapidly degrades to aldehyde functionalised products has yet to receive wide acceptance.

The way in which the oxidising species react with organic substrates will now be considered.

1.6.5 Primary oxidation processes

The initial steps in catalytic photooxidation have been widely studied. The majority of substrates investigated have been substituted benzenes, and of particular interest to the present work is the mechanism of degradation of phenols, an environmentally significant group of compounds. As previously described in the degradation of 4-hydroxybenzyl alcohol, free *OH radicals can undergo substitution of the aromatic ring systems, as in the
formation of dihydroxybenzyl alcohol or they can bring about side-chain oxidation, possibly via abstraction of a benzylic hydrogen, to give 4-hydroxybenzaldehyde. Surface-bound \( ^* \text{OH} \) may react in other ways with adsorbed substrates.

The \( ^* \text{OH} \) radical is electrophilic and hence adds preferentially to the position of the highest electron density within the benzene ring. Thus, the electron-donating/withdrawing properties of a substituent will determine the ratio of ortho : meta : para : ipso addition reactions (von Sonntag, 1996). Although in aromatic compounds, electron-donating substituents on the ring, e.g., HO and CH\(_3\)O groups, cause hydroxylation at ortho and para positions, electron-withdrawing substituents, such as in nitrobenzene (NO\(_2\)) and benzamide (CONH\(_2\)) have little effect on the orientation of hydroxylation. The intermediate products formed, hydroxyaromatics and quinones, are quite unstable and readily undergo further photodegradation. Peroxycyclohexadienyl and mucondialdehyde-type compounds are also proposed as primary intermediates.

Photocatalytic degradation studies with chlorophenols, 2,4-dichlorophenoxyethanoic acid (2,4-D), dimethoxybenzenes, benzamide, N-phenylethanamide, pyridine and nitrobenzene identified primary intermediates corresponding to the hydroxylation of the aromatic ring. Electron-donating substituents directed hydroxylation to ortho and para positions and if a chlorine atom or methoxy group occupied one of these positions, it was eliminated. Electron-withdrawing substituents, however, did not appear to influence hydroxylation. In the case of nitrobenzene approximately equal amounts of three hydroxylated derivatives were detected (Pichat, et al., 1993).

Studies of the degradation of \( p \)-cresol by polyoxometallates (POMs), e.g. oxides of tungsten and silicon, gives further evidence of the mechanism of degradation. Irradiated POMs react with water, producing \( ^* \text{OH} \) radicals, which can go on to oxidise organic substrates in solution. There is also the possibility of direct reaction of h\(_{vb}^+ \) with the substrate, but this generally appears to proceed to a lesser extent. Degradation of \( p \)-cresol by this system leads to hydroxylation products and opening of the ring, but the most abundant product is \( p \)-hydroxybenzyl alcohol. This suggests that the attack of \( ^* \text{OH} \) radicals
on the methyl group is predominant. Also, the relatively long lifetime of the $p$-hydroxybenzyl radical allows formation of dimeric products. Quinones were detected in trace amounts due to their direct photolysis even with $\lambda > 320$ nm. A possible scheme leading to these products is presented in Scheme 1-3 (Mylonas, et al., 1996).

Scheme 1-3 Oxidation of $p$-cresol in the presence of POMs.

Photocatalytic degradation of toluene by TiO$_2$ shows side-chain oxidation as opposed to hydroxylation. It is selectively transformed into benzaldehyde, with prolonged irradiation leading to further oxidation to benzoic acid and subsequent decarboxylation. Traces of other products attributed to the formation of benzyl radicals were also found. In UV-irradiated TiO$_2$ acetonitrile suspensions, the oxidation rate of the alkyl chain of alkyl benzenes decreases with the number of carbon atoms with the exception of toluene. The carbon atom in the $\alpha$ position with respect to the aromatic ring is the most reactive and leads to a carbonyl group (Scheme 1-4) (Pichat, 1994).
Scheme 1-4 TiO₂ photooxidation of an alkylbenzene in acetonitrile.

Another widely studied group of compounds are the halophenols. The oxidation of 4-chlorophenol in aqueous TiO₂ suspension was compared to the γ-radiolytic decay (Gray and Stafford, 1994). In the photocatalytic degradation of the substrate over TiO₂, the main intermediates were 4-chlorocatechol and hydroquinone. At higher substrate loadings, it was observed that the greater concentration of the primary product 4-chlorocatechol adsorbed on the surface encouraged direct hole oxidation resulted in an unidentified mixture of many non-aromatic fragments. Radiolytic studies are often used to elucidate free radical reaction mechanisms. By carrying out experiments in the presence of various scavengers Gray and Kamat deduced that, in γ-radiolysis, attack by *OH gives 4-chlorocatechol and hydroquinone as intermediates, indicating a common *OH-mediated pathway. In γ-radiolysis, however, the concentrations of intermediates were higher and the yield of hydroquinone relative to that of 4-chlorocatechol was lower than in the photocatalysed degradation. They concluded that, in the photocatalytic degradation of 4-chlorophenol by TiO₂, the degradation proceeds initially by *OH oxidations and, depending on experimental conditions, may be followed by direct oxidation by valence band holes at the semiconductor surface.

The TiO₂ photooxidation of pentachlorophenol (Mills and Hoffmann, 1993) revealed that the primary intermediates detected were p-chloranil (tetrachlorobenzoquinone), tetrachlorohydroquinone, o-chloranil, and hydrogen peroxide, while formate and acetate were observed after more prolonged irradiation. The mechanism proposed involves mainly oxidation of pentachlorophenol by surface-bound hydroxyl radicals, and in addition direct electron transfer to a surface-trapped hole forming the pentachlorophenoxy radical. The formation of p-chloranil and tetrachlorohydroquinone is explained by preferred orientation of *OH attack on the para position of pentachlorophenol (Scheme 1-5).
Scheme 1-5 The TiO₂ photooxidation of pentachlorophenol.

The reaction of *OH and N₃⁻ with a series of pentahalophenols (fluoro- (PFP-OH), chloro-(PCP-OH) and bromo- (PBP-OH)) was studied by pulse radiolysis (Serpone, 1994). Reaction of *OH with PCP-O⁻ and PBP-O⁻ gave 75% yield of the corresponding pentahalophenoxyl radicals, the proposed product of direct hole oxidation with TiO₂, and the remaining 25% of products consisting of dihydroxypentahalocyclohexadienyl radical anions, HO-PXP-O⁻, chloranil and bromanil, as formed by reaction with hydroxyl radicals in photocatalysis.

To conclude, primary oxidation processes are widely reported as involving attack by *OH, leading to either oxidation of aliphatic side-chains when present or nuclear substitution of hydroxyl, the position of substitution being directed largely by the presence of electron-donating substituents. Photocatalytic degradation and free hydroxyl radical oxidation show differences in intermediate profile for the same substrates, suggesting that surface-bound radicals are active in TiO₂ photooxidation. Dimerisation of radical intermediates and direct oxidation by photogenerated holes have also been reported.

1.6.6 Formation of ring-opened intermediates

Due to the complexity of primary oxidation processes in TiO₂-catalysed photodegradations, secondary and tertiary processes are difficult to follow, and therefore
even less well understood. Clearly, ring-opened intermediates must be formed from aromatic intermediates at some stage on the way to complete mineralisation. In an attempt to follow the degradation of hydroxylated biphenyl compounds through to aliphatic products, Bouquet-Somrani, et al. (1996) studied the photocatalytic degradation of the primary monocyclic primary intermediates, hydroquinone (HQ), benzoquinone (BQ) and catechol (CAT). They propose a complex mechanism, reproduced in Scheme 1-6, whereby 2,2'- and 4,4'-di- and 4-hydroxybiphenyl all give 1,2,4-trihydroxybenzene as a secondary product which undergoes ring-opening to form muconic acid (MUA), maleic acid (MA), and 1,3-butadiene (BU).

Scheme 1-6 Proposed mechanism for the formation of aliphatic compounds from hydroxylated biphenyls by photocatalytic degradation.

However, results from a study on substituted benzenes imply that ring-opened compounds could be formed as one of the primary stable intermediates. It is proposed that, for single-substituent aromatics, hydroxycyclohexadienyl radicals, formed either via *OH radical addition or via direct hole oxidation, undergo rapid reaction with oxygen to give
peroxyhydroxycyclohexadienyl radicals leading to the simultaneous formation of a phenol and the ring opened compound, mucondialdehyde. The mucondialdehyde is further degraded to carbon dioxide, water and a mineral acid (Scheme 1-7) (Matthews, 1988).

Scheme 1-7 Photocatalytic degradation of substituted benzenes.

A further study using GC-MS looked solely at the aliphatic compounds resulting from the photocatalytic degradation of dimethoxybenzenes. These were found to be mainly esters and acids. The dimethyl ester of hexadienedioic acid could result from ring opening of 1,2-dimethoxybenzene before hydroxylation. Scheme 1-8 (overleaf) shows the intermediates detected from the three dimethoxybenzene isomers. It is suggested that hydroxyl radicals are not the only oxidising species involved but speculation about superoxide and dimethoxybenzene radical-cations lacked supporting evidence. No aromatic intermediates were reported (Amalric, et al., 1995).

In summary, the multiplicity of oxidising species and degradation pathways obscures the nature of secondary and tertiary oxidation processes and few workers are prepared to speculate in detail on the subject. The results of these studies, however, indicate that ring-opened intermediates can be formed at an early stage in the oxidation of the substrate.
Scheme 1-8 Intermediates detected in the photocatalytic degradation of dimethoxybenzenes.

1.6.7 Conclusions

Absorption of light by a semiconductor catalyst leads to the excitation of an electron from the valence band to the conduction band, leaving a valence band hole. If they do not recombine, these charge carriers can go on to form oxidising species at the catalyst surface. The crystalline structure of titanium dioxide and the nature of adsorbed molecules both affect the efficiency of this process. There is a strong correlation between degradation rates and the concentration of adsorbed substrate, suggesting that oxidation occurs primarily on the catalyst surface. The structure of substrate molecules will affect the orientation of adsorption.
Surface-bound hydroxyl radicals are usually acknowledged as the principal oxidising species, being formed by abstraction of an electron at the hydroxylated surface by the valence band hole. This highly reactive species appears to attack adsorbed substrate. However, desorption of hydroxyl radicals and their reaction with substrate in the homogeneous medium cannot be ruled out. Oxidation may also occur directly by the valence band hole and some workers propose a central role for oxygen in the process, in addition to that of an electron sink.

Oxidation of organic substrates by hydroxyl radicals, whether on the catalyst surface or free, leads to hydroxylated intermediates and the oxidation of aliphatic side-chains in aromatic compounds. Direct hole oxidation seems to lead to rapid degradation to aliphatic fragments, with few detectable aromatic intermediates. Ring opened intermediates can be produced as the result of further oxidation of hydroxylated intermediates, etc., but there is some evidence that they could be formed in primary oxidation steps.

There is now broad agreement on the general mechanisms of semiconductor photocatalysis, although novel ideas are presented from time to time. However, there are still differences in the interpretation of the precise details of the way in which organic compounds are degraded due to the complexity of the processes in this heterogeneous system.
1.7 Scope and objectives of this project

Considerable research has been carried out on the photocatalytic degradation of phenolic compounds, particularly phenol itself and halophenols. The primary molecular processes in the reaction are revealed by the distribution of intermediates, but details of these remain unclear. Therefore this study attempted a systematic investigation of the relationship between intermediate distribution and the structure of the substrate.

Consequently, the objectives of this project were:

(a) To develop an effective procedure for photodegradation of a typical phenol, and appropriate methods of analysis of the reaction mixture to allow qualitative and quantitative determination of intermediates formed in the reaction.

(b) To establish correlations between the structure of a range of phenols (essentially the substitution pattern) and the ease of degradation by photocatalysis.

(c) To determine for each phenol the intermediates involved in the degradation process.

(d) To determine for each phenol, where possible, the primary processes in the reaction mechanism.

(e) To identify mechanistic concepts that may be usefully applied generally to the TiO$_2$ photocatalytic degradation of phenols.

These objectives were pursued through:

(i) the evaluation of the photocatalytic degradation of $p$-cresol under a range of photolysis conditions.

(ii) degradation studies on 2,6-, 3,5- and 3,4-dimethylphenols, 4-tert-butyl-, 2,6-, and 3,5-di-tert-butylphenols, and 2,6-di-tert-butyl-4-methylphenol.
(iii) photolysis of 3,5-dibromo-4-hydroxybenzonitrile and its 2-hydroxy isomer directly and in the presence of a photocatalyst.

An initial investigation of the photocatalytic degradation of p-cresol established both photolysis and HPLC analytical procedures for the remainder of the project and allowed comparison of the results of this study with those already published (Terzian, et al., 1991; Brezova, et al., 1993). The dimethyl and tert-butylphenols were examined in the light of the results from p-cresol to determine trends in degradation rates and intermediate profiles. Finally, the effect of substitution pattern on the photochemical degradation of two dibromohydroxybenzonitriles was investigated.

Therefore the rest of this thesis has the following structure. Firstly details of the experimental protocols will be described, followed by the results obtained from the photocatalytic degradation of p-cresol. Discussion and the conclusions drawn from this work leads on to an investigation of the degradation of tert-butylphenols, commencing with 2,6-di-tert-butyl-4-methylphenols (BHT). Confirmation of the trends observed are then sought by studies with isomeric dimethylphenols. Further information on substitution pattern effects are revealed from the degradation of dibromohydroxybenzonitriles. Finally, the results of the study are summarised and conclusions regarding the effect of substrate structure on the primary processes in photocatalytic degradation mechanisms are proposed.
CHAPTER 2
EXPERIMENTAL

2.1 Instrumentation

2.1.1 Physical measurements

Ultraviolet (UV) spectra were recorded in 1 cm quartz cuvettes using Kontron Model 860 or Cecil CE 5501 instruments. Infrared (IR) spectra were recorded as potassium bromide discs or in solution cells using a Nicolet 205 Fourier transform infrared spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Jeol EX400 (400 MHz) spectrometer (Departmental Service). Mass spectra (MS) were run on a VG-250 mass spectrometer (Departmental Service). Melting points were determined on an Electrothermal apparatus in capillary tubes and are uncorrected. Accurate weighing of small samples (< 0.1g) for quantitative HPLC measurements was carried out using a Perkin-Elmer AD2Z Autobalance. Gas chromatographic (GC) analyses were obtained with a Carlo Erba GC 6000 Vega Series 2 instrument, with BP10 capillary column and Shimadzu C-R1B integrator. Electrospray LC-MS data (negative ion mode) were supplied by Pfizer Central Research, Sandwich, Kent, UK. Accurate mass of photoproduct from 3,5-dibromo-2-hydroxybenzonitrile was supplied by SERC Mass Spectrometry Service Centre, University College of Swansea.

2.1.2 HPLC equipment

HPLC operations were performed using the following systems:

Instrument system 1: Varian 5060 ternary gradient LC pumping system, Varian 9065 Polychrom diode array detector (190-367 nm, 39 diodes), data acquisition using Varian Star software, version 4.01. This configuration allowed peak areas, UV-Vis spectra and calculated purity parameters to be obtained for individual peaks. The Purity Parameter calculation reduces the UV spectrum to an average wavelength which has been weighted by the absorbance squared by application of the following equation:
\[ \text{PuP}_{\lambda_1-\lambda_2} = \frac{\sum_{\lambda_1}^{\lambda_2} (A_i^2 \times \lambda_i)}{\sum_{\lambda_1}^{\lambda_2} A_i^2} \]

where \( \text{PuP}_{\lambda_1-\lambda_2} \) = peak purity parameter between wavelengths \( \lambda_1 \) and \( \lambda_2 \), and
\( A_i = \) absorbance at wavelength \( \lambda_i \)

Purity Parameters can also be used to evaluate peak purity across a peak in a chromatogram. If the peak is pure, the average wavelength of its spectrum will remain almost constant over the entire peak.

Diagnostic software features include extraction and reintegration of chromatograms at wavelengths other than that of primary detection, and identification of peaks by comparison with libraries of known compounds. Identity with an authentic compound was assumed when retention times (under identical analytical conditions) matched satisfactorily and the computed similarity parameter (based mainly on a comparison of Purity Parameters) exceeded 0.995. Details of procedures for qualitative and quantitative analyses are given in sections 2.4 and 2.6 respectively.

**Instrument system 2:** Waters 616 pump, 600S controller, 717 plus autosampler, 996 photodiode array detector, Millennium software, version 2.15. This software package was able to provide similar analytical information to the Varian Star software.

**Instrument system 3:** Waters Deltaprep 3000 pump, 600E System Controller, 484 Tunable Absorbance Detector, 745B Data Module and a Jones Apex ODS 8 µm, 250 \( \times \) 21 mm column. This system was used for all preparative scale separations.

**Instrument system 4:** Varian 5060 LC pump, Spectroflow 757 absorbance detector, Spectra-Physics ChromJet integrator.

**HPLC columns** The following stationary phases were used for analysis:

I Jones Apex II ODS, 250 mm \( \times \) 4.6 mm

II Waters Symmetry C18, 250 mm \( \times \) 4.6 mm
Mobile phase: All solvents were HPLC grade. For all analytical studies except dibromohydroxybenzonitriles and analysis of silver oxide oxidation products:

Reservoir A: 10% v/v ACN in water; Reservoir C: ACN.

Analyses to resolve 4MCC and 4MR had an additional reservoir, B: 10% v/v ACN in water + 0.1 mol dm\(^{-3}\) H\(_3\)PO\(_4\).

For dibromohydroxybenzonitriles:

Reservoir A: 5% v/v methanol in water; Reservoir B: 5% v/v methanol in water + 0.1 mol dm\(^{-3}\) phosphoric acid; Reservoir C: methanol.

For analysis of silver oxide oxidation products (instrument system 3, column IV):

Reservoir A: methanol; Reservoir B: water; Reservoir D: KH\(_2\)PO\(_4\) (40 cm\(^3\) of 1 mol dm\(^{-3}\) solution), H\(_3\)PO\(_4\) (4 cm\(^3\)) and methanol (50 cm\(^3\)) made up to 2 dm\(^{-3}\) with water.

All flow rates 1 cm\(^3\) min\(^{-1}\) unless otherwise stated.

Analytical conditions are described in Table 2-1.

Reproducibility of chromatogram peak areas. During the procedure to quantify the yield of the principal photoproduct from 35DB2HBN (section 2.3.2 j), six samples of the unphotolysed substrate solution were analysed consecutively, by HPLC, in order to determine the reproducibility of the peak areas. The results were as follows:

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean peak area</td>
<td>132 860</td>
</tr>
<tr>
<td>Standard deviation ((\sigma_n))</td>
<td>9530</td>
</tr>
<tr>
<td>Standard error ((\sigma_n / \sqrt{n}))</td>
<td>3890 = 2.9%</td>
</tr>
</tbody>
</table>
Table 2-1 HPLC analysis conditions.

<table>
<thead>
<tr>
<th>substrate</th>
<th>column</th>
<th>T/°C</th>
<th>mobile phase</th>
<th>λ/nm</th>
<th>analyte (retention times/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>p</em>-cresol 1</td>
<td>I</td>
<td>30</td>
<td>Program: 100% A to 30% A (0-20 min), 30% A (20-27 min)</td>
<td>278</td>
<td>4HBAC (2.8), 4HIBALC (6.7), HMC (6.5), HPMC (8.1), 4HBALD (10.3), 4MCC and 4MR (11.5), p-cresol (14.9), DBD (21.3), MQOL (25.7)</td>
</tr>
<tr>
<td><em>p</em>-cresol 2</td>
<td>I</td>
<td>30</td>
<td>Additional reservoir B: 10% v/v ACN in water + 0.1 mol dm⁻³ H₃PO₃ Program: 90% A, 10% B to 20% A, 10% B, 70% C (0-20 min).</td>
<td>220</td>
<td>4MCC (10.7), p-cresol (14.8),</td>
</tr>
<tr>
<td>BHT 1</td>
<td>II</td>
<td>35</td>
<td>Program: 60% A to 10% A (0-25 min)</td>
<td>220</td>
<td>BAC (10.1), BALC (13.6), BALD (18.5), MQOL (18.5), BQ (24.6), BHT (26.9)</td>
</tr>
<tr>
<td>BHT 2</td>
<td>II</td>
<td>30</td>
<td>Isocratic 30% A : 70% C</td>
<td>220</td>
<td>MQOL (8.8), bis(MQOL) (14.3), BHT (19.2)</td>
</tr>
<tr>
<td>BHT 3</td>
<td>II</td>
<td>30</td>
<td>Program: 50% A to 5% A (0-25 min)</td>
<td></td>
<td>MQOL (8.3), BHT (19.6)</td>
</tr>
<tr>
<td>BHT 4</td>
<td>II</td>
<td>30</td>
<td>Program: 50% A (0-10 min), 50 % A to 20% A (10-20 min)</td>
<td>215</td>
<td>MQOL (22.9), MHPQ (24.2)</td>
</tr>
<tr>
<td>4tBP</td>
<td>II</td>
<td>30</td>
<td>Program: 60% A to 10% A (0-15 min)</td>
<td>220</td>
<td>4tBP (10.4)</td>
</tr>
<tr>
<td>35DtBP</td>
<td>I</td>
<td>30</td>
<td>Program: 50% A to 25% A (0-25 min) then to 10% A (25-30 min)</td>
<td>215</td>
<td>35DtBCC (12.7), 35DtBP (14.0)</td>
</tr>
<tr>
<td>substrate</td>
<td>column</td>
<td>T/°C</td>
<td>mobile phase</td>
<td>λ/nm</td>
<td>analyte (retention times/min)</td>
</tr>
<tr>
<td>---------------------------</td>
<td>--------</td>
<td>------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
<td>--------------------------------------------------------</td>
</tr>
<tr>
<td>26DtBP</td>
<td>I</td>
<td>30</td>
<td>Program: 55% A to 30% A (0-25 min) composition held to 28 min then 0% A (from 28.1 min)</td>
<td>215</td>
<td>DtBBQ (26.9), 26DtBP (27.8)</td>
</tr>
<tr>
<td>26DtBP – long retention time peaks</td>
<td>III</td>
<td>35</td>
<td>Program: 50% H₂O : 50% ACN to 10% H₂O : 90% ACN (0-10 min) composition held to 20 min then 100% ACN (20-30 min)</td>
<td>220</td>
<td>26DtBP (10.1), DHDP (14.1), DPQ (22.0)</td>
</tr>
<tr>
<td>DMP</td>
<td>II</td>
<td>30</td>
<td>Program: 100% A to 30% A (0-25 min) then to 10% A (25-30 min)</td>
<td>220</td>
<td>26DMBQ (17.3), 34DMP (19.4), 35DMP (20.0), 26DMP (20.7)</td>
</tr>
<tr>
<td>DBHBN</td>
<td>II</td>
<td>30</td>
<td>Isocratic 20% A: 10% B: 70% C</td>
<td>220</td>
<td>35DB4HBN (6.5), 35DB2HBN (9.0)</td>
</tr>
<tr>
<td>silver oxide oxidation products</td>
<td>IV</td>
<td>35</td>
<td>Program: 5% A, 30% B, 65% D (0-5 min) then to 35% A, 65% D (5-10 min) (See mobile phases, section 2.1.2 for details of reservoirs)</td>
<td>225</td>
<td>photoproduct (8.8), photoproduct after oxidation (9.1), 35DB2HBN (21.7)</td>
</tr>
<tr>
<td>adsorption study</td>
<td>I</td>
<td>30</td>
<td>Isocratic 40% A: 60% C (for phenol, p-cresol, 26DMP); 30% A: 70% C (for 4tBP, 26DtBP)</td>
<td>220</td>
<td></td>
</tr>
</tbody>
</table>
2.1.3 Preparative HPLC

All preparative separations were performed using system 3.

