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PRD 1217-M

THE EFFECT OF CHLORINE AND OZONE ON ORGANIC COMPOUNDS IN WATER - A LITERATURE REVIEW

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THE EFFECT OF CHLORINE AND OZONE ON ORGANIC COMPOUNDS IN WATER - A LITERATURE REVIEW

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June 1987

UNRESTRICTED

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PERMISSION: This work was funded by the Department of the Environment whose permission to publish has been obtained

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SUMMARY

The presence of chemical by-products of drinking water disinfection in water supplies is a topic of interest to government departments, water authorities and companies and environmental pressure groups. The prediction of products of the reaction of disinfectants with organic compounds, particularly those originating from pollution incidents, is of considerable interest. This report reviews the recent literature on the effects of two of the most common disinfectants, chlorine and ozone, on organic compounds under aqueous conditions.

From the studies reviewed it is evident that both chlorine and ozone can react with a wide range of organic compounds, the extent and rate of reaction and the nature of the products formed being dependent on a number of parameters, such as pH, concentration of disinfectant and organic substrate, contact time, inorganic content and the nature of the organic substrate. The majority of the studies published during the period reviewed deal with reactions of chlorine and ozone with either humic substances or aromatic compounds. Humic substances react with both ozone and chlorine to produce a series of carboxylic mono-, di-, tri- and poly-acids. In addition, chlorine gives a series of chlorinated carboxylic acids, chloroaldehydes, chloroketones, chloroalkanes and chlorinated heterocyclic compounds.

Aromatic hydrocarbons give rise to chlorinated and oxygenated products on reaction with chlorine, but with ozone they are oxidised to produce C_2 and C_4 diacids. There are fewer studies on the reactions of chlorine or ozone with compounds such as amines, amino acids, aromatic heterocyclic compounds, pesticides and surfactants.

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1. INTRODUCTION

Drinking water supplies in most of the developed world have been treated with disinfectants for almost a century. Pioneering studies by Snow (see Prescott and Horwood 1935) established a link between sewage contamination of water supplies and the incidence of cholera during an outbreak of the disease in London. The increase in the number of water treatment plants at the turn of the century led to a massive decrease in the number of deaths due to typhoid (Greenberg et al 1980, Cantor 1982) in the USA.

Chlorine is both cheap and efficacious as an antibacterial and, in some instances, antiviral agent (Greenberg et al 1980, Tenno et al 1980, Kott et al 1980). Consequently, there has been widespread utilisation of chlorine as a disinfectant of public water supplies. Chlorine is added to water at concentrations between 1 and 10 mg l^{-1} for disinfection. It can also be added to water to remove tastes and odours and as an aid to clarification during the coagulation treatment process. Prior to the finished water being pumped into the distribution system, the concentration of chlorine is reduced to between 0.1 and 0.5 mg l^{-1}. Maintenance of this chlorine 'residual' permits the quality of the water supply to be monitored; the loss of the chlorine residual is usually an indicator of some problem with the finished water.

Ozone was first reported as a germicide after the experiments of de Meritems in France in 1886 in which it was shown that air containing only small amounts of ozone could sterilise polluted water. Studies by Frohlich in Germany in 1891 further demonstrated the bactericidal properties of ozone. Two years later the first drinking water treatment plant to employ ozone was erected at Oudshoorn in

Holland to treat water from the River Rhine. There are now many potable water treatment plants in Europe, USA and Canada using ozone as the sole disinfectant.

The development of sensitive analytical methods for separating and identifying minute quantities of organic substances extracted from water has permitted the accurate determination of many chemicals present in water at or below the nanogram per litre level. The identification of organic chemicals in water has stimulated concern regarding their potential long-term effects on public health and this concern has been heightened by several factors. Firstly, there has been an increased amount of re-use of surface water used for drinking water abstraction. Secondly, the presence of hundreds of organic compounds, albeit at low levels, in surface waters and derived drinking waters has been confirmed. Finally, Rook (1974) and Bellar et al (1974) found that chlorination of water containing organics can result in the formation of trihalomethanes and other chlorinated species. Individual organic constituents of water are usually present at or below the microgram per litre level (Fielding et al 1981) and it is unlikely that organic compounds present at such low levels would induce acute toxic effects in consumers. However, water is consumed on a daily basis for many tens of years and this chronic exposure to some organics present in drinking waters may have long-term health effects.

A study by Tardiff et al (1978) reported that organic extracts of some American tap waters possessed mutagenic activity, which was attributed to the trace organic compounds present. Work by Wilcox and Denny (1985) has shown that some of the mutagenic activity is sensitive to dechlorinating agents, particularly sulphite and other S(IV)

species. Recent work by Horth et al (1986) and Kopfler et al (1985) has shown that chlorination of waters during drinking water treatment can result in the formation of mutagenic activity that is associated with non-volatile contaminants in water. Consequently much effort has been expended developing methods for the identification and quantification of non-volatile organic compounds in water (Crathorne et al 1979, 1984, Watts 1979, Watts et al 1981, 1982) including off-line high-performance liquid chromatography (HPLC) using coupled columns, field desorption mass spectrometry (FD-MS) and fast atom bombardment mass spectrometry (FAB-MS).