*Separation of intermediates from 3,5-dibromo-2-hydroxybenzonitrile photolysis*

Mobile phase: Reservoir A: 5% methanol in PureOne water; Reservoir B: 0.1 mol dm⁻³ phosphoric acid in 5% methanol in PureOne water; Reservoir C: methanol.

Mobile phase composition: 49% A : 1% B : 50% C, flow rate 30 cm³ min⁻¹.

Sample injection size: 10 cm³ of a solution of extracted material (3 mg cm⁻³) in 50% methanol : water.

Fractions collected: fraction A, intermediate r.t. 2 minutes; fraction B (major intermediate), r.t. 4.8 minutes; fraction C, unchanged starting material. Fractions collected on each run were checked for purity by analytical HPLC, then combined.

Intermediates were extracted from LC fractions by continuous liquid-liquid extraction with dichloromethane.

2.2 Reagents

The following chemicals were supplied by Aldrich Chemical Company: 1,4-benzoquinone, bis(4-hydroxyphenyl)methane, 4-tert-butylicatechol, tert-butylhydroquinone, 4-tert-butyphenol, catechol, p-cresol, 2,6-di-tert-butyl-4-methylphenol, 3,5-di-tert-butylcatechol, 2,5-di-tert-butylhydroquinone, 2,6-di-tert-butylphenol, 3,5-di-tert-butylphenol, 4,4′-dihydroxy-3,3′,5,5′-tetra-tert-butylbiphenyl, 2,3-dihydroxybenzaldehyde, 2,4-dihydroxybenzaldehyde, 2,5-dihydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde, 2,2′-dihydroxy-5,5′-dimethylbiphenyl, 2,6-dimethylbenzoquinone, 2,3-dimethylhydroquinone, 2,6-dimethylphenol, 3,4-dimethylphenol, 3,5-dimethylphenol, 2,5-dimethylresorcinol, hydroquinone, 3-hydroxybenzaldehyde, 4-hydroxybenzaldehyde, 4-hydroxybenzoic acid, 2-hydroxybenzyl alcohol, 4-hydroxybenzyl alcohol, 4-methylcatechol, nordihydroguaiaretic acid, resorcinol, salicylaldehyde, salicylic acid, tetrabutylammonium fluoride (15 wt % on alumina and 1 mol dm⁻³ in tetrahydrofuran). 3,5-Di-tert-butyl-4-hydroxy-
(15 wt % on alumina and 1 mol dm\(^{-3}\) in tetrahydrofuran). 3,5-Di-tert-butyl-4-hydroxy-benzyl alcohol was supplied by Lancaster Chemicals and Rose Bengal bound to polystyrene by Fluka. 2,6-Di-tert-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one, 3,5-di-tert-butyl-4-hydroxybenzaldehyde, 3,5-di-tert-butyl-4-hydroxybenzyl alcohol, 3,5-di-tert-butyl-4-hydroxybenzoic acid, 2,6-di-tert-butylbenzoquinone and 3,3',5,5'-tetra-tert-butylidipheno-4,4'-quinone were obtained from A. J. Parry (see A. J. Parry, Ph.D. Thesis, Open University, 1995). 3,5-Dibromo-4-hydroxybenzonitrile and 3,5-dibromo-2-hydroxybenzonitrile were supplied by Rhône-Poulenc Ltd. Titanium dioxide (TiO\(_2\)) P25 was supplied by Degussa. Acetonitrile was HPLC grade and was supplied by Rathburn Chemicals Ltd and Fisher Scientific U.K. Ltd. Hexane was supplied by Rathburn and diethyl ether by Prolabo. All solvents were reagent grade, unless otherwise stated. Bottled, compressed gases were supplied by Air Products and nitrogen was high purity. Silica gel for chromatography was Sorbsil C60. All chemicals were used as supplied without further purification. Water used in solutions and eluents for HPLC was purified by reverse osmosis and ion exchange to produce Grade 2 purified water (according to ISO3696/BS3978) and finally by PureOne polishing.

2.3 Photolysis procedures

2.3.1 Standard photolysis procedure

All photocatalytic degradations with \(p\)-cresol and dibromohydroxybenzonitriles were carried out in wholly aqueous solution, unless otherwise stated. All photolyses with tert-butylphenols and dimethylphenols were in 20% ACN (vol : vol). Substrate solution (10\(^{-4}\) mol dm\(^{-3}\), unless otherwise stated) and titanium dioxide (0.5 g dm\(^{-3}\)) were placed in a Pyrex glass flanged vessel (~1.3 dm\(^3\) capacity) containing a magnetic follower. The flanged head was equipped with multiple inlets that permitted the introduction of (i) a water-cooled cold finger (ii) a compressed air inlet capped by a sintered frit and (iii) a sampling tube. TiO\(_2\) was suspended in the solution by sonication for ~5 minutes. The apparatus was then assembled and the reaction mixture left in the dark, with cooling, aeration and stirring, to equilibrate for 30 minutes.
Irradiation was by a Rayonet multilamp reactor fitted with eight 350 nm phosphor-coated lamps (total output 100 W). The flask was held concentrically to the lamps, the distance from the lamp ring to the outside of the flask being 12 cm.

Sample handling. Samples were taken with a syringe through the sampling tube. The suspension was drawn back and forth several times to ensure a representative sample. To remove suspended TiO₂, 4 cm³ aliquots were passed through a Gelman Acrodisc LC13 PVDF 0.2 µm filter, which was then washed with 2 × 500 µl ACN, the washings being added to the filtrate. To allow for the washings when calculating substrate and intermediate concentrations for quantitative analyses, the peak areas were multiplied by 1.25 before comparison with standard solutions.

Analysis was by HPLC system 1.

This procedure was repeated at intervals with p-cresol during studies with other substrates to ensure that the overall conditions remained unchanged.

In control experiments without TiO₂ the photolysis vessel was washed with dilute sodium hydroxide solution and rinsed with PureOne water before use to remove any residual TiO₂ from the glassware.

2.3.2 Other photolysis procedures

Photolyses were performed as for the standard photolysis procedure with the following changes:

(a) Initial p-cresol photolysis – substrate solution was 4 × 10⁻³ mol dm⁻³ and samples of 5 cm³ were taken. The filter was washed with 2 × 500 µl water, the filtrate and washings being analysed separately. Analysis was by HPLC system 4 for degradation measurements and system 1 for detection of intermediates.

(b) p-Cresol photolysis with a 400 W lamp – the photolysis was carried out in an Applied Photophysics Pyrex immersion-well reactor. The immersion-well had a water-cooled jacket and housed a 400 W medium pressure mercury arc lamp. Gas purge was via a
sintered frit in the base of the reaction vessel. 3 cm$^3$ samples were taken and the filter was washed with 2 × 500 µl water, the filtrate and washings being analysed separately. Analyses were by HPLC system 1. This apparatus was also employed for the initial photolyses with the 3,5-dibromohydroxybenzonitriles.

(c) $p$-Cresol photolysis with simulated daylight – irradiations were by an Applied Photophysics multilamp reactor fitted with twelve ‘cool’ daylight phosphor-coated lamps (total output 180 W).

(d) Samples for LC-MS analysis – a solution of $p$-cresol was photolysed for 8 hours using the method (a), the initial $p$-cresol photolysis. A 10 cm$^3$ sample of the photolysate (Sample A) was filtered and the filter washed with 3 × 1 cm$^3$ water, the filtrate and washings being combined. A further 10 cm$^3$ sample (Sample B) was passed through a C$_{18}$ Sep-Pak cartridge and the adsorbed material eluted with acetonitrile. Both samples were analysed by LC-MS (see section 3.2.3 for results).

(e) Preliminary $p$-cresol quantitation – procedure as for initial $p$-cresol photolysis but analyses carried out on HPLC system 4.

(f) Carousel reactor – solutions were placed into quartz tubes held in a circular rack which revolved around a 400W medium pressure mercury lamp. This apparatus was used to assess the effect of varying (i) concentration and (ii) solvent composition, under conditions of identical irradiation, on the direct photodegradation of 3,5-dibromo-2-hydroxybenzonitrile. The carousel holds 33 tubes, 12 in the inner rack closer to the lamp and 21 in the outer rack. There are no facilities, however, for aerating, cooling or stirring the solutions.

(g) Photocatalytic degradation of dibromohydroxybenzonitriles – the photolysate contained ~10 ppm of each isomer in aqueous solution. TiO$_2$ (0.75 g) was added to 1.65 dm$^3$ of substrate solution. The photolysis apparatus was the immersion-well reactor described in (b). Photolysate samples (2.5 cm$^3$) were filtered in the usual way and the filter washed with water (2 × 500 µl).
(h) Photocatalytic degradation of dibromohydroxybenzonitriles by sunlight – a mixed solution of the isomers (~10 ppm per isomer) in a Pyrex flask was magnetically stirred on a north facing window sill during February/March 1995. The irradiation with the catalyst contained 0.1 g TiO₂ per 250 cm³ photolysate. Sampling and analysis were as previously stated.

(i) Photolysis of 3,5-dibromo-2-hydroxybenzonitrile by daylight – irradiations were carried out in an Applied Photophysics multilamp reactor fitted with twelve ‘cool’ daylight phosphor-coated lamps (total output 180 W). The reaction flask describe in the standard photolysis procedures was used. Initially a 19 mg dm⁻³ substrate solution was used. Due to impurities, observed in the HPLC analysis of undegraded solution, 35DB2HBN was recrystallised from methanol : water before use. A more concentrated initial substrate solution was required to enable extraction of photoproducts. As the solubility of 35DB2HBN in water is low, the addition of an organic solvent (methanol or acetonitrile) allowed the concentration to be increased, but irradiation of these solutions showed changes in the product profile. Increasing the substrate concentration in water, however, did not alter the products observed. Subsequently a nearly saturated solution of 35DB2HBN in water was used in the preparative photolyses. In all non-TiO₂ photolyses the apparatus was washed with dilute sodium hydroxide solution and rinsed with PureOne water before use to remove any residual TiO₂.

(j) Quantitation of photoproduct from 35DB2HBN – a photolysis was carried out as in (i) with a 19 mg dm⁻³ substrate solution.

2.3.3 Preparative photolysis with 3,5-dibromo-2-hydroxybenzonitrile

3,5-Dibromo-2-hydroxybenzonitrile (35DB2HBN, 40 (see appendix V for structure)) solution (~100 mg dm⁻³ in PureOne water) was irradiated in an Applied Photophysics multilamp reactor using a Pyrex reaction vessel for ~21 hours. This apparatus had been used in previous degradation studies of the 3,5-dibromohydroxybenzonitrile isomers (2.3.2(i)).
Reaction intermediates were extracted with dichloromethane by continuous liquid-liquid extraction. Each 500 cm$^3$ batch of photolysate required ~18 hours processing for complete extraction. A total of 6 dm$^3$ of solution was irradiated. Dichloromethane extracts were evaporated on a rotary evaporator to give a yellow-white solid which was stored in a refrigerator until the components could be separated by HPLC (see section 2.1.3 for details of preparative separation).

2.4 Qualitative analysis of reaction intermediates from alkyl phenols

Information from HPLC analyses, e.g. peak retention times and UV spectra, and previously published work gave clues to the identity of degradation intermediates. When available, authentic commercial samples of suspected intermediates were analysed by HPLC, under the same analytical conditions and at similar concentrations to those found in the reaction suspension.

Figure 2-1 illustrates the use of HPLC/diode array analysis in assigning peaks to structures with essentially identical chromophores. It is proposed that for 3,5-di-tert-butylphenol (SM) (Figure 2-1(a)), a reduction in retention time, indicating an increase in the polarity of the molecule, suggests side-chain functionalisation of the substrate (SM-X), whilst a longer r.t. could be due to an increase in molecular weight implying coupling (SM-SM). The use of similar arguments with quinones is illustrated in Figure 2-1(b) (overleaf).

Computer-generated component matching is also available in the Polyview section of Varian Star software. Information from the analysis of authentic compounds can be stored in a library file for comparison with data from the analysis of partially degraded substrates. In each analysis for all peaks greater than the set minimum height, the retention time, purity parameter and peak height at $\lambda_{max}$ were recorded. Also stored were details of possible library matches with a computed similarity parameter. If retention times and UV-vis spectra of authentic material and intermediate matched satisfactorily and the similarity parameter was at least 0.995, the identity of the intermediate was taken to be confirmed.
Identification by library match was used with some caution as the search parameters programmed strongly influence the outcome. Imprecise parameters, however, usually produce obviously inaccurate matches rather than false positive identifications.

A list of the authentic compounds analysed and stored in the alkyl phenol library file by the end of this project is given below:

3,5-di-tert-butyl-4-hydroxybenzaldehyde, 3,5-di-tert-butyl-4-hydroxybenzyl alcohol, 3,5-di-tert-butyl-4-hydroxybenzoic acid, 2,6-di-tert-butylbenzoquinone and 3,3',5,5'-tetra-tert-butylidipheno-4,4'-quinone, 2,6-di-tert-butyl-4-methylphenol, 1,4-benzoquinone, 4-tert-butylicatechol, tert-butylhydroquinone, 4-tert-butylphenol, catechol, p-cresol, 4-hydroperoxy-4-methyl-2,5-cyclohexadien-1-one, 4-hydroxy-4-methyl-2,5-cyclohexadien-1-one, 2,6-di-tert-butyl-4-methylphenol, 3,5-di-tert-butylcatechol, 2,6-di-tert-butylphenol, 3,5-di-tert-butylphenol, 4,4'-dihydroxy-3,3',5,5'-tetra-tert-butylbiphenyl, 2,3-dihydroxybenzaldehyde, 2,5-dihydroxybenzaldehyde, 2,2'-dihydroxy-5,5'-dimethylbiphenyl, 2,6-dimethylenbenzoquinone, 2,3-dimethylhydroquinone, 2,6-dimethylphenol, 3,4-dimethylphenol, 3,5-dimethylphenol, 2,5-dimethylresorcinol, 4-formylcatechol, 4-formylresorcinol, hydroquinone, 3-hydroxybenzaldehyde, 4-hydroxybenzaldehyde, 4-hydroxybenzoic acid, 2-hydroxybenzyl alcohol, 4-hydroxybenzy alcohol, 4-methylcatechol, 4-methylresorcinol.
2,6-di-tert-butyl-4-hydroperoxy-4-methyl-2,5-cyclohexadien-1-one, 2,6-di-tert-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one, bis(4-oxy-4-methyl-2,6-di-tert-butylcyclohexa-2,5-dien-1-one, resorcinol, salicyaldehyde, salicylic acid.

The library created for comparison with analyses from dibromohydroxybenzonitrile experiments contained data from the two substrates and the degradation products only, as authentic samples of proposed intermediates were not commercially available. Identification of the photoproduct from 35DB2HBN was by the procedure described in section 2.5.

2.5 Qualitative analysis of the photolysis product from 3,5-dibromo-2-hydroxybenzonitrile

High Resolution mass spectrometry evidence suggested that the major photoproduct from 35DB2HBN was a bromodihydroxybenzonitrile. Consequently the following tests were carried out to determine which of the bromines in 35DB2HBN had been substituted.

2.5.1 Infrared spectroscopy

Para-substituted dihydroxybenzenes form intermolecular hydrogen bonds if sufficiently concentrated when dissolved in an aprotic solvent. Dilution of such a solution causes disruption of hydrogen bonding with a subsequent shift in the band due to the -OH stretch in the IR spectrum. Ortho-substitution, however, enables intramolecular hydrogen bonding to occur and the IR dilution effect is not observed (Silverstein, et al., 1991a).

The IR spectrum of a solution of the product (5 mg cm⁻³ in CH₂Cl₂) was recorded along with the spectra from two 1:2 (vol:vol) serial dilutions of the same solution.

2.5.2 Iron (III) chloride test

Addition of alkaline iron (III) chloride solution to a solution of an ortho-dihydroxy-compound leads to the formation a complex ion (44) with a characteristic green colour. A further addition of sodium carbonate solution turns the solution a burgundy colour.
The results of this test with authentic samples of dihydroxy compounds are shown in Table 2-2.

**Table 2-2** Reaction of dihydroxybenzene with iron (III) chloride and sodium carbonate.

<table>
<thead>
<tr>
<th>compound</th>
<th>colour with FeCl₃</th>
<th>colour with FeCl₃ + Na₂CO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dihydroxybenzene</td>
<td>dark green</td>
<td>burgundy</td>
</tr>
<tr>
<td>1,3-dihydroxybenzene</td>
<td>yellow (no change)</td>
<td>orange-yellow gelatinous precipitate</td>
</tr>
<tr>
<td>1,4-dihydroxybenzene</td>
<td>yellow (no change)</td>
<td>orange-yellow gelatinous precipitate</td>
</tr>
<tr>
<td>4-methyl-1,2-dihydroxybenzene</td>
<td>mid-green</td>
<td>deep violet</td>
</tr>
</tbody>
</table>

The test showed a clear distinction between 1,2- and other dihydroxy compounds, but does appear to be affected by other substituents on the ring.

### 2.5.3 Lead acetate test

A few drops of lead acetate solution added to an aqueous solution of a 1,2-diol gives a white precipitate.

**Table 2-3** Reaction of lead acetate solution with diols

<table>
<thead>
<tr>
<th>compound</th>
<th>reaction with lead acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dihydroxybenzene</td>
<td>white precipitate</td>
</tr>
<tr>
<td>1,3-dihydroxybenzene</td>
<td>no visible change</td>
</tr>
<tr>
<td>1,4-dihydroxybenzene</td>
<td>no visible change</td>
</tr>
</tbody>
</table>
2.5.4 Gas chromatography of aromatic boronic acids: on-column derivatisation of dihydroxyphenols.

In a further attempt to determine whether the hydroxyl groups were adjacent on the aromatic ring, derivatisation with phenylboronic acid on a gas chromatography (GC) was attempted. The experimental protocol was based on Rose, et al., (1982) and Longstaff and Rose, (1982).

Development of an experimental procedure was carried out with authentic samples of 1,2-, 1,3-, and 1,4-dihydroxybenzenes (catechol, resorcinol and hydroquinone). All solutions were 1 mg cm\(^{-3}\) in ethyl acetate. Solutions of a diol and phenylboronic acid were combined (100 µl of each) and injected onto the GC column.

GC oven temperature gradient: 110 °C (0-1 min), 110 -170 °C at 40 °C min\(^{-1}\), 170 -250 °C at 10 °C min\(^{-1}\), hold at 250 °C. Retention time of peaks for individual solutions and reaction mixture is given in Table 2-4.

Table 2-4 GC retention times for dihydroxyphenols analysed before and after reaction with phenylboronic acid.

<table>
<thead>
<tr>
<th>compound</th>
<th>retention time alone/min</th>
<th>retention time in reaction mixture/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dihydroxybenzene</td>
<td>6.4</td>
<td>8.6</td>
</tr>
<tr>
<td>1,3-dihydroxybenzene</td>
<td>7.7</td>
<td>7.7</td>
</tr>
<tr>
<td>1,4-dihydroxybenzene</td>
<td>7.4</td>
<td>7.5</td>
</tr>
<tr>
<td>phenylboronic acid</td>
<td>&gt; 20</td>
<td></td>
</tr>
</tbody>
</table>

Only 1,2-dihydroxybenzene formed a derivative with phenylboronic acid, the other diols being unchanged. Unreacted phenylboronic acid was retained on the column but could be removed by injection of 1,2-dihydroxybenzene. This procedure was used each time when a derivative was not formed.
2.5.5 Oxidation with silver oxide

Oxidation of hydroquinone by silver oxide gives benzoquinone, which has a characteristic UV spectrum (q.v. Figure 2-1b). The oxidation was carried out on authentic diols and the unknown photoproduct and HPLC data from analysis of the reaction mixtures compared.

To the substrate (10 mg) in methanol (10 cm³) was added silver (I) oxide (50 mg) and magnesium sulphate (60 mg). After stirring for one hour, the mixture was filtered and diluted 1:10 (vol:vol) with methanol before analysis by HPLC. The results with authentic compounds are described in Table 2-5, Figures 2-2 and 2-3.

Table 2-5 Oxidation of dihydroxybenzenes by silver (I) oxide

<table>
<thead>
<tr>
<th>compound</th>
<th>before oxidation</th>
<th>after oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>colourless solution</td>
<td>dark amber solution</td>
</tr>
<tr>
<td></td>
<td>r.t. 5 min</td>
<td>r.t. 7.4 min</td>
</tr>
<tr>
<td>1,2-dihydroxybenzene</td>
<td>λ_max 215 (sh), 276 nm</td>
<td>λ_max 263, 418 nm</td>
</tr>
<tr>
<td>1,4-dihydroxybenzene</td>
<td>colourless solution</td>
<td>yellow solution</td>
</tr>
<tr>
<td></td>
<td>r.t. 2.1 min</td>
<td>r.t. 5.1 min</td>
</tr>
<tr>
<td></td>
<td>λ_max 222, 289 nm</td>
<td>λ_max 246, 291 nm</td>
</tr>
</tbody>
</table>

Figure 2-2 UV spectrum of 1,4-dihydroxybenzene (a) before and (b) after oxidation by silver oxide
Figure 2-3 UV spectrum of 1,2-dihydroxybenzene (a) before and (b) after oxidation by silver oxide.

2.5.6 \(^{13}\text{C} \text{NMR}\)

It has been shown that chemical shifts of the ring carbon atoms of substituted benzenes in \(^{13}\text{C} \text{NMR}\) spectroscopy can be estimated by applying the principle of substituent additivity (Silverstein, et al., 1991b). The carbon shifts in a recorded \(^{13}\text{C} \text{NMR}\) spectrum of the photoproduct were compared to the calculated shift for the two proposed product structures.

2.6 Quantitative analysis of reaction intermediates

The area of a peak in a chromatogram is directly proportional to the amount of the compound in the solution being analysed. Accurate preparation of the photolysate solution enables the loss of substrate to be calculated. Analysis of a range of solution concentrations showed that detector response is linear, except near the extremes of detection i.e. 5 mAu < absorbance < 2 Au. Therefore analysis of a solution of a known concentration of a standard compound permits quantitative analysis of intermediates.
Although, as previously stated, tests carried out showed that detector response is linear, standard solutions were prepared to give similar peak areas to those observed in the photolysate.

The following is a sample calculation to illustrate the procedure.

Yield of 2,6-dimethylbenzoquinone (26DMBQ, 36) in the degradation of 2,6-dimethylphenol (26DMP, 28)

The initial substrate solution of $1.03 \times 10^{-4} \text{ mol dm}^{-3}$ gave a peak area 204 620 at 220 nm. After 15 minutes irradiation, the peak area was 129 130 indicating a substrate concentration of $6.5 \times 10^{-5} \text{ mol dm}^{-3}$, $3.8 \times 10^{-5} \text{ mol dm}^{-3}$ of substrate having been degraded.

For the authentic 26DMBQ, a solution of $8.8 \times 10^{-6} \text{ mol dm}^{-3}$ gave a peak area 44 940 at 254 nm. The 26DMBQ peak in the photolysate had an area of 41 660 (after correction for dilution). Therefore the concentration of 26DMBQ in the photolysate was $8.2 \times 10^{-6} \text{ mol dm}^{-3}$.

The product yields were calculated as follows

\[
\text{percentage product yield} = \frac{\text{intermediate formed / mol dm}^{-3}}{\text{substrate degraded / mol dm}^{-3}} \times 100
\]

for 26DMBQ

\[
\frac{8.2 \times 10^{-6} \text{ mol dm}^{-3}}{3.8 \times 10^{-5} \text{ mol dm}^{-3}} \times 100 = 21.6\%
\]

The calculation was repeated for each sample taken during the photolysis. A yield plot is a graph of percentage intermediate yield against percentage substrate degradation. If the line of the graph has a negative gradient or is horizontal, the intermediate is considered as a primary product in the reaction. A positive gradient defines a secondary intermediate.
2.7 Syntheses

2.7.1 4-Methylresorcinol (4MR, 3)

The synthesis was carried out by the literature method (Meirovics, et al., 1969).

4-Formylresorcinol: to resorcinol (5.5 g, 0.05 mol) in dimethylformamide (25 cm³, dried over anhydrous magnesium sulphate) was added dropwise with cooling phosphorus oxychloride (7.73 g, 4.7 cm³, 0.5 moles). During the reaction the mixture became semi-solid and additional dimethylformamide (20 cm³) was added. After 4 hours ice (19 g) and sodium acetate (19 g) were added. The white precipitate that formed after 15 minutes was filtered off. On standing, the filtrate produced a dark red precipitate that gave a 2,4-dinitrophenylhydrazone product with Brady’s reagent confirming the presence of an aldehyde.

A solution of the product in hexane was applied to a silica column (18 x 7 cm). The initial eluent was hexane, with diethyl ether gradually being added until the mixture was 1:1. The product was detected by spotting the fractions on to silica t.l.c. plates and adding a drop of Brady’s reagent. The fractions containing the aldehyde were pooled and the solvent removed. The white solid product gave a positive test with Brady’s reagent.

Yield of 4-formylresorcinol: 1.4 g (20%). Melting point: 127-130°C (Lit.: 130-132°C)

4-Methylresorcinol: zinc powder (1.2 g), mercury (II) chloride (0.06 g) and 2% hydrochloric acid were stirred together for 10 minutes. The aqueous layer was decanted off and the amalgamated zinc added to a 50 cm³ round bottom flask with water (1.5 cm³) and concentrated hydrochloric acid (3 cm³). Finally, 4-formylresorcinol (0.4 g, 0.003 moles) in toluene (10 cm³) was added. The mixture was stirred magnetically and refluxed. The reaction was followed by t.l.c. A further 1 cm³ of conc. HCl was added after 6 and 23 hours.

After 28 hours the zinc had been consumed. The reaction mixture was cooled to room temperature and the two layers separated. The aqueous layer was diluted with water (10 cm³) and extracted with diethyl ether (4 x 10 cm³). The combined toluene layer and ether
extracts were washed with water (2 x 20 cm3), dried over anhydrous magnesium sulphate, filtered and the solvents evaporated. The product was a brown oil but, when left overnight, white crystalline material formed in the flask. These crystals were confirmed by mass spectrometry to be 4-methylresorcinol.

Yield of 4-methylresorcinol: 0.3 g (80 %, white crystals). Mp: 100-101 °C. (Lit. :103-105 °C). MS (EI), M+ m/e = 124.

2.7.2 4-Hydroperoxy-4-methyl-2,5-cyclohexadien-1-one (HPMC, 8) and 4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (HMC, 7)

The synthesis was based on the method of Wasserman and Pickett, 1985. 

\( p \)-Cresol (2.2 g, 20 mmol) was dissolved in dry dichloromethane (100 cm3). The solution was added to tetrabutylammonium fluoride (1 mol dm\(^{-3}\) in tetrahydrofuran, 10 cm3) and Rose Bengal B (bound to polystyrene, 20 mg) in dry CH\(_2\)Cl\(_2\) (200 cm3). The photolysis flask was the Pyrex apparatus used in standard photolysis procedures (see section 2.3.1) which had been oven dried. The photolysate was purged with oxygen prior to irradiation, and a low flow rate maintained during the experiment. Irradiation was by an Applied Photophysics multilamp reactor fitted with twelve ‘cool’ daylight phosphor-coated lamps (total output 180 W).

The reaction was monitored by HPLC analysis. Samples of the photolysate (1 cm\(^3\)) were filtered, evaporated to dryness and redissolved in ACN : H\(_2\)O (50% by volume, 5 cm\(^3\)). Analyses were performed on instrument system 1 with \( p \)-cresol 1 analytical conditions. After 24 hours irradiation two peaks were observed, at retention times 6.7 and 8.1 min, both with very similar UV spectra (\( \lambda_{\text{max}} \sim 224 \text{ nm} \)). The analysis, however, still showed a large proportion of unreacted starting material.

After a total of 72 hours irradiation, a reactor panel (containing two lamps) was removed and a 50 W tungsten-halogen lamp placed close to the reaction flask. Eight hours irradiation with this additional lamp did not significantly increase the reaction rate and the reactor panel was replaced for the remainder of the photolysis. After a total of 169 hours
irradiation, a further 100 mg of Rose Bengal B was added to the photolysate which increased the rate of substrate loss.

At the end of 218 hours irradiation, the two peaks at r.t. 6.7 and 8.1 min were predominant in the HPLC analysis, with the starting material approximately 1/8th of initial concentration. The Rose Bengal was filtered off and the solvent removed on a rotary evaporator to give a brown oil (8.4 g).

Separation of the reaction products was attempted by column chromatography (silica gel, 50g, 3 x 20 cm). The brown oily product mixture was extracted with diethyl ether, the combined extracts evaporated and redissolved in the minimum volume of column eluent (hexane : diethyl ether, 1 : 1 by volume). An initial fraction of 50 cm³ followed by fractions of 20 cm³ were collected, the products being detected by thin layer chromatography (TLC) using the same eluent. Fractions showing a single compound by TLC were combined and the solvent removed to give an off-white solid (140 mg). HPLC analysis of the solid showed the presence of the two compounds observed in the photolysate at r.t. 6.7 and 8.1 min, with the peak at r.t. 6.7 min giving a computer generated similarity (see section 2.5) of 1.0000 to an unknown intermediate in the photocatalytic degradation of p-cresol.

The two components were separated by preparative HPLC using Instrument System 3. The eluent was 8% (by volume) ACN in water and 15 cm³ of a 2 mg cm⁻³ solution of the crude product mixture in eluent was separated in each run. The separation was followed by the detector output (absorbance units at 220 nm) and each fraction checked for purity by analytical HPLC. Fractions of the same compound were combined, the organic solvent removed on a rotary evaporator and the water by freeze drying.

The earlier eluting compound, 4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (HMC, 7), (18 mg) had a UV spectrum, \( \lambda_{\text{max}} 224.2 \text{ nm} \), PuP 225.13 nm. MS (EI), \( m/z = 124, 107 \) (base peak), literature values \( m/z = 124, 108 \) (base peak), 107, 96 (Endo, et al., 1989).

The later eluting compound, 4-hydroperoxy-4-methyl-2,5-cyclohexadien-1-one (HPMC, 8), (49 mg) had a UV spectrum, \( \lambda_{\text{max}} 223.6 \text{ nm} \), PuP 224.51 nm. After recrystallisation,
Mp 93-94.5 °C, literature value 102-104 °C (Endo, et al., 1989). NMR (CDCl₃, 400 MHz) δH : 1.43 (3H, s, Me), 6.31 (2H, d), 6.90 (2H, d), a small singlet at 1.58 was also visible. Literature values are ¹H NMR (CDCl₃) δ: 1.39 (3H s, Me), 4.22 (1H s, OOH), 6.23 (2H d, C3, 5-H), 6.97 (2H d, C2, 6-H) (Endo, et al., 1989) and (CDCl₃, 90 MHz) δ:1.40 (3H, s), 6.22 (2H, d), 6.92 (2H, d) and a small singlet at 2.46 was also visible (Wasserman and Picket, 1985).

2.7.3 2,6-Di-tert-butyl-4-hydroperoxy-4-methyl-2,5-cyclohexadien-1-one (MHPQ, 18) and 2,6-di-tert-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (MQOL, 17)

These compounds were provided by Mr Pravin Patel. The MHPQ preparation was according to the literature method (Kharash and Joshi, 1957). Characterisation was by HPLC Instrument System 1 with analysis system BHT 4 and by comparison with an authentic sample of the hydroxy compound, MQOL (17) (see appendix II for structure).

MQOL was synthesised by the reduction of MHPQ with triphenylphosphine after the method of Denney, et al. (1959) further confirming the identity of the substrate.

To a stirred solution of MHPQ (25.23 g, 0.10 mole) in 40 cm³ absolute ethanol and 30 cm³ H₂O was added triphenylphosphine (26.23 g, 0.10 mole) in absolute ethanol (100 cm³). After stirring at room temperature for two hours, the solvents were removed on a rotary evaporator. The solid residue was chromatographed on a silica column, eluent diethyl ether : hexane, 1 : 1. Detection of the product fraction was by HPLC, as was characterisation of the isolated material.

2.7.4 Bis(4-oxy-4-methyl-2,6-di-tert-butylcyclohexa-2,5-dien-1-one) (bis(MQOL), 27)

The synthesis was attempted by Mr Pravin Patel by the literature method (Benjamin, et al., 1978) from the synthesised sample of MQOL. Hydrogen peroxide and formic acid were added to MQOL in hexane. After stirring and heating at 40°C for 5 hours, the solution was
made basic with sodium hydroxide solution. The organic products, extracted with hexane were separated by column chromatography. The experimental protocol states that bis(MQOL) was isolated from the reaction mixture, it being one of five reported products. HPLC analysis of the material from the hexane extract obtained in the synthesis showed a small proportion of the required compound, but efforts to isolate it were unsuccessful.

**Preparative photolysis** (carried out by Mr Graham Jeffs)

The irradiation was carried out as for the standard photolysis procedure except the photolysate contained 0.53 g dm⁻³ BHT in 50% ACN : H₂O. The desired intermediate reached an optimum yield after 9 hours and was immediately extracted into hexane (2 × 150 cm³), the extracts dried over magnesium sulphate, filtered and stored in a refrigerator. A second irradiation with a 1.05 g dm⁻³ BHT solution gave a lower yield of the required material.

**Separation of intermediate** (development work GJ, separation GJ and JC)

Hexane extracts (100 cm³ portions) were extracted with acetonitrile (25 cm³ portions) until all the required material was removed. Water (~5 cm³) was added to each ACN extract to separate out any dissolved hexane. The required material was separated by preparative HPLC (Instrument System 3, eluent 70% ACN, product retention time ~11 min) and the purity of the collected fractions confirmed by analytical HPLC. The fractions were immediately extracted back into hexane (2 × fraction volume), dried over magnesium sulphate, filtered, and concentrated by a flow of nitrogen gas in a fume cupboard before being stored in a refrigerator. Solid samples were obtained by complete evaporation of the solvent, again by a stream of nitrogen.

**Characterisation** NMR (CDCl₃, 400 MHz) δ_H: 1.25 (21 H, s), 6.59 (2H, s); δ_C: 24.0 (C7), 29.4, 34.8 (tert-butyl), 79.2 (C4), 139.5 (C2,6), 148.4 (C3,5), 186 (C1).
2.8 Miscellaneous

2.8.1 Brady's reagent

2,4-Dinitrophenylhydrazine (0.25 g) was suspended in methanol (5 cm³). Concentrated sulfuric acid (0.5 cm³) was added dropwise and the warm solution filtered. Addition of the reagent to a solution of an aldehyde or ketone gives characteristic crystalline yellow to deep red 2,4-dinitrophenylhydrazone products.

2.8.2 Dark adsorption of alkyl phenols

The procedure used followed that of Cunningham, et al., 1994. The extent of dark adsorption of alkyl substituted phenols on the photocatalyst was determined by adding TiO$_2$ (0.5 g dm$^{-3}$) to a solution of a phenol (10$^{-4}$ mol dm$^{-3}$) in 20% acetonitrile. The suspension was initially sonicated for two minutes then stirred magnetically for one hour in the dark, before a 4 cm$^3$ sample was filtered (Acrodisc PDVF) and analysed by HPLC. The percentage of phenol adsorbed was calculated from the peak areas in the chromatogram before and after addition of TiO$_2$. 
CHAPTER 3
ALKYL PHENOLS

3.1 Introduction
As described in section 1.3, a number of alkyl phenols are environmentally relevant pollutants. These include the methylphenols (cresols), dimethylphenols (xylenols) and tert-butylphenols (Shui, et al., 1994). The first two groups of compounds are present in coal tar creosote and are often present in waste streams from, and in the ground surrounding, wood treatment plants. The third group comprises some of the phenolic antioxidants e.g. 2,6-di-tert-butyl-4-methylphenol (BHT, 13). Although not priority pollutants, they are widely used in the polymer and food industries, and are known to find their way into natural waters (Lopez-Avila and Hites, 1981).

This chapter begins by looking at catalytic photooxidations of p-cresol, carried out initially to develop experimental protocols, but the results of which prompted a comparative study with BHT. This, in turn, led on to work to investigate if there is a correlation between the substitution pattern in alkyl phenols and the primary molecular mechanism of photocatalytic degradation.

3.2 TiO₂ photocatalytic degradation of p-cresol
p-Cresol was chosen as a model pollutant for preliminary photocatalytic studies for the purpose of developing experimental and analytical techniques as ready comparison could be made with previously reported work (Terzian, et al., 1991; Brezova, et al., 1993). All of initial photolyses were carried out in wholly aqueous solutions, unless otherwise stated. Firstly, the rate of loss of p-cresol by two different sets of irradiation apparatus was determined. The intermediates formed in the degradation process were then identified, as far as possible, and their relative yields in the photolysate calculated.
3.2.1 Rates of loss of substrate

In an initial photolysis of a $4 \times 10^{-3}$ mol dm$^{-3}$ solution of $p$-cresol in the Rayonet apparatus (section 2.3.2a), less than 50% of the initial concentration of substrate had been lost after 48 hours irradiation. A control experiment performed under a nitrogen atmosphere showed no degradation after 142 hours irradiation.

Due to this slow degradation of $p$-cresol, the experiment was repeated with a 400W medium pressure mercury arc lamp resulting in 57% degradation after 26 hours irradiation, twice the rate observed for the Rayonet apparatus. Results from the two sets of apparatus are shown in Figure 3-1. Another control irradiation under N$_2$ indicated no degradation after 52 hours with the Hg lamp. A third apparatus was used in the preparation of a partially degraded sample for LC-MS analysis (see section 2.3.2d). The Applied Photophysics apparatus was fitted with “cool” daylight tubes and degraded 29% of the initial substrate concentration in 8 hours irradiation.

![Figure 3-1](image)

**Figure 3-1** Loss of $p$-cresol in Rayonet reactor and by 400W medium pressure mercury arc lamp.
The results obtained here are compared with those of Terzian and Brezova in Table 3-1.

**Table 3-1** Comparison of the rate of loss of \( p \)-cresol with experimental conditions in TiO\(_2\) catalysed photodegradation.

<table>
<thead>
<tr>
<th>Lamp</th>
<th>TiO(_2^a) loading/ g dm(^{-3})</th>
<th>photolysate volume/ dm(^3)</th>
<th>pH</th>
<th>substrate conc./ mol dm(^{-3})</th>
<th>irradiation time to 50% degradation/ h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rayonet</td>
<td>350 nm, 100 W</td>
<td>0.5</td>
<td>1</td>
<td>not controlled</td>
<td>4 \times 10(^{-3})</td>
</tr>
<tr>
<td>Hg lamp</td>
<td>400 W medium pressure mercury</td>
<td>0.5</td>
<td>0.4</td>
<td>not controlled</td>
<td>4 \times 10(^{-3})</td>
</tr>
<tr>
<td>'cool' daylight</td>
<td>daylight simulating 180 W</td>
<td>0.5</td>
<td>1</td>
<td>( b^b ) not controlled</td>
<td>4 \times 10(^{-3})</td>
</tr>
<tr>
<td>Terzian, et al.</td>
<td>( \geq 300 ) nm, 900 W Hg-Xe lamp</td>
<td>2</td>
<td>0.05</td>
<td>3</td>
<td>( 1.86 \times 10^{-4})</td>
</tr>
<tr>
<td>Brezova, et al.</td>
<td>125 W medium pressure mercury</td>
<td>0.8</td>
<td>0.12</td>
<td>not controlled</td>
<td>( 10^{-4})</td>
</tr>
</tbody>
</table>

\(^a\)Degussa P25 in all studies \(^b\)\( p \)-cresol solution had pH 6.1 and after irradiation with TiO\(_2\), pH 5.9 \(^c\)100% in \(<6\) hours \(^d\)95% in \(<1\) hour

All of the photolyses in this study had significantly slower rates of loss of substrate than those previously reported. We believe that this is partly due to the larger photolysate volumes and higher substrate concentration. There is no perceivable correlation between lamp wattage and degradation rate; a faster rate of loss occurred in Brezova’s work and here with the ‘cool’ daylight lamps than with Terzian’s more powerful 900 W lamp and the 400 W Hg lamp, respectively. The arrangement of lamps and irradiation path length were not described by either Terzian or Brezova. In this work the vessel used in the Rayonet and Applied Photophysics apparatus had a diameter of 7.5 cm and a 20 cm depth of photolysate. The outside of the flask was 12 cm from the lamps in the Rayonet and 7 cm in the Applied Photophysics reactor.
The results from these five studies show significant inconsistencies. The origins of these are believed to lie with a number of factors, e.g. light intensity, TiO$_2$ loading in the slurry, the rate of photoreaction and mixing of the photolysate (Stafford, et al., 1997). This range of variables can affect not only results between laboratories, but are subtle enough to influence experiments within a group. Consequently, at appropriate intervals during the study of further substrates, $p$-cresol degradations were repeated to check that conditions remained largely unchanged.

This lack of reproducibility was illustrated during the investigation of another substrate, 2,6-di-tert-butylphenol (26DtBP). The rate of degradation in two separate photolyses changed by a factor of four. Although the same experimental conditions were employed, the equipment had been moved to another location between the two experiments and a different magnetic stirrer was used. It is, however, unclear what caused such a notable change in the rate of loss of substrate. Despite the change in absolute rate, a comparative photolysis with $p$-cresol under the new conditions demonstrated that the relative rates of degradation remained essentially the same.

### 3.2.2 Qualitative analysis of reaction intermediates

A typical chromatogram of partially photocatalytically degraded $p$-cresol in aqueous solution, indicating the identified intermediates, is shown in Figure 3-2.

Intermediates observed by Terzian, et al. (1991) and Brezova, et al. (1993) include 4-hydroxybenzaldehyde (4HBALD, 4), 4-hydroxybenzoic acid (4HBAC, 5), 4-methylcatechol (4MCC, 2) and 4-methylresorcinol (4MR, 3) (see appendix I for structures). Authentic samples of the first three compounds were obtained, and the fourth synthesised. Comparison by HPLC analysis (diode array detection) with that of our photolysate analysed under the same conditions indicated the presence of 4HBALD. Addition of acid to the eluent system enabled resolution and identification of 4MCC and 4MR. 4HBAC was not detected, but the previously unreported 4-hydroxybenzyl alcohol (4HBALC, 6) was found to be present.
Figure 3-2 HPLC of p-cresol photolysate after irradiation in Rayonet reactor for 24 h (39% degradation, analytical conditions - p-cresol 1).

The UV spectrum of another peak in the HPLC analysis results, r.t. 6.5 min, was recognised as being similar to that of 2,6-di-tert-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (MQOL, 17), a compound used in another project in these laboratories involving 2,6-di-tert-butyl-4-methylphenol (BHT, 13) (see appendices II and III for structures). That work had shown that both MQOL and the equivalent hydroperoxy compound, 2,6-di-tert-butyl-4-hydroperoxy-4-methyl-2,5-cyclohexadien-1-one (MHPQ, 18) have virtually identical UV spectra (Parry, 1995). It was therefore proposed that the p-cresol degradation intermediate was either 4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (HMC, 7) or 4-hydroperoxy-4-methyl-2,5-cyclohexadien-1-one (HPMC, 8).

**LC-MS analysis**

In an attempt to identify more of the degradation intermediates, analysis of the photolysate by GC was attempted, with a view to further analysis by GC-MS. This was, however, unsuccessful and an opportunity arose for analysis by LC-MS. Analysis of the irradiated samples (section 2.2.3d) confirmed the presence of the aldehyde, 4HBALD and indicated that the cyclohexadienone was HMC (7) rather than HPMC (8).
An intermediate at r.t. 20 min, i.e. eluting after p-cresol, must be less polar or have larger molecules such as a dehydrodimer. Initial comparison of the UV absorption data with the literature values indicated that 2-(4'-hydroxyphenylmethyl)-4-methylphenol (9) (Higa, et al., 1975) rather than 2,2'-dihydroxy-5,5'-dimethylbiphenyl (12) (Beilstein) was the most likely structure for this compound. However, subsequent comparison with an authentic sample of compound 12 showed unequivocally that the peak in question was due to 2,2'-dihydroxy-5,5'-dimethylbiphenyl, and that the literature UV data (Beilstein) were in error.

The relative yields of both 12 and a product with a similar HPLC retention time increase significantly when irradiation is carried out with simulated daylight rather than UV-A radiation (Figure 3-3). The chromatographic properties and UV spectrum of the compound are consistent with a dimeric structure. It is not clear whether the influence of radiation wavelength on product distribution is due to differing photolability of the dehydrodimers under the two conditions or to an effect on pathways competing with their production.

The analysis conditions for this chromatogram and Figure 3-2 are the same, but a different column of the same type was used.

**Figure 3-3** HPLC of p-cresol photolysate after irradiation with 'cool' daylight tubes in Applied Photophysics multilamp reactor for 8 h (29% degradation, analysis conditions - p-cresol 14).
The identity of the highly retained peak at r.t. ~23 min remains elusive. UV data for possible \( p \)-cresol dehydrodimers is given in Table 3-2, along with data for \( p \)-cresol in various solvent systems for comparison of the effect of solvent on UV spectra.

**Table 3-2** Comparison of UV spectral data for \( p \)-cresol and highly retained intermediate (r.t. ~23 min) with data for possible dehydrodimeric products.