Since chlorination of water during drinking water treatment has been shown to produce potentially hazardous substances (Rook 1974, Bellar et al 1974, Tardiff et al 1978, Kopfler et al 1985) much effort has been expended over the last decade to determine the health effects of disinfection of water supplies. This has resulted in the publication of several reviews of the reactions of the two most commonly used disinfectants, chlorine and ozone, with organic compounds (for example Pierce 1978, Peters et al 1978). This report reviews the literature on chlorination over the period 1978 to 1985 and on ozonation over the period 1981 to 1985 and updates the previous reviews on chlorination (Peters et al 1978) and ozonation (Patience 1981) by-products published by WRc. However, since much of the basic chemistry of the reactions of ozone and chlorine with organic compounds in aqueous solution was published prior to 1981, the first section of the review presents a brief summary of this.

2. GENERAL REACTIONS OF CHLORINE AND OZONE WITH ORGANICS UNDER AQUEOUS CONDITIONS

2.1 Reaction pathways

Addition of chlorine to water results in almost instantaneous hydrolysis of the chlorine to equal amounts of hypochlorous and hydrochloric acids. The equilibrium and rate constants for this reaction are well documented (Pierce 1978 and Peters et al 1978).

Addition of chlorine to waters containing dissolved organic compounds can result in three possible reactions which are classified as:

(i) addition;
(ii) activated ionic substitution;
(iii) oxidation.

While all of the above reactions result in an increase of the oxidation state of the substrate, (iii) refers specifically to reactions resulting in unchlorinated products, eg

$RCHO \rightarrow RCO_2H$

Examples of these reactions with organic substrates are given in Figures 1 and 2; for more details the reader is referred to Pierce (1978) and Peters et al (1978).

Ozone may react with organic compounds in the following ways:

(i) dipolar cycloaddition;
(ii) electrophilic attack;
(iii) nucleophilic attack;
} (direct reactions)

(iv) radical reactions. (indirect reactions)

Examples of these are given in Figures 3-6 respectively. The direct reactions (i-iii) tend to be specific and occur at relatively slow reaction

rates. Radical reactions occur as a result of the decomposition of ozone in water, predominantly to produce hydroxyl radicals. Reactions of hydroxyl and other radicals occur at relatively fast rates and are less specific than the direct reactions.

2.2 Factors that influence the nature and amount of disinfection by-products

The nature and amount of organic by-products that result from disinfection by chlorine or ozone are influenced by a variety of factors which are summarised as follows.

2.2.1 The chemical nature of the substrate

This is of major importance. Detailed information on the manner in which different chemical compounds react is provided in Section 3.

2.2.2 Ratio of disinfectant to substrate

At low disinfectant-to-substrate ratios, reactions will be incomplete and by-products (and reaction intermediates) may react with the substrate, for example in the formation of dimers. If the disinfectant is in excess then, depending on the nature of the substrate, complete consumption of the substrate may occur. With a great excess of disinfectant some organic substrates can be completely oxidised to carbon dioxide. However, the conditions for such reactions are unlikely to be achieved in normal water treatment practice.

Natural surface waters contain organic material in the concentration range 0.5-30 mg l^{-1}. Between 50 and 90% of the dissolved organic material occurring in surface waters may be in the form of humic substances (Section 3.1). The remainder is usually in the form of a wide range of organic compounds (Fielding et al 1981, Crathorne et al 1984) usually present at concentrations of 1 µg l^{-1} or less. In exceptional circumstances, for example during a pollution incident, individual organic compounds

may be present at relatively high (mg l^{-1}) concentrations.

Under typical water treatment conditions, the ratio of disinfectant (either chlorine or ozone) to total organic substrate lies in the range 1-10 (wt/wt basis). Since individual organic compounds are usually present at very low concentrations - except in pollution incidents - the ratio of disinfectant to substrate for individual compounds is, in theory, very high (>>10). However, the disinfectants can react extensively with organic and inorganic matter (Sections 2.2.3 and 2.2.4). Thus, in practice, such reactions are competitive and for any particular reaction only a fraction of the amount of disinfectant added will be available. Therefore, in the case of reactions of individual substances an accurate estimation of the effective disinfectant to substrate ratio is difficult to make.

2.2.3
Reactions with inorganic species

Ozone and chlorine can react with many of the inorganic species that commonly occur in raw waters. Such reactions may affect the amounts and types of organic by-products formed from organic substrates (a) by competition for the oxidant (ie less oxidant available thus lower organic substrate-to-disinfectant ratios) or (b) reaction with inorganic species to form more reactive oxidants,

$$\text{eg } 2Br^- \xrightarrow{[O]} Br_2 \xrightleftharpoons{H_2O} HOBr + HBr$$

which can lead to entirely different by-products.

The presence of ammonia (and in some cases amines) in surface waters complicates the aqueous chemistry of chlorine. Hydrogen atoms on ammonia (and primary and secondary amines) are rapidly

substituted by chlorine to form chloramines. Although chloramines possess some disinfecting potential they are less powerful oxidants than the aqueous chlorine species (ie Cl_2 (aq), HOCl or OCl^-). In contrast, ammonia is resistant to reaction with ozone except under conditions of both high ozone to ammonia ratios and high pH.

Both chlorine and ozone can react with other inorganic species such as ferrous (Fe^{2+}) and manganous (Mn^{2+}) ions. These metal ions are oxidised to ferric (Fe^{3+}) and manganic (Mn^{4+}) species respectively. Ozone may also react with nitrite, sulphide and sulphite which produce nitrate and sulphate respectively. Bromide is rapidly oxidised to bromine by both disinfectants. Ozone can also oxidise both chloride and iodide to the respective halogens. Bicarbonate anions (HCO_3^-) can inhibit indirect (free radical) reactions of ozone with organic compounds, by acting as a radical scavenger.

2.2.4 Reactions with organic matter in general

Raw waters contain a wide variety of organic substrates, many of which will react with chlorine or ozone to produce organic by-products. If attempts are made to study the effect of disinfection by ozone or chlorine on a specific organic chemical in real situations then in a similar manner to that outlined above, the extent of reaction and the nature of the by-products may be influenced by numerous competitive reactions occurring in the water. At present it is not possible to predict whether or not these competitive reactions will influence the by-products that are formed in particular cases. It is therefore necessary to exercise great care in the design of laboratory experiments to simulate water disinfection and identify potential by-products.

2.2.5

pH

Potentially pH is a major factor in reactions of chlorine and ozone under aqueous conditions. The range of pH in water disinfection practice is not great (between 5 and 9) and only in specific cases will it exert significant effects on the extent, rate and by-products of reaction. Examples of such cases are discussed in Section 3.

3. PRODUCTS OF REACTION OF CHLORINE AND OZONE WITH SPECIFIC ORGANICS UNDER AQUEOUS CONDITIONS

3.1 Humic substances

Humic substances comprise a general class of biogenic, refractory, yellow to black, high molecular weight organic compounds that occur in virtually all terrestrial and aquatic environments (Aiken et al 1985). Aquatic humic substances usually represent >50% of the total organic carbon in natural water and can react with chlorine to produce a variety of oxidised and/or chlorinated products. Humic substances have been investigated extensively over the last few years because of the potential health risks arising from their chlorination by-products. However, humic substances are not well-characterised and consequently cannot be defined in unambiguous structural terms. Therefore, before discussing the reaction of humic substances with chlorine and ozone, it is useful to consider the definitions of the two most important types of humic substances:

Humic acid. The fraction of humic substances that is insoluble in water under acid conditions (<pH 2) but becomes soluble at greater pH (Aiken et al 1985).

Fulvic acid. The fraction of humic substances that is soluble in water under all pH conditions (Aiken et al 1985).

Since humic substances are heterogeneous chemical species of variable composition a study of the chemistry of the reactions of chlorine and ozone with humic substances will vary in the detail of the products formed depending on the source of the humics. Some of the investigations of the effect of chlorination and ozonation on humic substances, reviewed below, were conducted under conditions atypical of common water treatment practice in order to obtain sufficient amounts of reaction products for analysis.

3.1.1 Chlorination products

Rook (1974) and Bellar et al (1974) demonstrated that chlorination of river water resulted in the formation of trihalomethanes (THMs). These authors were of the opinion that the trihalomethanes were formed by the action of chlorine on the coloured matter in water, namely humic substances. It has since been discovered that halogenated compounds other than THMs are also formed upon chlorination of humic substances. These other halogenated compounds tend to be more difficult to isolate and identify because they are more polar than THMs and are usually present at lower concentrations. Several recent studies have shown that many types of compounds are formed during aqueous chlorination of humic material, the majority of these products being acids. Thus, aliphatic monobasic acids from acetic (C_2) to octacosanoic (C_{28}) and dibasic acids from ethanedioic (oxalic) (C_2) to decanedioic (C_{10}) (de Leer et al 1985, Johnson et al 1982) were identified. Several aromatic carboxylic acids were also observed (de Leer et al 1985, Johnson et al 1982) and were present in a range from benzoic to benzene pentacarboxylic acids. Furthermore, many chlorinated acids and poly-acids have been reported. Examples of these include mono-, di- and trichloroacetic acids (de Leer et al 1985, Johnson et al 1982, Christman et al 1983, Quimby et al

1980, Coleman et al 1984), chlorinated unsaturated acids such as chlorobutenoic and tetrachloropentenoic acids and chlorinated aromatic acids such as chlorobenzoic and 2,4-dichlorophenylacetic acids (de Leer et al 1985, Quimby et al 1980). Organic acids possessing other functional groups have also been reported, for example hydroxyl, oxo and cyano acids (de Leer et al 1985).

Products other than acids which have been identified include; monochloro- to pentachlorophenols (Quimby et al 1980, McCreary and Snoeyink 1981, Kringstad et al 1985); polychloroacetones and chloroaldehydes (Christman et al 1983, Coleman et al 1984, Kringstad et al 1983, 1985); haloacetonitriles such as dichloro- and dibromoacetonitrile (Coleman et al 1984, Oliver 1983); and chlorinated hydrocarbons (de Leer et al 1985, Johnson et al 1982, Christman et al 1983, Quimby et al 1980, Coleman et al 1984, McCreary et al 1981). Some chlorinated heterocyclic compounds have also been reported to form during the aqueous chlorination of humic acids, for example tetrachloro and tetrabromothiophene (Coleman et al 1984).