<table>
<thead>
<tr>
<th>compound</th>
<th>structure</th>
<th>( \lambda_{\text{max}}/\text{nm} ) (log ( \epsilon ))</th>
<th>solvent</th>
<th>source of data</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p )-cresol</td>
<td><img src="image" alt="OH" /></td>
<td>218, 275</td>
<td>70% ACN</td>
<td>HPLC analysis</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220 (3.74), 277</td>
<td>H( _2 )O</td>
<td>Kamlet, (1952)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>224(3.83), 280</td>
<td>ethanol</td>
<td>Kamlet, (1952)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>244, 280</td>
<td>ethanol</td>
<td>Hunter, <em>et al.</em>, (1950)</td>
</tr>
<tr>
<td>highly retained peak</td>
<td></td>
<td>201, 238 (sh), 286</td>
<td>85% ACN</td>
<td>HPLC analysis</td>
</tr>
<tr>
<td>(r.t. ~23 min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4,4'-dihydroxy diphenylethane</td>
<td><img src="image" alt="HO" /></td>
<td>227, 246, 279</td>
<td>ethanol</td>
<td>Hunter, <em>et al.</em>, (1950)</td>
</tr>
<tr>
<td>2-[(4-hydroxyphenyl)methyl]-4-methylphenol</td>
<td><img src="image" alt="OH" /></td>
<td>280, 283</td>
<td>methanol</td>
<td>Higa and Scheur, (1975)</td>
</tr>
<tr>
<td>Pummerer's ketone</td>
<td><img src="image" alt="O" /></td>
<td>222 (4.36), 302 (3.52)</td>
<td>ethanol</td>
<td>Phillips, <em>et al.</em>, (1963)</td>
</tr>
<tr>
<td>4-methyl-2-p-tolyloxyphenol</td>
<td><img src="image" alt="OH" /></td>
<td>212, 278</td>
<td>aqueous ethanol</td>
<td>Beilstein</td>
</tr>
</tbody>
</table>
Comparison of the unknown peak with an authentic sample of 4,4'-dihydroxydiphenylethane excluded this identity. Data for Pummerer's ketone were included as it is a commonly observed product of p-cresol oxidations (Anderson, et al., 1977).

The qualitative results are summarised in Figure 3-4 and compared with those reported previously.

**this work**

![Chemical structures](image)

**Terzian, et al.**

![Chemical structures](image)

**Brezova, et al.**

![Chemical structures](image)

**Figure 3-4** Identified intermediates in the photocatalytic degradation of p-cresol.

Both the nuclear substitution by OH and side-chain oxidation previously described were observed, but oxidation of the methyl group only went as far as the aldehyde. Radical dimerisation and the previously undetected nuclear addition of OH were also detected. Information on the relative importance of each of the products in the primary events of photocatalytic oxidation was sought through quantitation.
3.2.3 **Quantitative analysis of reaction intermediates**

The Rayonet irradiation apparatus was used in the quantitation experiment as the lower light levels and slower degradation rates allowed more detailed observation of reaction intermediates. The initial \( p \)-cresol photolysis procedure was used.

Yields of the five main products identified in the photolysis were determined by reference to solutions of known concentration of authentic samples except for 4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (for method see section 2.4). In the case of 4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (HMC, 7), 4-hydroperoxy-4-methyl-2,5-cyclohexadien-1-one (HPMC, 8) was used as reference as insufficient pure material was obtained in the synthesis. The very close similarity between the electronic spectra of the 2,6-di-tert-butyl analogues MQOL and MHPQ (Parry, 1995) indicates that 7 and 8 would have essentially identical responses in the diode array detector. The yield of 2,2'-dihydroxy-5,5'-dimethylbiphenyl (DBD, 12) was initially estimated by treating the molecule as two essentially non-interacting \( p \)-cresol chromophores. The yield was later confirmed by comparison with an authentic sample. Yields of the products at 30% degradation are given in Figure 3-5.

![Pie chart showing intermediate yields in the UV-A photocatalysed degradation of aqueous \( p \)-cresol at 30% degradation.](image)

**Figure 3-5** Intermediate yields in the UV-A photocatalysed degradation of aqueous \( p \)-cresol at 30% degradation.
The peak corresponding to the two dihydroxy intermediates (r.t. ~11.5 min, Figure 3-2) was poorly resolved and gave inconsistent quantitation data. Reanalysis of samples after the addition of acid to the eluent system (p-cresol 2 conditions, Table 2-1), improved their resolution. Yields for these intermediates were recalculated from these analyses to give the values reported.

The yield profiles for four intermediates are shown in Figure 3-6. The yield of a reaction product is taken to be the amount formed (in moles) divided by the number of moles of substrate consumed × 100 (q.v. section 2.6). It is helpful to distinguish between primary and secondary products. We consider a product as 'primary' if its yield remains unchanged or declines throughout the degradation. It is seen as the first formed compound in a reaction sequence with a significant lifetime. Correspondingly, a 'secondary' product would have values that increase with conversion. The nature and earliest reliable yield values of the primary products are most useful in considering the initial chemistry of these processes. Figure 3-6 indicates that 2 and 7 are both primary products. The yields of 3 and 12 are too small for reliable conclusions to be drawn, but the close shadowing of the yields of 4 and 6 may be significant.

![Figure 3-6 Yield profiles for four intermediates from the UV-A (Rayonet) photocatalysed degradation of aqueous p-cresol.](image-url)
3.2.4 Quantitation with 400 W medium pressure mercury lamp

In view of the dependence of results on reaction conditions noted earlier, a quantitative irradiation was also carried out with the mercury lamp and immersion well apparatus. The rate of loss of substrate was comparable to that in the previous photolysis under these conditions. Quantitation of the yields of 4HBALC and 4HBALD indicated that these products accounted for 20% of the mass of p-cresol lost at 11% conversion, after 4 hr irradiation. The yield profile (Figure 3-7) suggests that 4HBALC is a primary reaction intermediate, but the position for 4HBALD is unclear from these data. The discrepancies in the yields at low substrate conversion i.e. < 20% degradation, is due to the uncertainties in monitoring low concentrations of intermediates and small losses of substrate, but there does not appear to be the yield ‘shadowing’ observed in the other quantitation.

![Yield profiles for 4HBALC and 4HBALD.](image)

**Figure 3-7** Yield profiles for 4HBALC and 4HBALD.

3.2.5 Discussion

The results obtained in this study differ from those previously reported (Terzian, *et al.*, 1991; Brezova, *et al.*, 1993) not only in the rate of loss of substrate but also in the intermediate profile. There was, however, disagreement on the latter point between the two
intermediate profile. There was, however, disagreement on the latter point between the two groups, with Brezova reporting methyl group oxidation and hydroxy substitution intermediates whilst Terzian observed hydroxyl substitution intermediates only.


Terzian’s result suggests initiation by \( >\text{TiOH}^* \) whereas Brezova’s result could be interpreted as providing support for Heller’s proposed mechanism (q.v. p. 22).

Yield profiles for four of the intermediates observed in this study (Figure 3-6) indicates that 4MCC and HMC are both primary products. The yields of 4MR and 12 were too small to enable reliable conclusions to be drawn. The yield data for 4HBALC and 4HBALD are ambiguous. Two possible routes for the formation of 4HBALD are via 4HBALC, and directly from \( p \)-cresol possibly via Heller’s mechanism. In an investigation of the catalysed photooxidation of 4HBALC, Richard (1993) found that three products were formed – 4HBALD, 3,4-dihydroxybenzyl alcohol and hydroquinone. Identification of 4HBALD in this photolysate suggests that at least some of the aldehyde is formed as a secondary product via the alcohol. However, extrapolation of the yield to 0% conversion is sufficiently uncertain that an additional direct route such as that proposed by Heller cannot be ruled out (Scheme 3-1).

Scheme 3-1 Degradation of \( p \)-cresol via a hydrotetraoxide intermediate.
All the results from this study can be explained satisfactorily by the initial formation of a phenoxy radical although the involvement of a benzyl radical remains a possibility (Scheme 3-2). This implies that p-cresol can be adsorbed on the catalyst either via the hydroxy or methyl groups or, indeed, horizontal to the surface. In this interpretation, the function of oxygen is simply to act as an electron acceptor and prevent recombination with the valence band holes. Instead these migrate to the surface giving rise to surface-bound hydroxyl radicals. Direct oxidation by $h_{vb}^+$ as postulated by Richard (1993) cannot be ruled out for the formation of some of the products, however. 4-Methylresorcinol is most likely formed from HMC by rearrangement (Shine, 1967).

Scheme 3-2 Possible reaction pathways for the catalytic photooxidation of p-cresol.
3.2.6 Interim conclusions

Results from previous kinetic and product studies of TiO$_2$-promoted photooxidations of phenols have led to proposals for structures that may be important at the surface of the catalyst. For example, Serpone et. al. (1993; 1997) have considered surface-linked phenoxy radical, $45$, as a candidate and have described plausible ways this species could lead to observed intermediates. This structure finds some support in the increased dark adsorption of catechols (Vasudevan and Stone, 1996; Kesselman, et al., 1997), from surface hydroxylation (Kutty and Ahuja, 1995) and FTIR studies (Gray, et al., 1994). The present results, however, suggest it is less convincing as a participant leading to the formation of the highest yielding primary product from $p$-cresol, HMC ($7$). Given the increasing likelihood that hydroxyl radical attacks from a surface-bound location (Stafford, et al., 1997; Serpone, 1997), HMC is most likely to be formed when the para position of the molecule is close to the surface than when it is held away as would be the case in $45$.

![Structure 45](image1)

![Structure 13](image2)

In order further to investigate the plausibility of structures such as $45$ as intermediates in photocatalysis, we chose to study the photocatalytic degradation of the commercial antioxidant BHT ($13$). In this compound the two positions ortho to the hydroxyl are occupied by bulky tert-butyl groups which may prevent the formation of a structure such as a surface-linked phenoxy radical.

3.2.7 Photocatalytic degradation of $p$-cresol in 20% acetonitrile

For comparative studies with BHT, which has low solubility in water ($< 2$ mg dm$^{-3}$), it was necessary to add an organic component to the solvent. Other studies suggested that acetonitrile is the co-solvent least likely to cause any unwanted side reactions. It is known
Acetonitrile is the co-solvent least likely to cause any unwanted side reactions. It is known to decompose slowly under the conditions used for photocatalysis (Lichtin and Avudaithai, 1996) but the products are small molecules that are unlikely to interfere with the HPLC analysis. At least one other study has employed a similar strategy (Choudhry, et al. 1985).

A 20% vol:vol acetonitrile mixture was chosen as the least amount of ACN necessary to give reasonable solubility for BHT, enabling solutions of up to 80 mg dm⁻³ to be prepared. In photodegradation experiments with p-cresol (standard photolysis procedure, 4 × 10⁻³ mol dm⁻³ substrate solution), this solvent system had little effect on the initial rate (aqueous, 31% degradation in 24 hours; 20% ACN, 29% in 24 hours) but it did affect the product profile (q.v. Figure 3-2). Notably, compound 2 was not detected, but the dehydrodimers are more prominent with three times the concentration of compound 12 formed (Figure 3-8).

Figure 3-8 HPLC of p-cresol photolysate in 20% aq. ACN after irradiation in Rayonet reactor for 24 h (30% degradation, analysis conditions - p-cresol1).
Two new minor products not seen in the purely aqueous system were observed, one of which is compound 8, 4-hydroperoxy-4-methyl-2,5-cyclohexadien-1-one (HPMC). The presence of a less polar solvent such as acetonitrile is known to increase substrate adsorption compared to water (Cunningham et al., 1994) and this may offer greater opportunity for both radical dimerisation and interaction with adsorbed O₂ to give the hydroperoxy compound.

3.3 2,6-Di-tert-butyl-4-methylphenol

3.3.1 Preamble

As mentioned to in the introduction to this chapter, 2,6-di-tert-butyl-4-methylphenol (BHT, 13), a widely used antioxidant although not a priority pollutant, has been detected in some natural waters (Lopez-Avila and Hites, 1981). Its low solubility in water may be good news as far as water pollution is concerned, but it makes determining the course of the photocatalytic degradation in purely aqueous solutions difficult because intermediate concentrations would be too low to follow with any degree of certainty.

It was chosen as a substrate for photocatalytic degradation to provide a comparison with the results from p-cresol and to further investigate the plausibility of structures such as 45, which in the case of BHT, appears highly unlikely considering the steric bulk of the tert-butyl groups. The rate of loss of substrate compared to p-cresol was determined and then the intermediate profile examined. Quantification of the yields of identified intermediates enabled the relative significance of each to be evaluated.

3.3.2 Photocatalytic degradation of BHT with an internal standard

A preliminary irradiation, using the standard photolysis procedure, of BHT (80 mg dm⁻³, 3.6 x 10⁻⁴ mol dm⁻³) in the Rayonet reactor gave 90% degradation in 48 hours.

In an attempt to ensure that an accurate comparison could be made with other degradations in this study, the initial experiments with BHT included p-cresol in the photolysate as an internal standard. A TiO₂-catalysed photodegradation was carried out, using the standard
photolysis procedure, on a photolysate containing $10^{-4}$ mol dm$^{-3}$ of each substrate in the Rayonet reactor. The relative rates of loss are shown in Figure 3-9. 50% Degradation occurred after 6 hours irradiation for BHT and 30 hours for $p$-cresol. A dark control showed no loss of either substrate after 24 hours.

![Figure 3-9](image)

**Figure 3-9** Relative rates of degradation: $p$-cresol and BHT in the same photolysate.

An rapid initial phase followed by a slower steady rate of degradation was observed for $p$-cresol, an event not detected with wholly aqueous solutions.

To determine whether there was interference/competition between the substrates in the mixed photolysate, three further irradiations were carried out by the standard photolysis procedure but at the concentrations described in Table 3-3. The results suggest that the presence of another substrate in the photolysate does affect the rate of degradation of the test substrate. Indeed, in mixed photolyses different substrates may be affected to varying degrees. An alternative protocol was therefore employed where separate degradations of the standard substrate were repeated at appropriate intervals to ensure that largely similar experimental conditions were maintained.
Table 3-3 Relative rates of degradation of p-cresol and BHT.

<table>
<thead>
<tr>
<th>exp.</th>
<th>p-cresol conc. /mol dm(^{-3})</th>
<th>BHT conc. /mol dm(^{-3})</th>
<th>total substrate conc. /mol dm(^{-3})</th>
<th>p-cresol irradiation time to 50% degradation/h</th>
<th>BHT irradiation time to 50% degradation/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>10(^{-4})</td>
<td>10(^{-4})</td>
<td>2 \times 10(^{-4})</td>
<td>30</td>
<td>6</td>
</tr>
<tr>
<td>(ii)</td>
<td>10(^{-4})</td>
<td>0</td>
<td>10(^{-4})</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>(iii)</td>
<td>0</td>
<td>10(^{-4})</td>
<td>10(^{-4})</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>(iv)</td>
<td>5 \times 10(^{-5})</td>
<td>5 \times 10(^{-5})</td>
<td>10(^{-4})</td>
<td>28</td>
<td>4</td>
</tr>
</tbody>
</table>

A control photolysis of BHT in air without TiO\(_2\) led to 82% degradation after 22 h irradiation, with similar intermediates being eluted before the substrate but no long retention time peaks. However, a second control experiment showed no degradation. The loss of BHT in the first instance may have been due to residual TiO\(_2\) on the glassware, as it is difficult to remove. For all subsequent non-TiO\(_2\) photolyses the apparatus was washed with dilute sodium hydroxide solution and rinsed with PureOne water before use. The control experiment with TiO\(_2\) under nitrogen gave 77% degradation after 24 hours but the major intermediate in oxygenic degradations (below) was not observed.

3.3.3 Qualitative analysis of reaction intermediates

Consideration of the intermediates identified in p-cresol degradations suggested that analogous methyl group-oxidised and dienone-type intermediates might be formed from BHT. Accordingly authentic samples of 3,5-di-tert-butyl-4-hydroxybenzyl alcohol (BALC, 24), 3,5-di-tert-butyl-4-hydroxybenzaldehyde (BALD, 25), 3,5-di-tert-butyl-4-hydroxybenzoic acid (BAC, 26), 2,6-di-tert-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (MQOL, 17), and 2,6-di-tert-butylbenzoquinone (26DtBBQ, 21) were analysed by HPLC and the results stored in the software library. Comparison of data from the preliminary BHT photolysis with the library records identified BALC, along with MQOL and what was initially assumed to be MHPQ.
A solution of BHT (60 mg dm\(^{-3}\)) containing TiO\(_2\) was irradiated in the Rayonet reactor (standard photolysis procedure), the course of the reaction being followed by HPLC analysis using BHT analysis system 1. Figure 3-10 is a chromatogram of a photolysed sample at 32% degradation.

![HPLC Chromatogram](image)

**Figure 3-10** HPLC chromatogram of BHT photolysate after irradiation in Rayonet reactor for 5 h (32% degradation).

BALC (r.t. 14.0 min) and BALD (r.t. 18.5 min) were identified by comparison with the HPLC software library. The compound eluted at r.t. 31.5 min had a UV spectrum similar to that of the substrate, and therefore a chromophore which is largely unaltered, but the increase in r.t. indicated a higher molecular weight or a decrease in polarity. The compound was tentatively identified as a dehydrodimer of BHT.

As described in section 3.2.2, MQOL (17) and MHPQ (18) have virtually identical UV spectra, MQOL being eluted, in HPLC analysis, before MHPQ (Parry, 1995). In the chromatogram reproduced in Figure 3-10, the compounds eluting at 18.2 min and 24.1 min also had superimposable UV spectra, and where subsequently identified as MQOL and MHPQ, respectively. A purity check across the peak at 18.2 min initially suggested that only one compound was present. The peak at 24.1 min is one of the largest...
peaks in the chromatogram and, when the results were re-integrated at 234 nm, it dominated the trace. Subsequent analyses, where the eluent contained a lower percentage of ACN (analysis system BHT 4), resolved the 18.2 min peak into two. Consequently, there were three compounds present, all with virtually identical cyclohexa-2,5-dienone type UV spectra (Figure 3-11).

![UV spectra of three cyclohexa-2,5-dienone intermediates from the photocatalytic degradation of BHT.](image)

**Figure 3-11** UV spectra of three cyclohexa-2,5-dienone intermediates from the photocatalytic degradation of BHT.

Synthesis and HPLC analysis of an authentic sample of MHPQ (section 2.7.3) confirmed the co-elution of MQOL and MHPQ in Figure 3-10. The third compound was more highly retained than MQOL and MHPQ and, therefore, less polar and/or a larger molecule. The UV spectrum indicates that it has the characteristic cyclohexa-2,5-dienone chromophore. Oxidation of one or more of the tert-butyl groups of MQOL or MHPQ is likely to leave the chromophore unchanged (section 2.4), but would make the molecule more polar and therefore less retained. Substitution by hydroxyl at the 3-position or oxidation of the methyl group would affect both retention time and the chromophore. In the absence of other plausible structures, it was proposed that the compound eluted at 24.1 min was bis(4-oxy-4-methyl-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (bis(MQOL), 27). The elution of this compound before BHT may be possible due to hydrogen bonding by the molecule to
water in the eluent increasing the compounds solubility. A photochemical synthesis of subsequently supported this assignment.

3.3.4 Quantitative analysis of reaction intermediates

Intermediate yields were calculated by comparison with solutions of known concentration of authentic compounds, where available, or a close analogue with similar detector response, e.g. MQOL for bis(MQOL). Figure 3-12 shows the distribution of products at 33% degradation of the initial concentration of BHT. Compounds responsible for poorly retained HPLC peaks probably account for most of the unidentified material and, because of their polar nature, are attributed to secondary intermediates.

Figure 3-12 Yields of intermediates from the photocatalytic degradation of BHT after 5 h irradiation, 33% degradation.

The yield profile for bis(MQOL) together with the profile for HMC from p-cresol is shown in Figure 3-13 (overleaf).

The graph shows that at the lowest measurable conversions, bis(MQOL) is the major intermediate in the photocatalytic reaction of BHT. If the yield is extrapolated to very low conversion it could account for >80% of the degraded substrate. However, with no data available below 18% degradation (the reaction had a very fast initial phase) this assumption cannot be validated. The yields illustrate primary product behaviour for both
intermediates but HMC, a major product in \( p \)-cresol degradation, has a significantly lower yield than bis(MQOL) from BHT.

![Graph](image)

**Figure 3-13** Yield profiles of the principal primary intermediates from BHT and \( p \)-cresol.

### 3.3.5 Discussion

The rapid initial phase of degradation followed by a slower steady rate shown in Figure 3-9 has been observed by other workers (Upadhya and Ollis, 1997). It was attributed to the rapid consumption of preadsorbed substrate molecules followed by a slower stage when intermediates, oxygen and substrate are desorbing and readsorbing.

Replacing the *ortho* hydrogen atoms of \( p \)-cresol with *tert*-butyl groups accelerated rather inhibited the relative rate of degradation as might have been forecast on the grounds of steric hindrance. The increased rate of reaction could result from stronger adsorption of substrate molecules at the catalyst surface and, therefore, greater access to oxidising species.

Hydrophobicity affects the environmental fate of organic pollutants in that it influences the distribution of compounds between water and natural solids (e.g., soils, sediments, and
suspended particles), and organisms. Studies found that, within a series of compounds, the accumulation of non-polar compounds in an aquatic organism is directly proportional to the partition of compounds between water and water-immiscible solvents like octanol (Schwarzenbach, et al., 1993c). The octanol-water partition constant ($K_{ow}$) is therefore taken as a measure of the hydrophobicity of organic compounds: the higher the value, the more hydrophobic the molecule. The $K_{ow}$ for some alkyl phenols are given in Table 3-4.

**Table 3-4** Octanol-water partition constants for selected alkylphenols.

<table>
<thead>
<tr>
<th>compound</th>
<th>log $K_{ow}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$-cresol</td>
<td>1.94</td>
</tr>
<tr>
<td>3,4-dimethylphenol</td>
<td>2.35</td>
</tr>
<tr>
<td>3,5-dimethylphenol</td>
<td>2.35</td>
</tr>
<tr>
<td>2,6-dimethylphenol</td>
<td>2.36</td>
</tr>
<tr>
<td>4-tert-butylphenol</td>
<td>3.41</td>
</tr>
<tr>
<td>2,6-di-tert-butyl-4-methylphenol</td>
<td>4.17</td>
</tr>
</tbody>
</table>

The data show that BHT is significantly more hydrophobic than $p$-cresol. The hydrophobicity of the tert-butyl groups may cause the molecule to be adsorbed with the tert-butyl groups close to the catalyst surface as depicted in Scheme 3-3, an orientation which causes the minimum disturbance of the aqueous structure of the solvent layer outside. Direct bonding of the hydroxyl group, as envisaged in 45, is highly unlikely because of the steric bulk of the tert-butyl groups. Instead, a hydrogen-bond could be formed which can mediate electron transfer once a photogenerated hole is available.

![Scheme 3-3 Possible mechanism for oxidation of BHT at TiO$_2$ surface.](image)
The almost exclusive nature of the primary reaction which generates bis(MQOL) implies that BHT is oriented with its hydroxyl group associated with the TiO$_2$ surface, exposing the 4-position of the radical derived from oxidation to molecular oxygen on the outside of a monolayer. Two molecules of BHT are involved and, in spite of concentrations as low as 10$^{-4}$ mol dm$^{-3}$, the product could account for more than 80% of the reactant in the first phase of oxidation, and has a calculated yield of ~60% at 20% degradation of substrate (Scheme 3-4). The aggregation of neighbouring radicals may also be encouraged because the stability of adsorbed intermediates can be much higher than that of analogous species formed in homogeneous solution (Fox, 1993).

![Scheme 3-4 Proposed mechanism for the formation of bis(MQOL).](image)

Thus, hydrophobicity not only appears to steer molecules to a preferred orientation on the surface, but also encourages clustering to further minimise disruption to polar networks, and thereby set up a favourable reaction with nearby oxidants.

It has been proposed that an influence of considerable significance is exerted in the early stages of heterogeneous photocatalysis by hydrophobicity (Sherrard, et al., 1995; Amalric, et al., 1996). Detection of bis(MQOL) in the degradation of BHT appears to support this hypothesis. Accordingly, a series of other related alkylphenols (below) was examined in order to determine the nature and extent of this influence.