Although all of the studies discussed above described the isolation of compounds derived from the chlorination of humic material under aqueous conditions, few gave information on the mechanisms of formation of products. Without doubt this is due to the complex nature of both humic and fulvic acids. However, there are indications from several studies that the unchlorinated products produced during chlorination of humic substances are similar to those obtained by alkaline permanganate oxidation (Liao et al 1982). Indeed, it has been found that oxidation of humic acid resulted in the production of a range of acids and phenols. Subsequent chlorination of some of the individual

products led to the formation of many of the compounds found after aqueous chlorination of natural humic material (Sato et al 1985) such as the phenols formed by decarboxylation of aromatic acids similar to those found by Larson and Rockwell (1979). Similar results were reported by de Leer (1985) after the chlorination of 3,5-dihydroxybenzoic acid (Figure 10), a common product of oxidation of humic acid. This suggests that compounds formed initially by oxidation during aqueous chlorination of humic materials then undergo further reaction with chlorine and produce chlorinated products.

In summary, the chlorination of humic substances results in the formation of a range of chlorinated and unchlorinated organic acids, chlorinated phenols, chloroalkanes, chloroalkenes and chlorinated nitrogen-containing compounds. In the presence of bromide, brominated products may be formed.

3.1.2 Ozonation products

Ozonation of fulvic acids has been studied by various authors. Lawrence et al (1980) looked at solutions of fulvic acids ozonated under the conditions of a water treatment plant, with the oxidation products being identified by GC-MS. The predominant oxidation products were alkylphthalates, mono and di-carboxylic acids and a few cyclic-keto compounds. It was noted that after ozonation there was a marked increase in the number and relative concentration of the lower and intermediate molecular weight compounds. Fulvic acids were also studied by Rekhow and Singer (1984) who considered the THM formation potential of fulvic acid and its reaction products on ozonation. The effect of ozonation on the eventual THM concentration was studied and as expected, this varied depending on the compound involved although

ozone tended to reduce overall THM formation potential.

Fulvic acid was used in a study of the effects of bicarbonate and bromide on the ozonation of organic precursors (Legubé et al 1985, Doré et al 1987). This showed that bicarbonate (a radical scavenger) slowed down the reaction of ozone with fulvic acid and led to a greater degree of destruction of UV-absorbing substances and a reduction in the potential to form trihalomethanes and di- and tri-chloroacetic acids (Doré et al 1987).

A detailed study of the organic reaction products of ozonation of humic and fulvic acids with analysis by GC-MS and HPLC was reported by Watts (1985) and Watts et al (1982). Many volatile organic products were identified, eg short-chain diacids, hydroxy acids and aldehydes, but it was noted that the bulk of the organics were non-volatile and could not be identified with the techniques used.

3.2 Hydrocarbons

3.2.1 Chlorination products

Fielding et al (1987) reported that chlorine did not react with alkanes. However, these authors demonstrated that alkenes were readily consumed by chlorine and yielded chlorohydrins as the only detectable products.

The occurrence of polyaromatic hydrocarbons (PAH) in water has been the subject of several published surveys (Basu et al 1978, Benoit et al 1979, Crane et al 1981, Kveseth et al 1982, Shiraishi et al 1985, Coleman et al 1980, Suess 1976). Furthermore, the reactivity of many of these PAH under conditions typical of water treatment

chlorination has also been studied (Harrison et al 1976, Carlson and Caple et al 1978, Oyler et al 1982, Liukkonen et al 1983, Oyler et al 1978, Lin et al 1984, Oyler et al 1983, Rav-Acha and Blits 1985).

Carlson's group have been particularly prominent in the investigation of the effects of chlorination on PAH including naphthalene, methylnaphthalene, fluorene, anthracene, phenanthrene, fluoranthene and pyrene. As a result of their comprehensive studies many oxygenated, chlorinated, chloro-oxygenated and ring-ruptured derivatives of the parent PAH have been identified.

Incorporation of chlorine into the parent PAH ring structure is generally favoured at low pH (about 3). In contrast, chlorination at pH 8 favours production of oxygenated and ring-ruptured compounds (Oyler et al 1982, Liukkonen et al 1983). This effect has been confirmed in a kinetic study by Oyler et al (1983). The reaction scheme for aqueous chlorination of phenanthrene is outlined in Figure 14. In contrast, Fielding et al (1987) observed the formation of mono- and di-chloro pyrene after the chlorination of the hydrocarbon at pH 7.

Lin et al (1984) have also demonstrated that the consumption of aromatics (biphenyl and naphthalene) leading to halogenated products is enhanced in the presence of bromide ion. Bromide is rapidly oxidised by hypochlorous acid to form hypobromous acid which is more reactive (Morris 1978) than hypochlorous acid. Consequently, more of the substrate is consumed and brominated reaction products are formed. This effect was also observed by Rav-Acha and Blits (1985) who reported a faster rate of consumption of benz[a]anthracene in the presence of bromide.

In summary, aromatic compounds react with chlorine under a variety of conditions. The products which are formed during these reactions are dependent upon pH, mineral content of the aqueous solution, and ring substitution of the substrate.

3.2.2
Ozonation products

Fielding et al (1987) reported that ozone did not react with alkanes. However, these authors showed that alkenes were readily consumed by ozone to form aldehydes as the only observable products.

Patience (1981) in his review suggested that there were three modes of attack for ozone on PAH - 1,3-cyclo additions, electrophilic attack and finally conjugate addition reactions (when a reactive diene system was present). Various products of ozonation have been reported for a range of PAH compounds.

The reactions of ozone with acenaphthylene and acenaphthene in methanol and hexane (Figure 15) were studied by Chen et al (1979) with a view to predicting reaction products in water. They concluded that the two non-aqueous solvent systems used gave some indication of the reaction products that could be expected.