![Chemical Structures](image)

15 \( R = \text{C(CH}_3\text{)}_3 \)
16 \( R = \text{C(CH}_3\text{)}_3 \)
28 \( R = \text{CH}_3 \)
29 \( R = \text{CH}_3 \)
14
30
3.3.6 Dark adsorption study

Before the results of degradation studies with other substrates are presented, it is pertinent to consider the adsorption of alkyl phenols on TiO$_2$. The results of a dark adsorption study on a selection of substrates are given in Table 3-5.

Table 3-5 Percentage adsorbed after equilibration of $10^{-4}$ mol dm$^{-3}$ phenol in 20% acetonitrile in water with a suspension of 0.5 g dm$^{-3}$ TiO$_2$.

<table>
<thead>
<tr>
<th>phenol$^a$</th>
<th>4-R</th>
<th>2,6-di-R</th>
<th>3,5-di-R</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = Me</td>
<td>8 (&lt;1$^b$)</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>R = tert-butyl</td>
<td>4</td>
<td>88</td>
<td>25</td>
</tr>
</tbody>
</table>

$^a$unsubstituted phenol value = 2%  $^b$value in pure water

These results clearly demonstrate that the di-tert-butyl phenols have a considerable affinity for the catalyst. Any trends for the other compounds are ambiguous from the values obtained.

3.4 2,6-Di-tert-butylphenol

A comparative study of 2,6-di-tert-butylphenol (26DtBP) was carried out to determine the effect of the absence of the 4-methyl group on the rate of degradation and intermediate profile compared to BHT under, as far as possible, identical conditions (standard photolysis procedure). The results also enabled a comparison with 3,5-di-tert-butylphenol to study any effects the substituent pattern has on photocatalytic degradation.

3.4.1 Rate of loss of substrate

26DtBP was lost at about half the rate of BHT (Figure 3-14) (overleaf). Compared to p-cresol, rates were similar below 40% degradation but diverged after this point with 26DtBP showing a higher rate of loss. Both BHT and 26DtBP, and to some extent p-cresol, showed a rapid initial rate of loss of substrate followed by a slower, steady rate as previously discussed (section 3.3.5).
To further investigate this apparent two stage process, a 26DtBP photolysis suspension was irradiated (standard photolysis procedure) until HPLC analysis indicated that all substrate and intermediates were degraded, apart from some at short retention time (<5 minutes). A concentrated solution of 26DtBP was then added to the reaction flask to give approximately the same initial concentration in the bulk solution as used previously. A rapid initial phase was again observed with ~40% degradation in the first hour. Thus, no ageing effect on the catalyst is apparent, and the two stages are probably associated with first, initial occupation, and then replacement, by substrate molecules.

### 3.4.2 Qualitative analysis of reaction intermediates

HPLC analysis of the photolysate during the irradiation revealed twelve significant intermediates. The identity of nine of these has been resolved, while three remain elusive. Figure 3-15 (overleaf) is a typical HPLC chromatogram of the photolysate and Table 3-6 (p. 86) details the intermediates in order of elution.
Figure 3-15 HPLC chromatogram of 2,6-di-tert-butylphenol photolysate after irradiation in Rayonet reactor for 3 h (32% degradation, analysis conditions - 26DtBP).

2,6-Di-tert-butylbenzoquinone (DtBBQ, 21), 4,4′-dihydroxy-3,3′,5,5′-tetra-tert-butylbiphenyl (bis(26DtBP), 22) and 3,3′,5,5′-tetra-tert-butylpheno-4,4′-quinone (tBDPQ, 23) were identified by comparison with an authentic sample of the compound. As described in section 2.4, the peaks at r.t. 21.9 and 8.0 minutes were identified by comparison of their UV spectra with that of DtBBQ, both of them showing characteristic quinone absorption. They were consequently assumed to be quinones in which one or more of the tert-butyl groups had been oxidised, leaving the chromophore largely unaffected. Using the same principles, the intermediates at r.t. 9.6 and 6.3 are proposed to be a hydroquinone and side-chain oxidised hydroquinone respectively. The peak near the solvent front in the chromatogram (r.t. 2.7) is tentative assigned as a secondary ring-opened intermediate due to its low retention. Although not detected in this photolysis, small peaks with 2,5-cyclohexadienone-type spectra were observed in some photolyses.

The spectra of two significant unidentified peaks, r.t. 23.7 and 7.3 are reproduced in Figure 3-16 (p. 87). Comparison of these distinctive spectra with those of the compounds stored in the HPLC computer software library failed to provide any information as to their possible
identity (q.v. section 2.4 for a list of compounds included in the library) and, thus far, no matching data has been found in the literature for plausible chromophores.

Table 3-6 Reaction intermediates from the photocatalytic degradation of 2,6-di-tert-butylphenol.

<table>
<thead>
<tr>
<th>r.t./min</th>
<th>(\lambda_{\text{max/nm}})</th>
<th>purity parameter /nm (190-367 nm)</th>
<th>identity</th>
<th>degree of certainty and nearest library match</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7</td>
<td>206, 228</td>
<td>212.7</td>
<td>conjugated open chain</td>
<td>*</td>
</tr>
<tr>
<td>6.3</td>
<td>194, 289</td>
<td>197.2</td>
<td>side-chain oxidised hydroquinone (HQ-X)</td>
<td>** 23DMHQ</td>
</tr>
<tr>
<td>7.3</td>
<td>218, 265</td>
<td>223.8</td>
<td>unknown</td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>255</td>
<td>249.1</td>
<td>side-chain oxidised quinone (Q-X2)</td>
<td>** DtBBQ</td>
</tr>
<tr>
<td>9.6</td>
<td>193, 287</td>
<td>196.6</td>
<td>hydroquinone (HQ)</td>
<td>** 23DMHQ</td>
</tr>
<tr>
<td>13.9</td>
<td>237</td>
<td>236.5</td>
<td>unknown</td>
<td></td>
</tr>
<tr>
<td>21.9</td>
<td>252</td>
<td>239.8</td>
<td>side-chain oxidised quinone (Q-X1)</td>
<td>** DtBBQ</td>
</tr>
<tr>
<td>23.7</td>
<td>217, 275</td>
<td>219.5</td>
<td>unknown but similar chromophore as intermediate r.t. 7.3</td>
<td></td>
</tr>
<tr>
<td>26.9</td>
<td>252</td>
<td>239.8</td>
<td>2,6-di-tert-butylbenzoquinone</td>
<td>*** DtBBQ</td>
</tr>
<tr>
<td>27.8 (SM)</td>
<td>190, 215 (sh), 270</td>
<td>194.1</td>
<td>2,6-di-tert-butylphenol</td>
<td></td>
</tr>
<tr>
<td>(\times 1.7a)</td>
<td>204, 263</td>
<td>213.8</td>
<td>bis(26DtBP)</td>
<td>*** bis(26DtBP)</td>
</tr>
<tr>
<td>(\times 1.8a)</td>
<td>192, 220, 273</td>
<td>198.0</td>
<td>tert-butyl group linked dehydromer (SM-SM)</td>
<td>** 26DtBP</td>
</tr>
<tr>
<td>(\times 2.4a)</td>
<td>196, 421</td>
<td>247.1</td>
<td>tBDPQ</td>
<td>*** tBDPQ</td>
</tr>
</tbody>
</table>

Key to degree of certainty of assignment:

***exact match with spectrum and retention time of authentic material
**close match to standard containing the same chromophore
*speculative assignment

aSeparate analysis: value relative to r.t. of substrate.
Figure 3-16 Qualitative UV spectra of unidentified intermediates from the photocatalytic degradation of 2,6-di-tert-butylphenol.

3.4.3 Quantitative analysis of reaction intermediates

The total yield of identified intermediates accounted for about two thirds of the degraded material after 15 minutes irradiation. Figure 3-17 gives the relative yields of the identified intermediates.

Figure 3-17 Percentage intermediate yields in the photocatalytic degradation of 2,6-di-tert-butylphenol after irradiation for 0.25 h (32% degradation).
The dehydrodimeric intermediates accounted for over 40% of degraded material at this point in the reaction, the quinone, DtBBQ, being the next most abundant intermediate at 16% yield. Intermediates with 2,5-cyclohexadienone-type spectra were not observed in the photolysate to which these figures relate but, when present, they comprised <1% of the total yield. With no clues as to the identity of the peaks at r.t. 7.3 and 23.7, it is not possible to estimate their contribution to the yield, and so they are included in the unattributed losses.

3.4.4 Discussion

The rate of loss of 26DtBP was less than that observed for BHT but higher than for p-cresol. In a similar manner to the yield profile for BHT, dimeric intermediates again accounted for the majority of the degraded 26DtBP with reaction at the unsubstituted para position being predominant.

As with BHT, the directing force of the hydrophobic tert-butyl groups could bring about the molecular association as described in Scheme 3-5 possibly leading to the formation of bis (26DtBP) and tBDPQ (Scheme 3-6).

![Scheme 3-5 Proposed mechanism for molecular association.](image)

![Scheme 3-6 Suggested mechanism of formation of bis(26DtBP) and tBDPQ from associated 26DtBP radicals.](image)
Less closely adsorbed phenoxyl radicals may react with oxygen in solution prior to coupling, leading to a peroxy linked dehydrodimer. In the corresponding product from BHT, there are two methyl groups adjacent to the peroxy link. Here, with only two hydrogens at these positions, the molecule may be less stable. Aromatisation and cleavage would then account for the observed quinone and hydroquinone intermediates (Scheme 3-7). Thus, in effect, more than 70% of the primary chemistry of this degradation is associative in nature.

Scheme 3-7 Possible mechanism of formation of hydroquinone and quinone intermediates from 26DtBP.

If primary products do not desorb or if they desorb and are readsorbed, further oxidation could occur, leading to the side-chain functionalised hydroquinone and quinones detected.

While 2,6-di-tert-butylphenol forms a peroxy-linked dehydrodimer analogous to 27 as a precursor of the observed hydroquinones and quinones, there is no evidence that BHT forms the direct 4,4'-dehydrodimer, 46, analogous to the precursor of the 4,4'-directly-coupled products from 2,6-di-tert-butylphenol, even though 46 is now considered to be the principal product derived from BHT with radical reagents (Omura, 1991).
The difference made by the presence of the 4-methyl group in BHT may be explained by steric hindrance, as depicted in Figure 3-18. The \textit{tert}-butyl groups prevent close approach of the 4,4'-positions unless some tilting occurs. With BHT molecules, a further repulsion is introduced as the 4-methyl groups approach each other, and direct bonding is unlikely. The distance can be bridged, however, by the peroxy link that becomes available when one of the radicals reacts with oxygen. In the case of 2,6-di-\textit{tert}-butylphenol, the 4-position is bonded to a hydrogen atom and further tilting can take place so that some, but not all, molecules become coupled without a peroxide bridge.

\textbf{Figure 3-18} Steric hindrance in associative reactions at the 4,4'- positions of oxidised BHT molecules.

The apparently similar behaviour of BHT and 26DtBP in both rate of loss of substrate and intermediate profile strengthens the argument that the \textit{tert}-butyl groups control the way in which molecules adsorb and hence the interaction of substrate and oxidising species on the catalyst surface. It is proposed that the hydrophobic nature of the \textit{tert}-butyl groups would draw the molecule down onto the catalyst surface. In the case of BHT and 26DtBP this would lead to the hydroxyl group being in close proximity to the surface. In contrast, with
3,5-di-tert-butylphenol (35DtBP) the hydroxyl would be held out into the bulk solution. In order to further test the hypothesis and this postulated inversion of adsorption, compared to 26DtBP and BHT, on the mechanism of degradation, 35DtBP was irradiated under, as far as possible, identical conditions.

3.5 3,5-Di-tert-butylphenol

3,5-Di-tert-butylphenol (35DtBP) is a positional isomer of 26DtBP, with the tert-butyl groups meta to the hydroxyl rather than ortho. The para position is again unsubstituted. Because of the hydrophobic nature of the tert-butyl groups, the molecules are likely to be oriented with these closest to the surface. In this case, for 35DtBP the para position of the molecule will be closest to the catalyst surface with the hydroxyl held away into the surrounding solution. Much of the previously observed oxidation of 2,6-di-tert substituted compounds appears to occur at the para position when the hydroxyl is presumed to be close to the surface. In the case of 35DtBP, any attack by O₂ would be expected to take place at the hydroxyl, whilst attack at the para position, if it occurs, may well be affected by steric hindrance.

3.5.1 Rate of loss of substrate

The rate of loss of 35DtBP (standard photolysis procedure) was about half the rate observed for 26DtBP (Figure 3-19) (overleaf) and significantly slower than for p-cresol. Once again, a more rapid initial phase was observed followed by a slower steady rate. Irradiation of a solution of the substrate in the absence of TiO₂ led to <5% degradation in 24 hours, whilst photolysis with TiO₂ in the absence of oxygen gave a 12% loss in 24 hours. A dark control with TiO₂ showed no degradation.

3.5.2 Qualitative analysis of reaction intermediates

HPLC analysis of the photolysate after fourteen hours irradiation (39% degradation) revealed little accumulation of reaction intermediates (Figure 3-20) (overleaf). Earlier samples showed similar intermediate profiles.
Figure 3-19 Relative rates of degradation 2,6- and 3,5-di-tert-butylphenol.

Figure 3-20 HPLC chromatogram of 3,5-di-tert-butylphenol photolysate after irradiation in Rayonet reactor for 14 h (39% degradation).

Despite the expanded absorbance scale (20 mAU full scale) and a detector wavelength of 215 nm, at which most aromatic compounds would absorb strongly, nearly all of the intermediates have peak heights <5 mAU. Examination of the UV spectra of individual
peaks confirmed that none of them have strong absorbance at longer wavelengths. The largest intermediate peak in this plot is the one close to the solvent front at r.t. 1.6 minutes (eluent composition 50:50, ACN: H₂O). This may indicate one or more highly polar compounds, probably with molecules much smaller than the substrate, i.e. ring-opened intermediates. The UV spectrum reveals end absorption only with λ_max 194 nm, supporting the latter assumption. Spectroscopic details and possible identities of more retained components are given in Table 3-7.

Table 3-7 Reaction intermediates from the photocatalytic degradation of 3,5-di-tert-butylphenol.

<table>
<thead>
<tr>
<th>r.t./min</th>
<th>λ_max/nm</th>
<th>purity parameter /nm (190-367 nm)</th>
<th>identity</th>
<th>degree of certainty and nearest library match</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.6</td>
<td>194, 212 (sh), 270</td>
<td>195.6</td>
<td>tert-butyl group oxidation product (SM-X2)</td>
<td>* 35DtBP</td>
</tr>
<tr>
<td>5.7</td>
<td>195, 216(sh), 273</td>
<td>196.0</td>
<td>tert-butyl group oxidation product (SM-X2)</td>
<td>*35DtBP</td>
</tr>
<tr>
<td>6.7</td>
<td>193, 222, 270</td>
<td>197.4</td>
<td>unknown</td>
<td></td>
</tr>
<tr>
<td>9.6</td>
<td>230</td>
<td>229.4</td>
<td>substituted 2,5-cyclohexadienone</td>
<td>** MQOL/MHPQ</td>
</tr>
<tr>
<td>12.7</td>
<td>196, 217 (sh), 276</td>
<td>197.1</td>
<td>3,5-di-tert-butylcatechol ** 35DtBCC</td>
<td></td>
</tr>
<tr>
<td>14.0</td>
<td>194, 215(sh), 271</td>
<td>195.8</td>
<td>3,5-di-tert-butylphenol **</td>
<td>***</td>
</tr>
<tr>
<td>19.6</td>
<td>193, 214 (sh), 270</td>
<td>194.7</td>
<td>tert-butyl group linked dehydrodimer (SM-SM)</td>
<td>* 35DtBP</td>
</tr>
<tr>
<td>32.3</td>
<td>196, ~225 (sh), 273</td>
<td>199.0</td>
<td>tert-butyl group linked 35DtBCC oligomer (Cat-Cat)</td>
<td>* 35DtBCC</td>
</tr>
<tr>
<td>34.5</td>
<td>193, 220, 273</td>
<td>197.3</td>
<td>unknown but similar chromophore to intermediate r.t. 6.7</td>
<td>* tert-butyl group linked oligomer</td>
</tr>
</tbody>
</table>

Key to degree of certainty of assignment:
***/exact match with spectrum and retention time of authentic material
**close match to standard containing the same chromophore
*speculative assignment
Identities of intermediates were established by comparison of UV spectra using the principles previously described (section 2.4). Peak r.t. 9.6 had a 2,5-cyclohexadienone-type UV spectrum and the intermediate at r.t. 12.7 was identified by comparison with authentic material. The identities of the remaining intermediates are proposed based on subtle differences between the spectra of 35DtBP and 35DtBCC. The absence of pronounced differences between the spectra and the low photolysate concentration, and therefore weak absorbance in the spectra, hindered their definitive identification. Figure 3-21 shows the overlain UV spectra of 35DtBP and 35DtBCC and illustrates the differences between them. The first band in the catechol spectrum is broader and red-shifted 2 to 3 nm, although any assignment based on this band may be unreliable as it is at wavelengths near the limits of detection of the instrument. The shoulder less pronounced for the catechol and shifted to longer wavelengths by 2 to 3 nm and the third band is red shifted ~5 nm compared to 35DtBP. This further illustrates the possibility of distinguishing between such related compounds and their chromophorically close analogues.

Figure 3-21 UV spectra of 3,5-di-tert-butyphenol and 3,5-di-tert-butyicatehol.

Comparison of these spectra with those of the intermediates lead to these specilative assignments. Intermediates at r.t. 4.6, 5.7 and 19.6 have UV spectra closer to that of the substrate than the catechol. The first two intermediates, however, have a much shorter
retention time than 35DtBP and must be more polar. Oxidation of one or more -CH₃ groups of the tert-butyl substituents provide a possible explanation for their properties. Similarly, intermediate r.t. 19.6 min must be less polar and/or a larger molecule than the substrate and may be due to the coupling of two tert-butyl group oxidised molecules. In the spectra of the unidentified intermediates at r.t. 6.7 and 34.5 minutes the second band is more pronounced and red-shifted ~10 nm but otherwise they are also similar to that of the substrate. The peak at r.t. 32.3 had a spectrum closely similar to 35DtBCC, but its retention time relative to the proposed 35DtBP dehydrodimer (r.t. 19.6 min) suggest that it may be an oligomer.

In the control photolysis with TiO₂ in the absence of oxygen, dimeric and ring-open materials were more prominent and cyclohexadienones were not observed.

3.5.3 Quantitative analysis of reaction intermediates

The distribution of intermediates in this photolysate at 39% conversion is shown in Figure 3-22 and is in marked contrast to that for the 2,6 isomer at a comparable stage of degradation (Figure 3-17).

![Figure 3-22](image)

**Figure 3-22** Percentage intermediate yields in the photocatalytic degradation of 3,5-di-tert-butylphenol after irradiation for 14 h (39% degradation).

The low accumulation of intermediates meant that at no time during the photolysis could more than ten per cent of the degraded material be accounted for, with no individual
compound being observed in more than 2% yield. Consequently, the fate of over 90% of degraded substrate remains unclear, although most will probably account for the peak near the solvent front in the HPLC chromatogram. In the absence of CO₂ measurements, it may be surmised that the missing material had been rapidly degraded to smaller molecules, or perhaps fully mineralised.

3.5.4 Discussion

These results indicate that the position of the tert-butyl substituents on the substrate ring had a significant effect on both the rate of loss of substrate and on the profile of the degradation intermediates. The rate of loss of substrate was about half that recorded for 26DtBP and there was little accumulation of intermediates. Although the substrate was lost more slowly, the configuration of substituents in this isomer appears to lead to rapid processes towards mineralisation, once oxidation commences.

In contrast to those from BHT and 26DtBP, and apart from a small amount of a 2,5-cyclohexadienone, none of the identified intermediates arose from oxidation para to the hydroxyl group. The only detectable oxidation products occurred from either oxidation of the tertiary butyl substituents or by nuclear substitution of hydroxyl.

Hydrophobicity would encourage the 3,5-isomer to adsorb with the hydroxyl group held away from the surface. This orientation prevents radical formation via the hydroxyl group and hence rapid loss of substrate. The close proximity of the tert-butyl groups to the oxidising surface appears to bring about side-chain oxidation, both here and, to a lesser extent, in 26DtBP (Figure 3-23) (overleaf). Whether subsequent rapid degradation of 35DtBP to small polar molecules follows at this stage or is a consequence of much less frequent but highly reactive adsorption in the opposite orientation is not clear. Tightly bound substrates can be oxidised by direct hole transfer (Hoffmann, et al., 1995), but it is not possible, from the results obtained, to determine if it occurred in this degradation.

The final tert-butyl phenol substrate was 4-tert-butylphenol. Here the implications of replacing the methyl group of p-cresol with a single tert-butyl group were investigated.
3.6 4-tert-Butylphenol

In contrast to p-cresol, 4-tert-butylphenol (4tBP, 14) has a more hydrophobic tert-butyl group para to the hydroxyl rather than a methyl group. The results of an adsorption study (Table 3-5), however, did not detect an increase in adsorption for this compound compared to p-cresol. Bulky tert-butyl substitution ortho or meta to OH has been shown to have important effects on both the rates and reaction intermediate distributions. A number of p-cresol intermediates arose from oxidation of the methyl group or from nuclear addition of OH at the para position. Analysis of the outcome of the experiments with 4tBP must take into account that it both lacks benzylic hydrogen atoms and has a sterically protected 4-position. Nevertheless it was of interest to see if the expected hydrophobicity of this substrate is expressed in the results.

3.6.1 Rate of loss of substrate

The degradation of 4tBP (standard photolysis procedure) progressed at a rate less than half that of p-cresol (Figure 3-24) and slightly less than 35DtBP. Under the experimental conditions used, in comparison with p-cresol and the tert-butyl substituted phenols studied, 4tBP exhibited the slowest rate of loss of substrate. Control experiments with TiO$_2$ present, showed no degradation after 20 hours in the dark and $<10\%$ degradation after 26 hours with light in the absence of oxygen.
3.6.2 Qualitative analysis of reaction intermediates

Few intermediates were observed in the first 6 hours of irradiation (up to ~10% degradation). After further irradiation, and apart from peaks near the solvent front, only three significant intermediates were detected at r.t. 5.8, 9.8 and 13.6 minutes (substrate r.t. 10.4 minutes) (Figure 3-25) (overleaf). Intermediate r.t. 5.8 min. had a 2,5-cyclohexadienone-type spectrum, $\lambda_{\text{max}}$ 233.6 nm, and the other two had spectra largely similar to 4tBP suggesting oxidation of the tert-butyl substituent with the 13.6 minute peak probably being due to a dehydrodimer. None of the UV spectra recorded closely matched those for 4-tert-butylcatechol or 4-tert-butylresorcinol.

3.6.3 Quantitative analysis of reaction intermediates

Assuming that the identification of the 9.8 and 13.6 minute peaks is correct and the side-chain functionalised intermediates have the same chromophore as the substrate, they will also have approximately the same UV absorption coefficient and therefore an equivalent
Figure 3-25 HPLC chromatogram of 4-tert-butylphenol photolysate after irradiation in Rayonet reactor for 13 h (29 % degradation).

detector response to 4tBP. This enables the calculation of intermediate yields by direct comparison of peak areas for substrate solutions of known concentration to the intermediate peak area.

By applying this method, the yield of intermediate r.t. 9.8 min was found to remain near 10% and that of r.t. 13.6 min. ~6% of the degraded material above 10% degradation. The 2,5-cyclohexadienone intermediate had a yield of <1% throughout the photolysis.