Butkovic et al (1983) studied the reaction rates and constants for pyrene (py), phenanthrene (phen) and benzo(a)pyrene (benzo) on reaction with aqueous ozone. Reaction rates with ozone were found to be in the ratio of 5:2:1 py:phen:benzo. Complete loss of the PAH was observed, but no identification of the end products was carried out.

Helleur et al (1979) examined the ozonation of fluorene and fluoren-9-one (Figure 16). Partially oxidised intermediates, namely hydroxylated polynuclear aromatics, were formed initially and

then oxidised to aromatic dicarboxylic acids. These in turn reacted slowly with ozone to yield oxalic acid and an unknown aliphatic dibasic acid. A free radical mechanism was proposed for the reaction pathway observed.

Fielding et al (1987) noted that aromatic hydrocarbons containing more than one aromatic ring exhibited reaction with aqueous ozone in contrast to the unreactivity of compounds possessing only one aromatic ring, such as toluene and xylenes. These authors were only able to identify a few products, and observed that the ozonation of naphthalene and fluorene gave rise to phthalic acid and fluoren-9-one respectively.

3.3 Aromatic compounds (excluding hydrocarbons)

The reactions between discrete aromatic compounds (as opposed to aromatic moieties incorporated in humic and fulvic acids) and chlorine have been the subject of many investigations (Peters et al 1978 and references therein). This interest resulted from the discovery that chlorination of aromatic compounds in water samples can cause water quality problems, for example the production of tastes and odours (Pierce 1978, Peters et al 1978). Several groups of workers have reported the occurrence of aromatic compounds (Fielding et al 1981, Basu et al 1978, Benoit et al 1978, Crane et al 1981, Kveseth et al 1982, Shiraishi et al 1985, Coleman et al 1980) in raw and drinking waters. In all of the studies described, the authors generally found the individual aromatics to occur at the ng l^{-1} level. The nature of the aromatics found varied from single ring structures such as benzene, toluene, phenols and phthalates to multi-ring compounds such as pyrene, fluoranthene, benzopyrenes and their oxidation products.

3.3.1

Chlorination products

The aqueous chlorination of aromatic compounds with respect to formation of THMs (Hasegawa et al 1983) and total organic chloride (Aizawa et al 1984) has been investigated. These studies demonstrated that aromatic compounds generally produced larger amounts of total organic chloride but less chloroform than aliphatic compounds. It was also shown that the amount of chloroform produced during chlorination of phenol was strongly affected by the type of substitution of the aromatic ring. Meta substituted phenols were shown to produce higher levels of chloroform than either ortho or para substituted phenols. This effect was not observed for either anilines or acetophenones, although chloroform was formed from these compounds.

Chlorination of aniline (Figure 7) has been shown (Jenkins et al 1978) to result in formation of ortho-chloroaniline and another compound, probably para-chloroaniline. Evidence exists that hydroxylation of the aromatic ring takes place during chlorination. Prolonged contact (about 24 h) between aniline and chlorine was shown to result in polymerisation of the amine (Figure 7).

The same authors described the reaction between chlorine and dimethylaniline. Gas chromatographic analysis of the reaction products showed that dimethylaniline yielded greater amounts of monochlorinated product than aniline. The authors suggested that this was probably due to the greater ring activation by the $-N(CH_3)_2$ group compared to the $-NH_2$ group. With dimethylaniline no polymerisation reactions occurred. It is interesting to note that in the cases of both aniline and dimethylaniline, all of the starting material consumed could not be accounted for as products. Finally, these authors examined the effect of aqueous chlorination on benzidine and

concluded that it did not undergo ring chlorination but instead polymerised rapidly.

Reviews by Pierce (1978), Peters et al (1978) and Morris (1975) describe in detail the reaction products that are formed during the chlorination of phenol under aqueous conditions. Recent work by Nazar et al (1981) has shown that catechol (Figure 8) and some substituted catechols form chloro derivatives under aqueous conditions. Additionally, these authors found that some of the chlorination products are mutagens, namely ortho-benzoquinone and chloro-ortho-benzoquinone. Ring-cleavage products including fumaric, maleic and muconic acids and their derivatives were also produced.

Onodera et al (1984) examined the products formed during the chlorination of phenol (Figure 9). In addition to the expected products (Pierce 1978, Peters et al 1978) viz chlorophenols, chlorobenzoquinones and chlorinated carboxylic acids these authors also tentatively identified chlorinated phenoxyphenols on the basis of GC retention time (packed column) and mass spectrometry. The chlorinated phenoxyphenols were found in higher yield at low pH.

The same authors (Onodera et al 1983, 1985) examined the effects of aqueous chlorination on phenylphenol isomers over a range of pH (4-10). The products identified (using GC-MS) from the ortho isomer included chlorophenylbenzoquinones and chlorophenylhydroquinones, phenyl substituted dibenzodioxins and chlorinated dimers of the starting materials. The meta isomer did not produce a dioxin but did undergo multiple incorporation of oxygen and chlorine and dimerisation. The para isomer underwent chlorination, hydroxylation, dimerisation and

oxidation as well as forming a substituted dibenzodioxin (Figure 10).

In a further study, Onodera et al (1982) investigated the effect of aqueous chlorination on naphthols. GC-MS analyses of the products of chlorination have shown that mono- and dichlorinated naphthol, chlorinated naphthoquinones, dimerisation products and ring cleavage products are formed (Figure 11).

In summary, phenolic compounds can form ring chlorinated and oxygenated derivatives and dimeric products as a result of aqueous chlorination.

In contrast to the studies described above, Smith et al (1977) demonstrated that the action of chlorine on aromatic compounds that did not possess an activating substituent, such as $-NH_2$, or -OH, resulted in the formation of only chlorinated products. This agreed with studies reviewed by Carlson and Caple (1978). In addition, Smith et al (1977) showed that the fate of the substrates under both homogeneous and heterogeneous reaction conditions was broadly similar.

3.3.2 Ozonation products

Previous work on the ozonation of aromatic compounds (reviewed by Patience 1981) dealt mainly with identification of reaction products. Recent studies have concentrated on the specific reaction mechanisms involved. The majority of these studies relate to phenolic compounds and these are reviewed together in a separate section.

As noted by Patience (1981) attack by ozone on phenols rapidly yields hydroxylated aromatic intermediates (ie hydroquinone, catechol and trihydroxybenzene) which undergo further oxidation with ring opening to give unsaturated aliphatic

diacids or aldehydoacids. These acidic intermediates can also react further with ozone but at a slower rate. However, it was reported in the review of Patience (1981) that there was some confusion as to the exact mechanism involved. Phenols have been studied by various authors (Legubé et al 1981a, 1981b, Doré et al 1980a, Brunet et al 1980) who concluded that phenol, like other aromatics, follows a similar reaction path to that described previously (Section 2.2) for electrophilic attack.

Rice et al (1980) and Sokratova et al (1982) reported the initial oxidation products of phenol to be hydroxylated derivatives which on further oxidation gave rise to quinones, cis-cis-muconic acid, oxalic and cis-butenedioic (maleic) acids. The oxidation proceeds via di- and tri-hydroxyaromatic compounds and quinones, with continued oxidation breaking the aromatic ring to form acids, such as oxalic acid which are much less reactive to ozone.

Chrostowski et al (1983) suggested that under alkaline conditions and low ozone dose, aqueous solutions of phenol (10-50 mg l^{-1} of substrate) may react along an oxidative coupling pathway (Figure 12) which yields polymerised products. The mechanism proposed by these workers includes the formation of a phenol free radical. Further work on coupling/polymerisation reactions of phenolic compounds has been conducted by Duguet et al (1985). They compared the effect of ozone with that of hydroxyl radicals produced by enzymatic decomposition of hydrogen peroxide on the polymerisation of 2,4-dichlorophenol (2,4-DCP). They observed that at both 1 and 100 mg l^{-1} concentrations of 2,4-DCP and an ozone to carbon ratio of 1:1 (wt/wt) the consumption of substrate was greater than 95%. It was shown that this

reduction in concentration was achieved by an oxidative coupling resulting in the formation of insoluble compounds with apparent molecular weights (measured by gel permeation chromatography) for the most part less than 5000 daltons. It was noted also that ozone produced higher molecular weight polymers that were more polar than those produced by HRP-H_2O_2 induced polymerisation. The degree of elimination of chlorine from the organic compounds was much greater with ozonation than with the enzyme reaction. Mass spectrometry showed the presence of condensation products up to and including hexamers and chlorinated polyaromatic compounds.

4-Phenylazo-1-naphthol was treated with ozone in a study by Matsui et al (1981) on the decolorisation reaction of hydroxyazo dyes. The reaction products identified were phenol, 1,4-naphthoquinone and nitrogen. A mechanism (Figure 13) was suggested in which ozone reacts initially with the azo group and further reaction proceeds via the 'ene' mechanism (1,3-cyclo addition, Figure 3).

Various authors have described the reaction mechanism for aromatic compounds in terms of a two step process, firstly loss of aromaticity which has a fast reaction rate and secondly a much slower ozonation of the organics so produced. Brunet et al (1980) noted that the second stage of ozonation of aromatics into more polar compounds was confirmed by the formation of haloform precursors. Their work consisted mainly of the reactions of phenol, polyhydroxybenzenes, amines and phenoxyacetic acid derivatives. During the ozonation of these aromatic compounds, small quantities of products resulting from ring opening (ie loss of aromaticity) were found. By comparing the reaction of ozone with a geometric isomer of one of these ring-opened products, trans,trans

muconic acid, to the reaction with the aromatic compounds, Gilbert (1980a) showed that the range of end products, namely oxalic and mesoxalic acids and carbon dioxide, and reaction intermediates, fumaraldehyde, glyoxal, glyoxylic and formic acids was similar to those obtained from the aromatic compounds. The differences in the products obtained can be explained as arising from the use of trans,trans muconic acid instead of the geometrical isomer formed on the ozonation of aromatics, namely cis,cis muconic acid. On the basis of the formation of similar products the authors concluded that (as with phenols) ring opening is part of the action of ozone on aromatic compounds. It was also noted that the specific products for aromatic compounds were dependent on the ozone dose used. Low doses of ozone and high substrate concentrations produced high concentrations of intermediates containing 4 and 6 carbon atoms. High doses of ozone produced lower amounts of 4 and 6 carbon intermediates and rapid production of products with one to three carbon atoms.