3.6.4 Discussion – 4-tert-butylphenol

4-tert-Butylphenol degrades slowly under these experimental conditions with little accumulation of reaction intermediates. As with 35DtBP, it is possible that the hydrophobically favoured orientation is dominant but slow reacting giving the few intermediates observed in very low yield, while the much less frequent but highly reactive orientation with OH next to the surface leads to rapid secondary degradation reactions.
3.6.5 Discussion – tert-butylphenols

The relative rates of loss of substrate for \(p\)-cresol and the four \(tert\)-butylphenols are shown in Figure 3-26. Following experiments involving periodic illumination of an aqueous TiO\(_2\) suspension, Upadhya and Ollis (1997) proposed that the turnover rate for dioxygen molecules following reduction by conduction band electrons is the rate-limiting step in photocatalytic oxidation. These results seem to contradict this assertion as the steady state rates differ. Also, a clear trend was observed; the rates of the 2,6-di-\(tert\)-substituted phenols on the one hand, and those for the 3,5-di- and 4-\(tert\)-butylphenols on the other, fell consistently either side of the rate for \(p\)-cresol.

![Diagram](image)

**Figure 3-26** Comparative rates of reaction of BHT, 26DtBP, \(p\)-cresol, 35DtBP, and 4tBP irradiated with TiO\(_2\) suspended in 20% acetonitrile in water.

The intermediate profiles detected also fell into two distinct groups. The 3,5-di and 4-\(tert\)-butyl phenols showed little accumulation of primary intermediates in which the ring remained intact, but appeared to degrade directly to small polar molecules. Those identified were principally products of side-chain functionalisation. In contrast, the 2,6-di-\(tert\)-substituted phenols showed abundant primary intermediates. Methyl group oxidation was detected, but the mechanism was dominated by radical coupling reactions.
3.6.6 Interim conclusions

The photocatalytic degradation of tert-butyl phenols is significantly affected by the pattern of substitution, both with regard to the rate of reaction and the intermediates formed. It is proposed that the hydrophobic nature of the tert-butyl groups steers adsorption, the preferred orientation being with the tert-butyl groups close to the catalyst surface and away from the bulk of the water. Thus, the position of the substituents on the ring determines the proximity of the hydroxyl group to the oxidising species on the surface. When the hydroxyl group is near the surface, the mechanism of reaction encourages rapid loss of substrate and the formation of numerous, often aggregated intermediates, whereas when the hydroxyl is held away from the surface the degradation proceeds at a slower rate with few detectable ring-retained intermediates.

The influence of substitution pattern was further investigated by examining the catalytic photooxidation of three isomeric dimethylphenols. The hydrophobicity of these compounds lies between p-cresol and the tert-butylphenols (Table 3-4) and the intention was to determine whether it was sufficient to affect the reaction mechanism in such cases.

3.7 Dimethylphenols

Results previously described indicate that the alkyl substitution pattern for tert-butylphenols has a pivotal effect on the TiO2 photocatalysed degradation. Three isomeric dimethylphenols (DMP, xylenols), 2,6-, 3,5-, and 3,4-, were degraded by TiO2 photocatalysis to determine whether any pattern of reaction occurred. Firstly, the photocatalytic degradation of 26DMP and 35DMP is compared. If adsorption is directed as previously observed, it would be expected that 26DMP would be degraded at a faster rate, and a more diverse intermediate profile would be observed, when compared with 35DMP. Finally in this chapter, the results of the catalytic photooxidation of 34DMP are described. 34DMP, like p-cresol, has an alkyl group para to the hydroxyl and might be expected to give similar oxidation products.

The results obtained are also compared to those from other studies of the photooxidation of dimethylphenols. A study of the mineralisation of dimethylphenols by illuminated TiO2
(Terzian and Serpone, 1995) was followed by an exploration of the mechanism of the reaction by pulse radiolysis (Terzian, et al., 1995). The degradation was also investigated using excited uranyl ions as the oxidising species (Sarakha, et al., 1997).

### 3.7.1 Rate of loss of substrate – 26DMP and 35DMP

When 26DMP and 35DMP were irradiated (standard photolysis procedure), initial rates of degradation mirrored those for the analogous di-tert-butylphenols, with 26DMP being lost more rapidly and 35DMP showing rate of loss of substrate around one third of that of 26DMP (Figure 3-27). The rate of loss of 26DMP was comparable with that for p-cresol.

The now familiar rapid initial phase followed by a slower steady rate was again observed.

![Figure 3-27](image)  
**Figure 3-27** Relative rates of degradation of p-cresol, 2,6- and 3,5-dimethylphenol

### 3.7.2 Qualitative analysis of reaction intermediates from 2,6-DMP

Twelve significant intermediates were detected in the TiO₂ catalysed degradation (standard photolysis procedure) of 26DMP (Figure 3-28 (overleaf) and Table 3-8 (p. 104)).
Figure 3-28 HPLC chromatogram of 2,6-dimethylphenol photolysate after irradiation in Rayonet reactor for 15 min (39 % degradation).

The presence of the quinone, 26DMBQ (36), was confirmed by comparison to the analytical data from an authentic sample, but the hydroquinone was not detected. Additionally a 2,5-cyclohexadienone, from nuclear addition of •OH, was identified by comparison with MQOL and 2,6-dimethylresorcinol from the closest available analogue 2,5-dimethylresorcinol. Eight aggregated products are proposed resulting from either methyl group coupling or coupling at the para position. There was no evidence of oxygen coupling at the para position and none of the long r.t peaks observed showed 2,5-cyclohexadienone-type spectra.

So it appears that as with 26DtBP a number of intermediates were formed from initial oxidation at the para position, leading to the formation of a benzoquinone and dimerisation.

3.7.3 Quantitative analysis of reaction intermediates from 26DMP

Calculation of percentage yields of intermediates after 15 minutes irradiation using standard photolysis procedure (38% degradation) revealed that 26DMBQ was the most
<table>
<thead>
<tr>
<th>r.t./min</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;/ nm</th>
<th>purity parameter /nm (190-367 nm)</th>
<th>identity</th>
<th>degree of certainty and nearest library match</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.0 (not observed until 74% degradation)</td>
<td>231</td>
<td>227.9</td>
<td>substituted 2,5-cyclohexadienone</td>
<td>** MQOL/MHPQ</td>
</tr>
<tr>
<td>16.5</td>
<td>216, 257</td>
<td>227.6</td>
<td>unknown but chromophore similar to intermediates r.t. 7.3 and 23.7 from 26DtBP</td>
<td>** 26DMBQ</td>
</tr>
<tr>
<td>17.3</td>
<td>252</td>
<td>249.9</td>
<td>2,6-dimethylbenzoquinone</td>
<td>*** 26DMBQ</td>
</tr>
<tr>
<td>18.0</td>
<td>194, 275</td>
<td>196.6</td>
<td>2,6-dimethylresorcinol</td>
<td>** 2,5-dimethylresorcinol</td>
</tr>
<tr>
<td>20.7 (SM)</td>
<td>215(sh), 266</td>
<td>195.8</td>
<td>2,6-dimethylphenol</td>
<td>***</td>
</tr>
<tr>
<td>23.4</td>
<td>205, 265</td>
<td>217.1</td>
<td>bis(26DMP)</td>
<td>** bis(26DtBP)</td>
</tr>
<tr>
<td>24.5</td>
<td>197, &gt;367</td>
<td>243.9</td>
<td>side-chain functionalised DMDPQ</td>
<td>* tBDPQ</td>
</tr>
<tr>
<td>26.3</td>
<td>196, &gt;367</td>
<td>253.9</td>
<td>DMDPQ</td>
<td>* tBDPQ</td>
</tr>
<tr>
<td>29.1</td>
<td>208, 265</td>
<td>192.0</td>
<td>side-chain linked dimer</td>
<td>** 26DMP</td>
</tr>
<tr>
<td>29.9</td>
<td>285</td>
<td>197.8</td>
<td>1,2-bis(2,5-dihydroxy-3-methylphenyl)ethane</td>
<td>** 2,3-dimethyl hydroquinone</td>
</tr>
<tr>
<td>32.6</td>
<td>192, 219, 275</td>
<td>195.5</td>
<td>oligmeric intermediate</td>
<td>*</td>
</tr>
<tr>
<td>38.9</td>
<td>193, 219</td>
<td>197.1</td>
<td>oligmeric intermediate</td>
<td>*</td>
</tr>
<tr>
<td>48.9</td>
<td>193, 220</td>
<td>197.2</td>
<td>oligmeric intermediate</td>
<td>*</td>
</tr>
</tbody>
</table>

Key to degree of certainty of assignment:
***exact match with spectrum and retention time of authentic material
**close match to standard containing the same chromophore
*speculative assignment
abundant intermediate at that stage in the reaction (Figure 3-29). The corresponding peak in the chromatogram shown (Figure 3-28) appears relatively small due to the detector wavelength of 220 nm ($\lambda_{\text{max}}$ 254 nm). The second highest yield was for the methyl group linked dimer, bis(26DtBP). All the other intermediates had yields of 5% or less. Yields for aggregated intermediates were calculated on the assumption that they have a similar detector response to the substrate. Almost half of the reacted substrate was not, however, accounted for.

![Figure 3-29 Percentage intermediate yields in the photocatalytic degradation of 2,6-dimethylphenol after irradiation for 15 minutes (39% degradation).](image)

**Figure 3-29** Percentage intermediate yields in the photocatalytic degradation of 2,6-dimethylphenol after irradiation for 15 minutes (39% degradation).

### 3.7.4 Qualitative analysis of reaction intermediates from 3,5-DMP

HPLC analysis of a partially degraded photolysate (Figure 3-30) showed little in the way of reaction intermediates. Again, typically for a meta alkyl substituted phenol, a large peak was observed near the solvent front probably indicating the presence of ring-opened material.

The small peaks that were present gave information on their possible identities and data on them are recorded in Table 3-9 (p.107). The chromatograms recorded during the photolysis were reintegrated at 205, 234 and 254 nm to obtain the data for this table.
2,6-Dimethylbenzoquinone was identified from a sample of authentic material. Although the peak corresponding to 26DMBQ appears insignificant in Figure 3-30, this is again due to the low absorbance of the molecule at the detector wavelength. The identity of all other intermediates was assigned by comparison with compounds with similar chromophores. A peak at r.t. 11.8 min had a UV spectrum indicative of a 2,5-cyclohexadienone and is tentatively assigned to be a substituted dimethyl-2,5-cyclohexadien-1-one. Comparison of the spectrum of the peak r.t. 15.2 min with hydroxybenzaldehydes suggested that it may be a product of the oxidation of a methyl group, e.g. 3-hydroxy-5-methylbenzaldehyde. The peaks at r.t. 12.5 and 8.3 min have UV spectra reminiscent of a catechol and are tentatively assigned to 3,5-dimethylcatechol and a side-chain functionalised catechol, respectively. Finally, the intermediate at r.t. 16.0 min has a similar UV spectrum to the substrate and may be the product of side-chain functionalisation e.g. 3-hydroxy-5-methylbenzyl alcohol.
Table 3-9 Reaction intermediates from the photocatalytic degradation of 3,5-dimethylphenol.

<table>
<thead>
<tr>
<th>r.t./min</th>
<th>$\lambda_{\text{max}}$/nm</th>
<th>purity parameter/nm (190-367 nm)</th>
<th>identity</th>
<th>degree of certainty and nearest library match</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.9</td>
<td>204</td>
<td>203.8</td>
<td>ring-opened material</td>
<td>*</td>
</tr>
<tr>
<td>8.3</td>
<td>194</td>
<td>197.4</td>
<td>side-chain oxidised 35DMCC</td>
<td>* 4MCC</td>
</tr>
<tr>
<td>11.8</td>
<td>231</td>
<td>223.6</td>
<td>substituted 2,5-cyclohexadienone</td>
<td>** MQOL/MHPQ</td>
</tr>
<tr>
<td>12.5</td>
<td>196</td>
<td>199.3</td>
<td>3,5-dimethylcatechol</td>
<td>* 4MCC</td>
</tr>
<tr>
<td>15.2</td>
<td>213, 256, 316</td>
<td>224.8</td>
<td>3-hydroxy-5-methylbenzaldehyde</td>
<td>** 2-hydroxy-benzaldehyde</td>
</tr>
<tr>
<td>16.0</td>
<td>197, 221, 274</td>
<td>198.0</td>
<td>side-chain functionalised 35DMP SM-X</td>
<td>* 35DMP</td>
</tr>
<tr>
<td>17.0</td>
<td>252</td>
<td>250.8</td>
<td>2,6-dimethylbenzoquinone</td>
<td>*** 26DMBQ</td>
</tr>
<tr>
<td>20.0 (SM)</td>
<td>196, 213 (sh), 275</td>
<td>197.6</td>
<td>35DMP</td>
<td>***</td>
</tr>
</tbody>
</table>

Key to degree of certainty of assignment:
***exact match with spectrum and retention time of authentic material
**close match to standard containing the same chromophore
*speculative assignment

3.7.5 Quantitative analysis of reaction intermediates from 35DMP

The only intermediate present in any significant quantity in the photocatalytic degradation of 35DMP using the standard photolysis procedure was 26DMBQ. Although it made up nearly 50% of the degraded material in the initial stages of the reaction, it is itself rapidly degraded. All other intermediates occurred at a low percentage yield i.e. ≤ 2%.

Figure 3-31 (overleaf) compares yield profiles for the common benzoquinone intermediate observed in the degradations of both 2,6- and 3,5-dimethyl phenol. In the 35DMP reaction, the quinone appeared to be present at nearly 50% yield at low conversion of substrate, but
was lost rapidly. For the 2,6- isomer, the quinone produced the same yield at around twice the percentage degradation of substrate.

Figure 3-31 Comparison of yield profiles of the common benzoquinone intermediate from 2,6- and 3,5-dimethylphenol.

3.7.6 Discussion

The same trend in the rate of loss of substrate in relation to substitution pattern was observed for these two dimethylphenols as with the di-tert-butylphenols, the 3,5-isomer being degraded more slowly than the 2,6-isomer (Figure 3-27). This supports the results reported for degradation in pure water (Terzian and Serpone, 1995).

Terzian and Serpone studied the mineralisation of dimethylphenols by illuminated TiO\(_2\) and Terzian et al. (1995) investigated the mechanism of degradation by pulse radiolysis. In the first study, irradiations were performed in aqueous solutions at pH 3 with TiO\(_2\) (Degussa P25, 2 g dm\(^{-3}\)). The initial rates of degradation are shown in Table 3-10.

The relative rates for 2,6- and 3,5-dimethylphenols are largely in agreement with those observed in this study, the 2,6-isomer being lost at about twice the initial rate.
Table 3-10 Initial rates of loss of dimethylphenols by irradiated TiO$_2$ in air-equilibrated suspension at pH 3 (Terzian and Serpone, 1995).

<table>
<thead>
<tr>
<th>dimethylphenol</th>
<th>initial rate$^a$ / $\mu$M min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,6</td>
<td>20±1</td>
</tr>
<tr>
<td>2,4</td>
<td>18±2</td>
</tr>
<tr>
<td>2,5</td>
<td>12.2±0.7</td>
</tr>
<tr>
<td>3,4</td>
<td>12±2</td>
</tr>
<tr>
<td>2,3</td>
<td>10.1±1.5</td>
</tr>
<tr>
<td>3,5</td>
<td>8.9±0.5</td>
</tr>
</tbody>
</table>

$^a$No significant variation in initial rates was observed between different batches of Degussa P25.

A third study examined the photooxidation of 26DMP by excited uranyl ions, *UO$_2^{2+}$ (Sarakha, et al., 1997). The degradation intermediates from 26DMP observed in this study are compared with those cited in the literature in Figures 3-32(a) and (b).

Figure 3-32(a) Intermediates identified in the photooxidation of 2,6-dimethylphenol in the present work.
2,6-Dimethylbenzoquinone is the only intermediate commonly observed. The corresponding hydroquinone was identified by Terzian and Serpone, but was not detected elsewhere. The dehydrodimer, bis(26DMP), was present in this study and in that of Sarakha, et al. Once again, a more extensive group of intermediates was found in this work than in the literature.

2,6-Dimethylbenzoquinone is a product of the photooxidation of both 3,5- and 2,6-dimethylphenols, but the differing routes to its formation are emphasised by the yield profiles obtained in the present work (Figure 3-31). It appears that its formation from the 3,5-isomer occurs via a comparatively direct route and in an environment that promotes further oxidation in situ. In contrast, the same quinone is formed from the 2,6-isomer at the end of a longer sequence, at which point it is not immediately available for further oxidation, and so accumulates. This latter proposition is fully consistent with the mechanism proposed for the formation of the analogous compound from 2,6-di-tert-butylphenol (Scheme 3-7, p.89) and with the absence of its analogue in the photolysate of 3,5-di-tert-butylphenol. The mechanism, with a peroxy-linked 4,4'-dehydrodimer as intermediary, may also apply in some of the frequently reported observations of quinones in the photocatalytic oxidations of phenols, avoiding the need to invoke quinone reduction (Richard, 1994) as the origin of the observed hydroquinones in those cases.
For 35DMP, the comparison in identified intermediates is shown in Figure 3-33.

*This work*

![Diagram of intermediates](attachment:intermediates.png)

*Terzian and Serpone*

![Diagram of intermediates](attachment:intermediates.png)

**Figure 3-33** Intermediates identified in the photooxidation of 3,5-dimethylphenol.

Again, 26DMBQ is commonly observed, as is the possibility of hydroxyl substitution on the ring. Terzian and Serpone did not, however, indicate the presence of any intermediates from the oxidation of the methyl groups or substituted 2,5-cyclohexadienones, although the presence of other unidentified intermediates was acknowledged. Although they did not consider orientation of the molecule on the catalyst surface, it was acknowledged that the substitution pattern directly affects the reaction mechanism and the nature of the products.

Degradation of 2,6- and 3,5-dimethylphenols has followed the pattern observed for 2,6- and 3,5-di-tert-butylphenols, i.e. 2,6- isomers degraded more rapidly but formed more observable reaction intermediates, whereas 3,5- substrates were lost at a slower rate with fewer detectable intermediates.
The hydrophobicity of dimethylphenols is significantly less than for di-tert-butylphenols (q. v. Table 3-4), but the trends in reaction rates and intermediate profiles suggest that the position of the methyl groups on the ring, particularly with respect to the hydroxy group, can still influence surface orientation and hence the mechanism of degradation. It is probably also true that the weakness of the directing force permits adsorption to occur in more than one orientation.

The final dimethylphenol considered was 3,4-dimethylphenol (34DMP). If there is a hydrophobic steering force at work with these substrates, the position of the methyl groups might be expected to encourage a reaction mechanism similar to that for 35DMP. However, it has a methyl group substituted para to the hydroxyl and may therefore behave more like p-cresol.

3.7.7 Rate of loss of substrate – 3,4-DMP

Degradation of 34DMP by the standard photolysis procedure occurred at a comparable rate to p-cresol (Figure 3-34) and 26DMP and more rapidly than 35DMP.

![Figure 3-34](image)

**Figure 3-34** Relative rates of degradation: p-cresol and 3,4-dimethylphenol.
3.7.8 Qualitative analysis of reaction intermediates from 34DMP

Eight intermediates were detected in the TiO₂ catalysed degradation of 3,4-dimethylphenol (34DMP) which gave the above results, including four with 2,5-cyclohexadienone-type UV spectra. Details of the intermediate profile are recorded in Figure 3-35 and Table 3-11 (overleaf).

![HPLC chromatogram of 3,4-dimethylphenol photolysate after irradiation in Rayonet reactor for 30 minutes (24 % degradation).](image)

**Figure 3-35** HPLC chromatogram of 3,4-dimethylphenol photolysate after irradiation in Rayonet reactor for 30 minutes (24 % degradation).

By comparison with intermediate profiles from the degradation of p-cresol and BHT, considering both the UV spectra (Figure 3-36) and the order of elution, the peaks at r.t. 9.0 and 10.5 are assigned to the corresponding 4-hydroxy (HDMC, 37) and 4-hydroperoxy-2,5-cyclohexadienones (HPDMC, 38), respectively. Similarly, applying the same reasoning used for the BHT degradation, the peak at r.t. 16.8 min may be the peroxy-linked dimer. The identity of the fourth 2,5-cyclohexadienone-type peak (at r.t. 12.4 mins) remains unclear. Examination of the UV spectra of authentic samples of 4-hydroxybenzaldehyde and 3-hydroxybenzaldehyde suggested the intermediates with r.t. 13.6 and 14.9 min could be the analogous 4-hydroxy-2-methyl- and 5-hydroxy-2-methylbenzaldehydes, respectively.
Table 3-11 Reaction intermediates from the photocatalytic degradation of 3,4-dimethylphenol.

<table>
<thead>
<tr>
<th>r.t. / min</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; / nm</th>
<th>purity parameter/nm (190-367 nm)</th>
<th>identity</th>
<th>degree of certainty and nearest library match</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0</td>
<td>230, 266 (sh)</td>
<td>231.4</td>
<td>4-hydroxy-3,4-dimethyl-2,5-cyclohexadien-1-one</td>
<td>** MQOL</td>
</tr>
<tr>
<td>10.5</td>
<td>228, 266 (sh)</td>
<td>229.3</td>
<td>4-hydroperoxy-3,4-dimethyl-2,5-cyclohexadien-1-one</td>
<td>** MHPQ</td>
</tr>
<tr>
<td>12.4</td>
<td>236</td>
<td>236.4</td>
<td>possible 2,5-cyclohexadien-1-one type compound</td>
<td>* MQOL/MHPQ</td>
</tr>
<tr>
<td>13.6</td>
<td>199, 222, 278</td>
<td>228.1</td>
<td>4-hydroxy-2-methylbenzaldehyde</td>
<td>** 4-hydroxy-benzaldehyde</td>
</tr>
<tr>
<td>14.9</td>
<td>219, 253, ~325</td>
<td>245.2</td>
<td>5-hydroxy-2-methylbenzaldehyde</td>
<td>** 3-hydroxy-benzaldehyde</td>
</tr>
<tr>
<td>16.8</td>
<td>227</td>
<td>227.5</td>
<td>bis(4-oxy-3,4-dimethyl-2,5-cyclohexadien-1-one)</td>
<td>* bis(MQOL)</td>
</tr>
<tr>
<td>19.4 (SM)</td>
<td>215 (sh), 275</td>
<td>194.8</td>
<td>3,4-dimethylphenol</td>
<td>***</td>
</tr>
<tr>
<td>21.9</td>
<td>195, 220</td>
<td>207.9</td>
<td>unknown</td>
<td></td>
</tr>
<tr>
<td>27.6</td>
<td>204, 244, 288</td>
<td>211.2</td>
<td>2,2′-hydroxy-4,4′,5,5′-tetramethylbiphenyl</td>
<td>** 2,2′-dihydroxy-5,5′-dimethylbiphenyl</td>
</tr>
</tbody>
</table>

Key to degree of certainty of assignment:
***exact match with spectrum and retention time of authentic material
**close match to standard containing the same chromophore
*speculative assignment
The highly retained peak at r.t. 27.6 min exhibited a spectrum resembling 2,2'-dihydroxy-5,5'-dimethylbiphenyl (12), a dehydrodimer detected in the degradation of p-cresol and is proposed to be 2,2'-hydroxy-4,4',5,5'-tetramethyl-biphenyl (31).

Figure 3.36 UV spectra of four intermediates from the photocatalytic degradation of 34DMP.

3.7.9 Quantitative analysis of reaction intermediates from 34DMP

The most significant peak in the HPLC analysis of partially degraded 3,4-dimethylphenol is the peak at r.t. 16.8 min. This intermediate accounted for a third of the degraded substrate at low conversion (assuming the same response factor as MQOL), with all other intermediates having yields of <5%. Figure 3.37 (overleaf) presents the relative yields of the identified intermediates.
Figure 3-37 Percentage intermediate yields in the photocatalytic degradation of 3,4-dimethylphenol after irradiation for 30 minutes (24% degradation, standard photolysis procedure).

3.7.10 Discussion – 34DMP

The intermediate profiles and yields appear somewhat anomalous compared with the other dimethylphenol results, but a previous study on the sensitised photooxidation of alkyl phenols (Faust and Hoigné, 1987) suggests that the reactivities of 4-alkylphenols may be influenced by hyperconjugation effects of the alkyl group. They also infer that the hydroxyl group is important in sensitised photooxidation as the reactivity of 4-dimethoxybenzene was found to be less than that of 4-methoxyphenol. Here, the yield profile suggests that oxidation of the methyl para to the hydroxyl is more prevalent than functionalisation of the other substituent.

There are several similarities with the results from p-cresol, i.e. 2,5-cyclohexadiene-type intermediates, methyl group oxidation, dehydrodimer formation and, indeed, near identical rates of degradation. The intermediates identified appear to indicate that 34DMP can adsorb in two orientations i.e. with the methyl groups on the surface or via the OH group. Close proximity of the methyl groups to oxidising species would promote methyl group oxidation, addition of OH and associative radical reactions (Figure 3-38). If the speculative
assignment of the 16.8 min peak to a bis-dienone turns out to be true, however, then the opposite orientation is implicated as described earlier (section 3.2.5). This would raise the question as to why such a compound was not observed with p-cresol itself in 20% ACN. Clearly 3,4-dimethylphenol merits a closer and more detailed study.

![Possible influence of orientation on product profile in the photocatalytic degradation of 3,4-dimethylphenol.](image)

**Figure 3-38** Possible influence of orientation on product profile in the photocatalytic degradation of 3,4-dimethylphenol.

### 3.8 General discussion

Considering the results obtained for all the alkyl phenols in this study, a number of trends have emerged amongst the substrates. The 3,5-disubstituted substrates were lost at the slowest rates and the 2,6-disubstituted at the fastest. Differences between, and consistency within, effects of substitution in the two groups were also reflected in the intermediate profiles. The 3,5-dialkyl and the 4-tert-butylphenols showed little accumulation of primary carbocyclic products, but appeared to degrade largely to small polar molecules without observable interruption. In contrast, BHT and the 2,6-dialkyl-phenols showed abundant primary intermediates.

Very small peaks in the HPLCs of photolysates of 4-tert-butylphenol, 3,5-di-tert-butylphenol and 3,5-dimethylphenol showed spectra closely similar to those of the corresponding reactant, suggesting sidechain-functionalised monomeric and dehydrodimeric derivatives were responsible. Each chromatogram also showed a peak
corresponding to <1% of oxidised reactant with a spectrum typical of 2,5-cyclohexadienones, and that for the 3,5-dimethylphenol included small peaks consistent with a catechol and 2,6-dimethylbenzoquinone. Oxidation of the sidechains and coupling are best envisaged with a hydrophobically selected orientation that places these groups next to the oxidising surface, although the other minor intermediates could arise plausibly from either orientation.

The metastable products from the two 2,6-dialkylated phenols were broadly similar and, like that from BHT, are derived almost entirely via radical coupling of two oxidised molecules of reactant (Table 3-12) (overleaf). Thus, the direct 4,4'-linked products seen with the tert-butyl compounds were evident in the photolysate of the corresponding dimethyl derivatives. (Both sets of compounds are seen in radical-promoted reactions with concentrated solutions of the phenols in benzene (Magnaterra, et al., 1996)). Similarly, the quinones and hydroquinones seen among the products may be an outcome of aromatisation and cleavage of the peroxydehydrodimer analogous to bis(MQOL) (27), where the 4,4'-methyl groups are replaced by hydrogen atoms (Sarakha, et al., 1997). The HPLC of the dimethylphenol photolysate also shows retained constituents that remain to be identified (notably one with \( \lambda_{\text{max}} \) at 216 and 257 nm; similar spectra are seen for two minor constituents in the product mixture from 2,6-di-tert-butylphenol), further emphasising the accumulation of intermediates seen for phenols with this substitution pattern.

3,4-Dimethylphenol also shows a complex array of metastable products. Unlike the 3,5-dialkyl- and 4-tert-butylphenols, this compound can react at a benzylic position and thereby offer additional oxidative pathways. Cyclohexadienones, catechols and benzaldehydes were observed among the intermediates, mirroring the profile identified for \( p \)-cresol and suggesting that the para methyl substituent has a significant role in the degradation mechanism.

Such subtle effects may be seen to support the hypothesis that specific orientations play an important part in heterogeneous photocatalysis and that those proposed for these compounds reflect a significant influence by hydrophobicity. This is clearly demonstrable
for the two di-tert-butylphenols in dark absorption equilibration data for the series of compounds in Table 3-4. The implications of other comparisons of the data appear questionable and indicate a need for caution when considering groups as small as methyl.

Table 3-12 Product distribution (%) at 35% TiO$_2$-catalysed photooxidation of 2,6-dialkylphenols in 20% acetonitrile in water

<table>
<thead>
<tr>
<th>product</th>
<th>alkyl group, R</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>methyl</td>
</tr>
<tr>
<td>![image 1]</td>
<td>8</td>
</tr>
<tr>
<td>![image 2]</td>
<td>$3^a$</td>
</tr>
<tr>
<td>![image 3]</td>
<td>4</td>
</tr>
<tr>
<td>![image 4]</td>
<td>26</td>
</tr>
<tr>
<td>Q-X$^b$</td>
<td>$&lt;1^c$</td>
</tr>
<tr>
<td>HQ-HQ$^c$</td>
<td>$&lt;1^c$</td>
</tr>
<tr>
<td>HQ-X$^b$</td>
<td>$&lt;1^c$</td>
</tr>
<tr>
<td>HQ-HQ$^d$</td>
<td>3</td>
</tr>
</tbody>
</table>

$^a$includes sidechain-functionalised derivative $^b$sidechain-functionalised $^c$below detectable limits $^d$sidechain-linked dehydrodimer
A reasonable case for either orientation could be made for \( p \)-cresol, for example. Moreover, plausible pathways can be envisaged for all intermediates observed in the photocatalytic oxidation of that compound using either orientation, with the possible exception of the abundant primary intermediate, 4-hydroxy-4-methylcyclohexa-2,5-dien-1-one. Scheme 3-8 shows how this, and other intermediates found to be significant in this study, may be readily explained using the hydrophobically favourable orientation with the methyl groups adjacent to the catalyst surface. It represents a conceptual development from the scheme displayed earlier (3-2) in which both substrate orientation and the surface location of the hydroxyl radical are taken into account.

![Scheme 3-8 Proposed reaction mechanism for the TiO\textsubscript{2}-catalysed photodegradation of \( p \)-cresol adsorbed at the surface via the methyl substituent.](image)

**Scheme 3-8** Proposed reaction mechanism for the TiO\textsubscript{2}-catalysed photodegradation of \( p \)-cresol adsorbed at the surface via the methyl substituent.
Oxidation by a surface-trapped hole at the 4-position of the molecule and hydrogen atom abstraction from phenolic hydroxyl leads to a surface structure which releases the hydroxycyclohexadienone by solvolysis. In pure water, attack at the 2-position to the hydroxyl group, leads to 4-methylcatechol while in 20% acetonitrile, water is displaced at the catalyst surface (Cunningham, et al., 1994), allowing hydrophobically-induced clustering to be expressed through similar nucleophilic attack by the 2-position of another molecule of p-cresol. Elimination at the methyl group affords a quinone methide that aromatises with the addition of water to the benzyl alcohol, which is further oxidised to the aldehyde.

3.9 Conclusions

Employing relatively low intensity radiation and apparatus that exposes substrate adsorbed on the catalyst serially for short periods, although inefficient as regards mineralisation, allows primary products in photocatalytic oxidations to be observed. The TiO₂-catalysed photooxidation by UV-A of p-cresol in water involves at least four competing steps following hydrogen abstraction. The two earlier studies each uncovered one of these but failed to detect one of the major processes, namely hydroxyl addition. Evidence to support the intermediacy of a hydrotetroxide as proposed by Heller is equivocal.

Surface-bound hydroxyl radicals are involved directly in product formation and oxygen acts primarily as an electron sink for conduction band electrons; it plays little or no part in product formation from aqueous p-cresol. Oxygen is involved, however, in product formation to a minor extent when the solvent is aqueous acetonitrile and as a major participant in the photooxidation of 2,6-dialkylphenols.

Substituent pattern is an important determinant in the choice of pathway for the photocatalytic degradation of alkyl phenols. 2,6-Dialkylated phenols are degraded most rapidly and undergo associative reactions, almost exclusively when the alkyl group is tert-butyl, as a prelude to photooxidative degradation in 1 : 4 acetonitrile in water catalysed by TiO₂. Monomer radicals are linked directly and/or via the insertion of molecular oxygen according to structure, the latter generating quinones and hydroquinones by aromatisation

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and fragmentation when the 4-position is unsubstituted. Minor, but significant dehydrodimerisation of side-chain radicals also occurs. 3,5-Dialkyl substitution promotes primary products that react faster than the substrate, and hence gives rise to ring-opened material with little accumulation of intermediates.

The hydrophobic nature of the alkyl groups promotes their adsorption on the catalyst surface and, furthermore, clustering of molecules encourages associative reactions. This orientation shields the alkyl substituents from the bulk solution causing minimal disruption of polar networks.

Phenols with other alkyl substitution patterns also tend to hydrophobic clustering and, at least in part, select orientations that place the alkyl groups close to the oxidising surface, a phenomenon that may have significance in the photocatalytic degradation of other organic compounds.

Part of this behaviour may be attributable to the presence of acetonitrile in the solvent, a change from water to a less polar solvent such as acetonitrile has been found to increase dark adsorption of a substrate in TiO$_2$ suspensions (Cunningham, et al., 1994). However, it seems that the hydrophobic profile of a substrate for heterogeneous photocatalytic oxidation in water is a significant factor of the molecular pathway selected in the first phase of its degradation.
CHAPTER 4
DIBROMOHYDROXYBENZONITRILES

4.1 Introduction

The photocatalytic degradation of a commercially available phenolic compound, the herbicide bromoxynil (3,5-dibromo-4-hydroxybenzonitrile, 39, 35DB4HBN), was investigated as an example of a compound which could, potentially, pollute the aqueous environment. Continuing the theme of the influence of substituent pattern, its behaviour was compared with that of its isomer 3,5-dibromo-2-hydroxybenzonitrile (40, 35DB2HBN).

\[
\begin{align*}
39 & \quad & \text{3,5-dibromo-4-hydroxybenzonitrile} & & \text{35DB4HBN} \\
40 & \quad & \text{3,5-dibromo-2-hydroxybenzonitrile} & & \text{35DB2HBN}
\end{align*}
\]

Bromoxynil is used for post-emergent control of annual broad-leaf weeds, primarily as a contact herbicide. Its mode of action is due to inhibition of the second light reaction of photosynthesis and also to uncoupling of the oxidative phosphorylation of respiration (Halmann, 1996d).

4.2 Photocatalytic degradation of dibromohydroxybenzonitriles

An initial irradiation was undertaken of an aqueous solution containing ~10 ppm of each isomer in the presence of TiO₂, both compounds being present in the same solution to enable rapid screening of their degradation. Photolysis in a Pyrex vessel by a 400W medium pressure mercury arc lamp degraded nearly all of the 35DB2HBN and 80% of 35DB4HBN after 2 hours (Figure 4-1, overleaf) with few intermediate peaks observed by HPLC analysis.
Figure 4-1 Photocatalytic degradation of 35DB4HBN and 35DB2HBN by 400W medium pressure mercury arc lamp.

A series of control experiments were performed on a solution containing both isomers (Table 4-1).

Table 4-1 Control experiments with dibromohydroxybenzonitriles

<table>
<thead>
<tr>
<th>exp. no.</th>
<th>TiO₂</th>
<th>O₂</th>
<th>light</th>
<th>35DB4HBN</th>
<th>35DB2HBN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>100% loss &lt; 4.5 hr</td>
<td>100% loss ~ 2 hr</td>
</tr>
<tr>
<td>2</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>100% loss &lt; 5.5 hr</td>
<td>100% loss &lt; 1 hr</td>
</tr>
<tr>
<td>3</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
<td>no degradation</td>
<td>no degradation</td>
</tr>
<tr>
<td>4</td>
<td>×</td>
<td>×</td>
<td>✓</td>
<td>100% loss ~ 5 hr</td>
<td>100% loss &lt; 1.5 hr</td>
</tr>
</tbody>
</table>

Both isomers were degraded when irradiated, with or without TiO₂ and oxygen, and 35DB2HBN was also lost more rapidly than the 4-hydroxy isomer in the absence of a photocatalyst. Two intermediates were observed in the irradiations without TiO₂. The
results of experiment 4 show that both isomers are photolabile with radiation, \( \lambda > 260 \text{ nm} \) and that 35DB2HBN is the more reactive.

One of the ultimate aims of photocatalytic technology for the remediation of aqueous pollutants is the use of sunlight as the source of irradiation. The possibility of degrading the two dibromohydroxybenzonitriles with TiO\(_2\) and sunlight was first examined speculatively by leaving suspensions adjacent to the laboratory window (but shielded from direct sunlight) over a two day period. Figure 4-2 illustrates that, although slower than with a lamp, degradation is significant even with relatively low levels of radiation. The 2-hydroxy isomer is again lost more rapidly. No significant intermediate peaks were observed in the analysis of the photolysate.

![Figure 4-2](image)

**Figure 4-2** Photocatalytic degradation of 35DB4HBN and 35DB2HBN on exposure to daylight during February 1995.

In the absence of TiO\(_2\) the 2-hydroxy isomer was degraded by exposure to sunlight; there was no measurable loss of the 4-hydroxy isomer under these conditions (Figure 4-3). The presence of three reaction intermediates was observed in the photolysate, the one giving
the largest apparent concentration in the chromatogram reaching a maximum after 3 hours exposure. A control flask, covered with aluminium foil, was also placed on the window sill. No loss of either isomer was detected from this solution.

Figure 4-3 Degradation of 35DB4HBN and 35DB2HBN in the absence of TiO$_2$ on exposure to daylight during early March 1995.

Comparing the UV-vis spectra of the two isomers (Figure 4-4, overleaf), it can be seen that the 2-hydroxy isomer absorbs at considerably longer wavelength than the 4-hydroxy isomer. Moreover, the spectrum of the former extends into the UVA region of the solar spectrum thus making it potentially photolabile in daylight.
The contrasting behaviour of the two isomers may have a bearing on the degradation of environmentally relevant compounds by sunlight. Consequently, an investigation of the direct photolysis of 35DB2HBN was undertaken.

### 4.3 Photolysis of 3,5-dibromo-2-hydroxybenzonitrile by daylight

#### 4.3.1 Initial photolysis results

The only reaction intermediates observed in this study were those from the direct photolysis of 35DB2HBN. In an attempt to determine the primary photolysis mechanism for this compound, direct photolyses were carried out under controlled conditions. Irradiation with cool daylight lamps degraded 95% of the substrate in 7 hours. Figure 4-5 is a chromatogram of a partly degraded solution and shows three degradation products. UV-vis spectra of the most prominent of these is shown in Figure 4-6 (overleaf). Although the photoproduct is very much less retained than the substrate (r.t.. 6 min compared to 13.3 min), suggesting that it was a more polar compound, comparison of the UV spectra shows near identity with the substrate chromophore.
Figure 4-5 HPLC chromatogram of 35DB2HBN photolysate after irradiation in Applied Photophysics reactor without TiO$_2$ for 3 h (63% degradation, 220 nm detection, DBHBN analysis conditions).

<table>
<thead>
<tr>
<th>Name</th>
<th>PuP (nm)</th>
<th>r.t./min</th>
</tr>
</thead>
<tbody>
<tr>
<td>photoproduct</td>
<td>208.4</td>
<td>6.0</td>
</tr>
<tr>
<td>35DB2HBN</td>
<td>209.3</td>
<td>13.3</td>
</tr>
</tbody>
</table>

Figure 4-6 UV-vis spectrum of the principal product (r.t. 6 min, Figure 4-5) from the direct photolysis of 35DB2HBN (purity parameter range 190-367 nm).
4.3.2 Identity of principal photoproduct

The identity of the major product was investigated by a number of analytical techniques utilising a sample of the compound extracted from the photolysate. It has a molecular weight of 213 and HRMS gives a molecular ion with the likely formula \( C_7H_4BrNO_2 \), indicating that one of the bromine atoms in the substrate has been replaced by OH, i.e. structure 41 or 42. Results of the qualitative tests on the photoproduct are summarised in Table 4-2. Details of the procedures and results observed with authentic compounds are given in Section 2.5.

![Structures 41 and 42](image)

**Table 4-2** Results of analytical procedures used to investigate the identity of the principal photoproduct.

<table>
<thead>
<tr>
<th>procedure</th>
<th>result with photoproduct</th>
<th>structure suggested by result</th>
</tr>
</thead>
<tbody>
<tr>
<td>solution IR spectrum</td>
<td>no hydroxyl band shift on dilution(^a)</td>
<td>5B23DHBN</td>
</tr>
<tr>
<td>( \text{FeCl}_3 )</td>
<td>green colour</td>
<td>5B23DHBN</td>
</tr>
<tr>
<td>( \text{FeCl}_3 + \text{Na}_2\text{CO}_3 )</td>
<td>pink solution with red/brown gelatinous precipitate</td>
<td>inconclusive</td>
</tr>
<tr>
<td>lead acetate</td>
<td>no precipitate</td>
<td>3B25DHBN</td>
</tr>
<tr>
<td>derivatisation with phenyl boronic acid/GC analysis</td>
<td>no change in r.t.</td>
<td>3B25DHBN</td>
</tr>
<tr>
<td>HPLC analysis before oxidation with ( \text{Ag}_2\text{O} )</td>
<td>colourless solution, r.t. 8.8 min, ( \lambda_{\text{max}} ) 213, 317 nm</td>
<td></td>
</tr>
<tr>
<td>HPLC analysis after oxidation with ( \text{Ag}_2\text{O} )</td>
<td>yellow solution, r.t. 9.1 min, ( \lambda_{\text{max}} ) 257, 290, 458 nm(^b)</td>
<td>3B25DHBN</td>
</tr>
</tbody>
</table>

\(^a\)IR spectrum indicates that CN group is retained. \(^b\)see Figure 4-7.
The solution IR spectrum was recorded to look for the effects of intermolecular hydrogen bonding. Para-substituted dihydroxybenzenes form intermolecular hydrogen bonds in solution with an aprotic solvent. Dilution of such a solution causes disruption of hydrogen bonding with a subsequent shift in the -OH stretching maximum in the spectrum. Ortho-substitution, however, encourages intramolecular hydrogen bonding and the IR dilution effect is not observed (Silverstein, et al., 1991a). In this case no shift was observed but, due to low solubility, the undiluted solution may have been too weak for the effect to be detected.

Addition of alkaline iron (III) chloride solution to a solution of a 1,2-dihydroxybenzenes leads to the formation a complex ion with a characteristic green colour. A further addition of sodium carbonate solution turns the solution burgundy. The green colour formed on addition of iron (III) chloride to the photoproduct suggested that it was 5B23DHBN, but the result on addition of sodium carbonate was inconclusive. Similarly, lead acetate solution added to an aqueous solution of a 1,2-diol gives a white precipitate; the test compound gave a negative result.

1,2-Dihydroxybenzenes can be derivatised by phenylboronic acid on a gas chromatography (GC) column, the derivative having a different retention time (Rose, et al., 1982; Longstaff and Rose, 1982). Exploratory experiments with 1,2-, 1,3-, and 1,4-dihydroxybenzenes confirmed that only 1,2-dihydroxybenzene was derivatised. Considerable difficulty was encountered in obtaining satisfactory and reproducible GC traces for the photolysis products. Changes made from the preliminary investigation include a different solvent and modified GC oven temperature gradients. However, even when conditions were optimised for the photolysis products, while still giving a positive result with 1,2-dihydroxybenzene, no changes were observed in the chromatogram of the product with phenylboronic acid.

Oxidation of hydroquinone by silver oxide gives benzoquinone, which has a characteristic UV spectrum (q.v. Figure 2-1b). Oxidation with authentic diols confirmed that this is so.
Results with the unknown photoproduct are reported in Table 4-2 and Figure 4-7 and suggest that it is 3B25DHBN.

**Figure 4-7** UV spectrum of photoproduct (a) before and (b) after oxidation by silver oxide.

It has been shown that chemical shifts of the ring carbon atoms of substituted benzenes in $^{13}$C NMR spectroscopy can be estimated by applying the principle of substituent additivity (Silverstein, *et al.*, 1991b). For example, the shift from benzene for C-2 of the disubstituted compound 4-chlorobenzonitrile is calculated by adding the effect for an ortho CN group (+3.6) to that for a meta Cl group (+1.3). When the carbon shifts in a recorded $^{13}$C NMR spectrum of the photoproduct were compared to the calculated shift for the two candidate structures under consideration (Table 4-3) the shifts were found to be in closer agreement with those obtained for the para dihydroxy compound, 3B25DHBN.
Table 4-3 $^{13}$C NMR shifts for the ring carbon atoms of the 35DB2HBN photoproduct and its candidate structures.

<table>
<thead>
<tr>
<th>carbon number</th>
<th>calculated values</th>
<th>photoproduct shifts</th>
<th>calculated values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3B25DHBN</td>
<td></td>
<td>5B23DHBN</td>
</tr>
<tr>
<td>C1</td>
<td>103.5</td>
<td>101.8</td>
<td>103.5</td>
</tr>
<tr>
<td>C2</td>
<td>155.1</td>
<td>150.7</td>
<td>144.7</td>
</tr>
<tr>
<td>C3*</td>
<td>112.3</td>
<td>111.2</td>
<td>145.0</td>
</tr>
<tr>
<td>C4</td>
<td>124.5</td>
<td>125.5</td>
<td>124.5</td>
</tr>
<tr>
<td>C5*</td>
<td>150.4</td>
<td>148.5</td>
<td>117.7</td>
</tr>
<tr>
<td>C6</td>
<td>119.2</td>
<td>123.0</td>
<td>129.6</td>
</tr>
</tbody>
</table>

*C3 in 3B25DHBN is in a corresponding electronic environment to C5 in 5B23DHBN.

There are some inconsistencies in the results obtained from these investigations with the photoproduct from 35DB2HBN. These may be caused by interference from the other substituents on the ring; the comparative compounds were simple dihydroxybenzenes. There is little positive evidence for the photoproduct being a ortho-dihydroxy compound. Although a characteristic green colour was observed on addition of iron (III) chloride, sodium carbonate failed to give the expected burgundy colour. Negative results with lead acetate and phenyl boronic acid may mean that these reactions do not proceed with this compound rather than indicating that it is not a 1,2-diol. The change in UV spectrum on oxidation and comparison of $^{13}$C NMR data appear to give the strongest indication that a para-dihydroxy compound was present and consequently the structure of the principal photoproduct is proposed to be 3B25DHBN (42).