Legubé et al (1981b) observed that during ozonolysis the absorption maxima in the UV spectra corresponding to a $\pi \rightarrow \pi^*$ transition of the aromatic ring disappeared. Various intermediates were identified. The first step of the reaction was proposed to involve either electrophilic attack or 1,3-dipolar-cycloaddition. Additionally Legubé et al (1981a) showed that the mechanisms and resulting kinetics were more complicated than a simple two-step approach, furthermore the substituents exerted a major influence in directing the site of attack by ozone. Thus phenol and aniline, which both have electron-donating substituents, underwent electrophilic attack at the ortho and para positions. However, no identifiable aromatic intermediates were observed on reaction of

ozone with phenoxyacetic acids and therefore ring opening was assumed to be the principal reaction. Substituent effects were also briefly discussed by Doré and Legubé (1983) in a study of monocyclic and polar aromatic species and the end products were quoted as short-chain compounds such as aldehydes, acids and diacids.

Both Legubé *et al* (1983) and Decoret *et al* (1984) have suggested a general mechanism of aromatic ozonation in terms of three stages with the rate of reaction decreasing for each stage, *viz*:

1) consumption of the starting material with formation of polyhydroxyaromatic compounds and loss of aromaticity *via* electrophilic attack;

2) ozonation of intermediate unsaturated aliphatic compounds;

3) ozonation of intermediate saturated oxygenated products.

The effect of substituents on reactivity with ozone was studied by Legubé *et al* (1983). High reactivity was conferred by *ortho* and *para* directing (electron-donating) functional groups such as hydroxyl and amino during electrophilic attack. Both naphthalene and styrene reacted with ozone *via* the 1,3-dipolar-cycloaddition mechanism. Low reactivity was exhibited by compounds with *meta*-directing (electron-withdrawing) substituents, which resulted in electrophilic substitution. The reactions were noted to be pH dependent and this aspect was considered by Decoret (1984) who suggested that an acidic solution is more likely to promote a direct attack by ozone rather than a free radical attack.

1,2-Benzenedioic (phthalic) acid was studied by El Dine et al (1984). They analysed its ozonation products using HPLC and mass spectrometry and found that ozonation led to the formation of monohydroxyphthalic acids. The reaction then proceeded via decarboxylation to give ortho-hydroxybenzoic (salicylic) acid. Subsequent ozonation of salicylic acid resulted in the formation of dihydroxybenzoic acid. Muconic acid and a series of polar short-chain oxidation products were obtained as the final products of ring cleavage.

Gilbert and Zinecker (1980b) studied the ozonation of substituted aromatic amines. Total consumption of the amines occurred after approximately 4-6 m.mole ozone/m.mole amine had been applied. Coloured intermediates were produced which disappeared on further reaction with ozone. Generally, loss of chloro, nitro and sulphonic acid substituents occurred and 20-40% of the amino group nitrogen was converted to ammonia. Patience (1981) indicated that the intermediates found on ozonation of aromatic amines contained an imine functional group and this was also found by Legubé et al (1981a).

In a later study by Gilbert (1983) aniline was again observed to form red intermediates during ozonation but no identification of these was made. The end products were oxalic acid, 2,3-dioxopropanoic acid (mesoxalic semi-aldehyde), 2-oxopropanedioic acid (mesoxalic acid), glyoxal and an unknown nitrogen-bearing compound. Caprio et al (1984) looked at ozonation of nitrobenzene in aqueous solution. They found that complete loss of nitrobenzene occurred in a short period of time (20 mins), with no appreciable accumulation of unsaturated intermediates. Other intermediates were oxidised at a slower rate than nitrobenzene to give oxalic acid and carbon dioxide.

3.4 Nitrogen and/or sulphur containing compounds

3.4.1 Chlorination products

3.4.1.1 Heterocyclic compounds

Over the past seven or eight years several authors have reported the occurrence of heterocyclic compounds in raw, drinking and waste waters (Watts et al 1982, Crathorne et al 1984, Stuermer et al 1982, Ellis et al 1982). Additionally, several studies of the reactions between chlorine and heterocyclic compounds have been reported (Gould and Hay 1982, Gould and Richards 1984, Gould et al 1984a, 1984b, Dennis et al 1979, Lin and Carlson 1984, Watts et al 1982). The majority of these studies have examined the reactions between purines, pyrimidines, their derivative nucleotides and nucleosides, and chlorine (Gould and Hay 1982, Gould and Richards 1984, Gould et al 1984a, 1984b, Dennis et al 1979).

Gould and co-workers (1982, 1984) have shown that caffeine reacts slowly with chlorine to yield 8-chlorocaffeine, ring-ruptured derivatives and rearrangement products (Figure 17). Also, this group of investigators examined the products of uracil chlorination. They found that 5-chlorouracil was produced at low chlorine to uracil ratios (approximately 1:1). However, when proportionally more chlorine was present dichlorouracil could be detected, along with evidence of ring-ruptured products (1982, 1984a). The detection of 5-chlorouracil after treatment of uracil with a similar quantity of chlorine was also reported by Watts et al (1982). Although these authors did not determine the ultimate fate of uracil, they established that the compound was not

converted to chloroform. Poncin and Martin (1986) also found that chlorination of uracil yielded 5-chlorouracil as an intermediate with eventual oxidation to CO_2 depending on the amount of chlorine applied. Finally, Gould and co-workers (1982, 1984) identified the products of chlorination of cytosine and methylcytosine (Gould et al 1984b). They found that chlorohydrins were formed along with several organic chloramines containing up to three chlorine atoms. In the case of 5-methylcytosine, a major product, consistent with pyrimidine ring cleavage, was detected but not identified.