4.3.3 Quantitative analysis of 3B25DHBN

Quantitation of the yield of the photoproduct (q.v. Section 2.6 for method) revealed that 3B25DHBN is the predominant primary product in the direct photolysis of 35DB2HBN by cool daylight lamps. Figure 4-8 shows that, at low substrate conversion, it accounts for almost all of the degraded material.
4.4 Discussion

4.4.1 Photodegradation of dibromohydroxybenzonitriles

Both 3,5-dibromo-4-hydroxybenzonitrile and 3,5-dibromo-2-hydroxybenzonitrile were degraded when irradiated by a 400W medium pressure mercury arc lamp in solution in the presence of TiO$_2$ without the formation of observable persistent intermediates. However, degradation also occurred on irradiation in the absence of TiO$_2$ and/or oxygen indicating that both isomers are photolabile with radiation $\lambda > 260$ nm.

An investigation of the degradation of these two compounds by sunlight gave the results summarised in Table 4-4 (overleaf).

35DB4HBN is not degraded by weak daylight in the absence of TiO$_2$ but it is susceptible to photocatalytic degradation, without the formation of detectable intermediates, under these conditions. The 2-hydroxy isomer is rapidly degraded by daylight, but persistent photoproducts are detected. The lower rate of loss of this substrate in the presence of TiO$_2$
may be the result of scattering by the catalyst which prevented penetration of light into the flask or, possibly, competition by the other substrate for oxidising species at the catalyst surface.

Two groups have reported on the direct photolysis of bromoxynil and its main photoproducts (Kochany et al., 1990; Machado, et al., 1995) and the results will be considered here in relation to the reaction of the 2-hydroxy isomer. Kochany reported the formation of 3-bromo-4-hydroxybenzonitrile (47) and 4-hydroxybenzonitrile (48), both compounds being identified by GC-MS. Machado, however, did not observe 47 or 48 but found instead 3-bromo-4,5-dihydroxybenzonitrile (49) and a second unidentified compound. Compound 49 was isolated from a photolysed solution and characterised by $^1$H NMR and EI mass spectrometry. Quantitation revealed it to be a primary photoproduct and accounted for 65% of the converted material. The same behaviour was also observed in deoxygenated solution, indicating that oxygen is not involved in this reaction and leading them to propose that it is most likely a heterolytic photohydrolysis.

The EI mass spectrum recorded in Machado’s paper has close similarities with that obtained for the isomeric principal photoproduct (42) from 35DB2HBN in this study. 3B25DHBN is formed by photochemical aromatic substitution, a well known reaction of haloaromatics (Coyle, 1986), but mechanistic details relevant to the selectivity observed in this case remain unclear. It is possible that the minor product of the reaction is the alternative dihydroxy isomer or, possibly, the trihydroxy compound, but this was not further investigated. Figure 4-8 suggests the trihydroxy compound, being a secondary product, is the more likely assignment as there seems little room for the competing reaction necessary to generate the isomer.
It has been shown that 35DB2HBN is more susceptible to direct photolysis under the conditions used in these experiments. The UV absorption spectra of the two isomers (Figure 4-4) shows that the 2-hydroxy isomer has an absorption band at 315 nm, in the UV-A region of the spectrum which, in sunlight, is largely unattenuated by the atmosphere (Phillips, 1982). Its isomer, bromoxynil, however, has no significant absorption above 300 nm and is therefore largely unaffected by sunlight. So the differing photochemical responses of the two isomers comes down to differences in their electronic absorption spectra. The question to be answered, preferably in simple terms, is the source of the difference.

4.4.2 Comparative study of UV spectra of 3,5-dibromo-2-hydroxybenzonitrile and 3,5-dibromo-4-hydroxybenzonitrile

The region of photochemical interest in the UV spectrum is the absorption above 300 nm. As has already been noted, this leads to the differing photochemical susceptibilities in ambient daylight. The reason for this difference may be addressed by considering the influence of substituents on the electronic structure of the isomers, a matter considered recently by Roberts and McCullough (1997).

The absorption band in question corresponds to the lowest energy weak band which, in the parent compound benzene, occurs at 254 nm ($\varepsilon_{\text{max}} \sim 200$) and was called the $\alpha$ band by Clar (1952) or the $1L_b$ band by Platt (1949). This band is symmetry forbidden and would be even weaker were it not for vibrational distortions. However, any substituents that destroy the symmetry cause an increase in intensity of this band.

Platt (1951) devised a semi-empirical method to calculate the extent of this enhancement as a function of the nature, number and relative positions of a range of substituents. He introduced the concept of a 'spectroscopic moment' and proposed that a substituent would alter the intensity of the $1L_b$ band and give rise to a small additional transition moment. By considering the symmetry properties of the excited state involved, he concluded that the direction of the transition moment at each position is as shown in Figure 4-9(a): for mono-substituted derivatives, the direction is immaterial, but for substitution by two or more
substituents, the moments add vectorially to give the overall resultant spectroscopic moment. The additional intensity of the $1L_{b}$ band is then proportional to the square of the spectroscopic moment.

Platt obtained the values of the substituent moments from the band intensities of suitably substituted benzene derivatives. They may be positive or negative depending on the nature of the substituent, with ortho/para directing groups (e.g. $-\text{OH}$ (+34), Br (+4)) being positive in general, and meta directing groups (e.g. $-\text{CN}$ (-19)) being negative. The individual group moments for 35DB4HBN and 35DB2HBN are shown in Figures 4-9(b) and 4-9(c) respectively: the overall transition moments are calculated to be 11 for 35DB4HBN and 50 for 35DB2HBN. The $1L_{b}$ band for the latter is therefore predicted to be some 20 times more intense, qualitatively in agreement with that found experimentally though quantitatively an overestimate.

![Figure 4-9](image)

**Figure 4-9** (a) The relative directions of the spectroscopic moments induced by substituents at different positions on the benzene ring; (b) the moments for 35DB4HBN; (c) the moments for 35DB2HBN.

Among the quantum mechanical methods available for calculating the electronic spectra of relatively large molecules containing atoms with high atomic number, the semi-empirical ZINDO method developed by Zerner et al. (Zerner and Ridley, 1973; Zerner, 1991) gives the most reliable results at relatively low computational cost. The version used by Roberts and McCullough (1997) was that implemented on the Oxford Molecular CAChe system. The ZINDO program is parametrized for the spectroscopic properties of molecules and enables UV-visible spectra to be calculated at the INDO (intermediate neglect of diatomic
overlap) level of approximation. Both 35DB4HBN and 35DB2HBN have a total of 56 valence electrons and 47 valence atomic orbitals, and so there will be 28 occupied and 19 unoccupied molecular orbitals for each. The results obtained show net charge distributions broadly as expected from simple ideas of inductive effects (Figure 4-10).

![Figure 4-10](image)

**Figure 4-10** The net atomic charges calculated by the ZINDO method for (a) 35DB4HBN and (b) 35DB2HBN.

By symmetry, whatever the method used, the two highest occupied and the two lowest unoccupied valence orbitals for benzene are degenerate. In benzene derivatives, such as 35DB4HBN and 35DB2HBN, the energies remain nearly degenerate and consequently, in order to get a realistic picture of the transitions involved, a further calculation involving configuration interaction has to be carried out. The resulting synthesised spectra are shown in Figure 4-11 (overleaf).

The agreement between the calculated spectrum for 35DB2HBN and the experimental one is excellent: the wavelengths for the three main bands are 210, 230 (sh) and 315 nm (exp.) and 215, 245 and 290 nm (calc.). The lowest energy transition for 35DB4HBN is calculated to be at 34 975 cm\(^{-1}\) with an oscillator strength of 0.011 (a value of 1 corresponds roughly to an absorption coefficient of \(10^5\)), and that for 35DB2HBN is at 34 395 cm\(^{-1}\), with an oscillator strength of 0.047. Again, the calculated results are qualitatively in accord with the experimental observations, though this time the difference is perhaps slightly underestimated.
The main configurations contributing to the lowest energy excited state for the two molecules are shown in Table 4-5; all the other contributing configurations have coefficients of less than 0.15 (the coefficients are normalised, that is the sum of all the squares of the coefficients equals one). The involvement of more configurations in

<table>
<thead>
<tr>
<th>transition between orbitals</th>
<th>coefficient</th>
<th>transition between orbitals</th>
<th>coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>28 → 29</td>
<td>+0.06</td>
<td>28 → 29</td>
<td>+0.71</td>
</tr>
<tr>
<td>28 → 30</td>
<td>+0.77</td>
<td>28 → 30</td>
<td>+0.40</td>
</tr>
<tr>
<td>27 → 29</td>
<td>−0.61</td>
<td>27 → 29</td>
<td>−0.42</td>
</tr>
<tr>
<td>27 → 30</td>
<td>+0.04</td>
<td>27 → 30</td>
<td>+0.37</td>
</tr>
</tbody>
</table>
35DB2HBN has produced a larger resultant transition moment. In simple terms, it is a consequence of the lower symmetry of 35DB2HBN compared with 35DB4HBN.

In conclusion, both methods predict a more intense band for the lowest energy transition of 35DB2HBN compared with 35DB4HBN simply as a result of the arrangement of substituents, without the need to invoke any additional interaction between ortho substituents such as the –OH and –CN in 35DB2HBN. This principle, perhaps supported by the simple analysis using Platt’s spectroscopic moments, could be used to predict the possible occurrence of significant long-wavelength bands in other benzenoid molecules that might render them susceptible to photodecomposition by sunlight.

4.5 Conclusions

1 Both isomers of these relatively highly substituted phenols are rapidly degraded to small molecules, and possibly mineralised, by TiO₂ photodegradation without the accumulation of potentially toxic persistent intermediates.

2 In contrast with the alkyl phenols, photocatalytic pathways for these compounds are complicated by the fact that they undergo direct photolysis. The detection and identification of the principal primary photoproduct from the direct photolysis of 35DB2HBN by daylight indicates that this degradation commences with the substitution of the bromine in the 5-position by hydroxyl.

3 The higher rate of loss of 35DB2HBN by direct photolysis with daylight as opposed to photocatalytic degradation can be explained by the presence of the 315 nm absorption band in its UV spectrum resulting simply from the electronic environment caused by this pattern of substitution.
CHAPTER 5
OVERVIEW

5.1 Summary

Pollution of the aqueous environment is a topic of serious concern because of not only its potential effects on human health but also the damage caused to natural habitats. One of the techniques currently under development for waste water remediation is semiconductor photocatalysed degradation. It is potentially a safe, effective method of waste treatment where the pollutant in oxygenated solution is irradiated in the presence of a catalyst to give water, carbon dioxide and mineral acids as the only by-products. Many workers have already investigated the photocatalytic degradation of a range of organic compounds (Mills and Le Hunte, 1997 and references therein) and this research group has compiled its own database which, at the time of writing, contains details of nearly 900 papers.

The ultimate aim of photocatalytic water treatment is the rapid and complete destruction of organic compounds, but incomplete mineralisation may produce intermediate materials that are potentially more toxic or harmful than the original pollutant. It is important, therefore, to monitor any intermediates formed in mineralisation studies. Moreover, a study of the intermediates will provide a greater understanding of the mechanism by which photocatalytic degradation occurs. This knowledge may be useful when considering the design of remediation systems.

A widely accepted view of the mechanism of photocatalytic degradation of organic compounds in aqueous solution is that the process is initiated by absorption of light by a semiconductor catalyst. This results in the excitation of an electron from the valence band to the conduction band, leaving a valence band hole. The hole abstracts an electron at the hydroxylated surface of the catalyst giving rise to a surface-bound hydroxyl radical. These radicals are believed to be the principal oxidising species, reacting with adsorbed organic material. The conduction band electron is scavenged by an electron acceptor which, in aerated solution, is thought to be oxygen.
Many workers propose hydroxylated compounds as products resulting from the initial oxidation step, further attack by hydroxyl radicals leading to small polar compounds. Some studies have suggested that adsorbed materials can be oxidised directly by the valence band hole, without the intermediacy of hydroxyl radicals, a process which appears to promote mineralisation without the formation of detectable intermediates. The degradation can, however, involve several routes and following it beyond the initial stages becomes increasingly more complex.

Among the many toxic materials that pollute natural waters are a variety of phenols. Of these, the chlorophenols have received particular attention as model substrates for photocatalytic degradation. A group that has attracted less attention is the alkyl phenols, the subject of a large part of the present study. They include cresols and xylenols which are found in many wood preservatives, and some phenolic antioxidants. Preliminary investigations in this work with p-cresol revealed that the experimental protocol chosen, although extremely inefficient in mineralising the substrate, permitted the observation of early intermediates in the degradation pathway and hence revealed details of some of the primary processes in the reaction mechanism. A number of the intermediates detected had not been identified by other workers, possibly because their experimental methods gave higher rates of loss of the substrate. Two previously unreported types of intermediate were discovered, substituted 2,5-cyclohexadienones from the addition of hydroxyl and dimers from the aggregation of phenoxy radicals. Comparison of the product profiles for wholly aqueous systems with those containing additional organic solvent revealed that, in the presence of 20% acetonitrile, ring coupling was more favoured and there was some addition of oxygen.

The results from p-cresol suggested that the initial pathways in photocatalysed oxidations might be determined to a large extent by the orientation of the substrate molecules on the catalyst surface. Some authors propose that phenols are adsorbed through the hydroxyl group. If so, the introduction of bulky substituents ortho to the hydroxyl group should significantly affect both the rate of loss of the substrate and intermediate profile resulting from steric hindrance of this mode of adsorption. In order to test this hypothesis the
photooxidation of 2,6-di-tert-butyl-4-methylphenol, the antioxidant BHT, was compared with that of p-cresol. It was discovered, however, that rather than reacting more slowly, BHT was lost at a higher rate under comparable conditions. The addition of the tert-butyl groups also appears to have influenced the reaction pathways, with aggregation of substrate molecules in the presence of oxygen being the predominant primary process in the reaction.

Tert-butyl substituents are relatively hydrophobic and to determine precisely what effect they had on the semiconductor photooxidation of phenols, three other tert-butyl substituted phenols were investigated. The outcome was that substrates with 2,6-substitution were lost at a faster rate than p-cresol, and 3,5- or 4-tert-butyl compounds more slowly. Ortho-substituted compounds also formed more detectable carbocyclic intermediates. With meta- and para-tert-butyl phenols, on the other hand, few detectable photooxidation products were observed. We propose that the more hydrophobic parts of the molecule are oriented towards the catalyst surface, thereby minimising the disturbance caused to polar networks in the solvent. Hydrophobicity may also lead to clustering of substrate molecules which, paradoxically, encourages molecular aggregation as a preliminary to degradation. For 2,6-disubstituted compounds, association of the hydroxyl group with the surface exposes to the outside of the monolayer the 4-position of the radical derived from oxidation. This species is able to react further to form the ring-retained intermediates identified. Conversely, adsorption of the molecule with the hydroxyl group held away from the surface, encouraged by meta- and para-tert-butyl substitution, appears to be a largely unreactive orientation. We suggest that the infrequently attained inverse orientation enables degradation to small, ring-opened compounds.

A similar pattern was discovered with 2,6- and 3,5-dimethylphenols, although the benzoquinone was the predominant intermediate rather than any aggregated material for the 2,6-isomer. The presence of some dimeric material was again in contrast with published work.
The influence of substituent pattern was also evident in an investigation with the herbicide bromoxynil (3,5-dibromo-4-hydroxybenzonitrile) and its isomer 3,5-dibromo-2-hydroxybenzonitrile. Here, the 2-hydroxy isomer was degraded more quickly than the 4-hydroxy, but no intermediates were detected for either of them when irradiated with TiO$_2$ in aqueous solution. In the absence of TiO$_2$, however, the principal primary photoproduct of 35DB2HBN was formed by hydrolysis, in which substitution of one of the bromines occurred to give 3-bromo-2,5-dihydroxybenzonitrile.

5.2 Conclusions

The use of low intensity light and relatively long pathlength reactors exposes substrates adsorbed on a photocatalyst to radiation for short periods before being carried into the unilluminated bulk of the photolysate. This results in a relatively low rate of loss of material, but allows primary products from the photooxidation to be identified.

Whilst phenol adsorption on the catalyst surface can be via the hydroxyl group, other substituents and their position on the ring can significantly influence the orientation of the molecule at the surface and thereby the mechanism of degradation. 2,6-Dialkylated phenols undergo associative reactions as the initial step of photocatalytic degradation particularly when the substituents are tert-butyl. Radicals are linked directly when the 4-position is unsubstituted or, via an oxygen link, to form substituted 2,5-cyclohexadienone dimers which may be directly detected or may decompose to give quinones and hydroquinones. The presence of acetonitrile in the solvent may also promote aggregation, by enhancing adsorption of the substrate, and the participation of oxygen in product formation, as was the case with p-cresol.

3,5-Dialkylated phenols are lost from the photolysate at a slower rate, but the intermediate stages in their degradation are not readily detected by the techniques employed in this study. Uninterrupted progress towards ring opened products seen with these compounds may be a consequence of the infrequently attained orientation that places the hydroxyl group next to the surface while the dominant, hydrophobically-favoured orientation leads
to comparatively slow reaction involving the sidechains. Alternatively, the latter orientation may promote pathways that in some way lead to ring opening.

This study has uncovered more aggregated intermediates than is generally reported in photocatalytic degradation studies with organic compounds, despite the fact that the concentration of majority of the substrate solutions were in the region of $10^{-4}$ mol dm$^{-3}$. This may be due to the hydrophobic nature of alkyl phenols, which orients the molecules with the alkyl groups close to the catalyst surface and encourages clustering.

It therefore appears that the hydrophobic profile of a substrate is a significant factor in determining the initial reaction pathway in its degradation.

This work has shown that all of the substrates considered can be degraded by TiO$_2$ photocatalysis. Although some further insights into the primary processes have been gained, the very nature of heterogeneous reactions implies much complexity, and almost certainly involves a number of different pathways for any given substrate. The present project has illustrated the potential value of contributions from organic chemistry in addressing this complexity and in obtaining a better understanding of the molecular basis of this environmentally promising technology.

5.3 Future Work

This study found that 2,6-dialkylated phenols were lost at a faster rate than their 3,5-isomers but produced a range of metastable products. None of the substrates were, however, irradiated through to complete mineralisation. Since the aim of photocatalytic degradation is the complete removal of organic compounds, determining whether one substitution pattern was more persistent in this respect would provide information which might be useful in practical applications, e.g. when two or more isomers were present in a waste stream. The most appropriate method for following the degradation, in this case, would be to monitor carbon dioxide emissions.

Further investigation of the hydrophobic effect of substituents could be carried out by degrading other alkyl phenols using the same experimental protocol as used in this study.
Comparisons could be made between the 2,6 and 3,5 isomers of each compound and between the different substituent sizes, either straight chain or branched, for the same substitution. Application of our methods of photolysis and product analysis to series of closely-related organic compounds may uncover further details of primary processes in TiO₂ photocatalysis.

Although modern HPLC techniques have greatly assisted the identification of many of the intermediates observed in this work, their usefulness is limited by prior knowledge suggesting possible intermediates and the recognition of previously encountered chromophores. Regular analysis of photolysate samples by LC-MS would provide valuable additional information regarding the identity of reaction intermediates, enabling a more complete picture of the mechanistic pathways to be resolved.

The inclusion of acetonitrile in the solvent produced significant effects with p-cresol. Although not of practical environmental value, studies of the effect of acetonitrile at different concentrations may prove to be useful in the investigation of surface processes.

In addition to such product identification studies, a full understanding of the many competing pathways requires a detailed study of the reaction kinetics of one or more of these substrates.

Following on from the work with the dibromohydroxybenzonitriles, comparative studies could be carried out on similar, but less substituted compounds, i.e. bromo and dibromo-phenols and 2- and 4-cyanophenols. The results from this work may give further insight into the way in which the substituents interact in the dibromohydroxybenzonitriles.
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Appendix I: p-cresol structures

1. p-cresol

2. 4-methylcatechol (4MCC)

3. 4-methylresorcinol (4MR)

4. 4-hydroxybenzaldehyde (4HBALD)

5. 4-hydroxybenzoic acid (4HBAC)

6. 4-hydroxybenzyl alcohol (4HBALC)

7. 4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (HMC)

8. 4-hydroperoxy-4-methyl-2,5-cyclohexadien-1-one (HPMC)

9. 2-(4'-hydroxyphenylmethyl)-4-methylphenol

10. 3,4-dihydroxy benzyl alcohol

11. Hydroquinone

12. 2,2'-dihydroxy-5,5'-dimethylbiphenyl (DDB)
Appendix II tert-butyl structures

13 2,6-di-tert-butyl-4-methylphenol  
   BHT

14 4-tert-butyl phenol  
   4tBP

15 2,6-di-tert-butyl phenol  
   26DtBP

16 3,5-di-tert-butyl phenol  
   35DtBP

17 2,6-di-tert-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one  
   MQOL

18 2,6-di-tert-butyl-4-hydroperoxy-4-methyl-2,5-cyclohexadien-1-one  
   MHPQ

19 2,6-di-tert-butyl hydroquinone  

20 4-tert-butyl catechol  
   4tBCat

21 2,6-di-tert-butyl benzoquinone  
   26DtBBQ

22 4,4'-dihydroxy-3,3',5,5'-tetra-tert-butylbiphenyl bis(26DtBP)

23 3,3',5,5'-tetra-tert-butyl-dipheno-4,4'-quinone  
   tBDPQ
Appendix III tert-butyl structure

24 3,5-di-tert-butyl-4-hydroxybenzyl alcohol  
BALC

25 3,5-di-tert-butyl-4-hydroxybenzaldehyde  
BALD

26 3,5-di-tert-butyl-4-hydroxybenzoic acid  
BAC

27 bis(4-oxy-4-methyl-2,6-di-tert-butylcyclohexadien-1-one)  
bis(MQOL)
Appendix IV dimethylphenol structures

28 2,6-dimethylphenol
26DMP

29 3,5-dimethylphenol
35DMP

30 3,4-dimethylphenol
34DMP

31 2,2'-dihydroxy-4,4',5,5'-tetramethylbiphenyl

32 1,2-bis(2,5-dihydroxy-3-methylphenyl)ethane

33 2,3-dimethylhydroquinone

34 4,4'-dihydroxy-3,3',5,5'-tetramethylbiphenyl bis(26DMP)

35 3,3',5,5'-tetra-tert-butyl-dipheno-4,4'-quinone
DMDPQ

36 2,6-dimethylbenzoquinone
26DMBQ

37 4-hydroxy-3,4-dimethyl-2,5-cyclohexadien-1-one
HDMC

38 4-hydroperoxy-3,4-dimethyl-2,5-cyclohexadien-1-one
HPDMC
Appendix V bromohydroxybenzonitrile structures

39 3,5-dibromo-4-hydroxybenzonitrile
*Bromoxynil*
35DB4HBN

40 3,5-dibromo-2-hydroxybenzonitrile
35DB2HBN

41 5-bromo-2,3-dihydroxybenzonitrile
5B23DHBN

42 3-bromo-2,5-dihydroxybenzonitrile
3B25DHBN

47 3-bromo-4-hydroxybenzonitrile

48 4-hydroxybenzonitrile

49 3-bromo-4,5-dihydroxybenzonitrile