Lin and Carlson (1984) have reported results obtained from the chlorination of sixteen aromatic heterocyclic compounds. One of the compounds studied, benzothiazole, was of particular interest since it has been identified in some ground waters. Chlorination of benzothiazole resulted in oxygen incorporation to yield benzothiazol-2-ol. Additionally, these authors observed that other sulphur-containing heterocyclic compounds viz benzo[b]thiophene and dibenzothiophene yielded only oxygenated products after chlorination.

In summary, it has been observed that nitrogen-containing heterocyclic compounds yielded both chlorinated and oxygenated products on chlorination whereas sulphur-containing heterocyclic compounds yielded only oxygenated products.

3.4.1.2
Amino acids

Amino acids have been found in many natural waters at concentrations between 2 and 400 µg l^{-1} (Le Cloirec and Martin 1985). They are thought to originate mainly from the decomposition of peptides and proteinaceous material present in natural waters (Le Cloirec and Martin 1985, Mallevialle

et al 1984). Consequently there has been much interest in the effect of chlorination on these compounds. Glaze et al (1982) reported the effect of super-chlorination under aqueous conditions (albeit atypical of drinking water treatment practice) on a series of amino acids including alanine, valine, leucine, phenylalanine, tyrosine and tryptophan. Le Cloirec and Martin (1985) discussed the chlorination of alanine under conditions typical of water treatment. Both groups reported that aldehydes and nitriles were the principal products of chlorination and were produced in high yield. The likely mechanism for their formation is outlined in Figure 18. In addition, Glaze et al observed ring-chlorinated derivatives of the aldehydes and nitriles derived from tyrosine as well as ring-chlorinated tyrosine. He also found that tryptophan yielded chlorinated and/or oxygenated products on treatment with chlorine.

Earlier (Section 3.1) it was stated that dichloroacetonitriles are found as products of the chlorination of humic substances. Bieber and Trehy (1983) have shown that these substances can also arise from the chlorination of proteinaceous material including free amino acids. These authors suggested a mechanism for the conversion of polypeptide chains to cyanoacetic acid and halogenated cyanoacetic acid and finally by decarboxylation to haloacetonitrile (Figure 19).

Fielding and Horth (1986) reported additional chlorination productions of amino acids formed under conditions similar to those used during water treatment. These included chloroform, 1,1,1-trichloroethane and dichloroacetonitrile from the methionine; chloroform, indolylacetonitrile, indol-3-carboxaldehyde and 2-benzoxazalinone from

tryptophan; and 2-phenyl-2-chloroethanol and 2-phenyl-2,2-dichloroethanol from phenylalanine.

In conclusion, it can be stated that several amino acids react readily with chlorine in water to produce oxidised and chlorinated products.

3.4.1.3
Mercaptans

Ethanethiol (ethyl mercaptan) was shown to react with chlorine to form the corresponding disulphide. This compound was in turn consumed by chlorine to form unspecified products (Faujour et al 1980).

3.4.2
Ozonation products

3.4.2.1
Aliphatic amines

Faujour et al (1980) conducted a study of the action of chlorine and ozone on amines, in particular tri- and dimethylamine and ethylamine. Among the reaction products identified were dimethylhydroxylamine and trimethylamineoxide produced by ozonation of dimethylamine and trimethylamine respectively.

Elmghari-Tabib et al (1982) have suggested a reaction pathway for aliphatic amines (Figure 20). The reaction products were hydroxylamines, oximes and amides with condensation products of the amine or intermediate amides also being produced at high substrate concentrations. A general reaction scheme was presented in which the initial oxidation phase involved an electrophilic attack by ozone on the hetero-atom followed by either oxidation of the carbon chain adjacent to the nitrogen atom, producing amides, or by the general destruction of the molecule producing inorganic nitrogen compounds, carboxylic acids and aldehydes. Secondary condensation reactions may then take place at high substrate concentrations.

3.4.2.2
Amino acids

Work on the amino acid glycine has been reported by Duguet et al (1980). Glycine was oxidised to a noticeable extent over a period of 20 minutes demonstrating first-order kinetics with respect to glycine concentration at a pH >7. The rate of reaction increased with increasing pH. Since ozone decomposition also increased with increasing pH the authors concluded that in a basic solution a free radical pathway existed and noted that in acidic or neutral media only partial degradation of the amino acids was observed.

Glycine and leucine were studied by Yamada and Somiya (1980) who identified formaldehyde as a common product, which under alkaline conditions (>pH 9) or high ozone concentration (>40 mg l^{-1}) was found to be oxidised further to carbon dioxide and water. Formation of oxo-acids was observed, either pyruvic or glyoxylic acid depending on the particular amino acid involved.

Laboratory studies of the ozonation of ethylenediaminetetraacetic acid and hydroxyethylenediaminetriacetic acid in alkaline waste solutions showed that there was some removal of these compounds. The authors (Lutton et al 1979) proposed that the reaction involved hydroxyl free radicals. Oxalate ion was tentatively identified as a reaction intermediate. These authors observed that nitrates could act as radical scavengers in a similar manner to bicarbonate.

3.4.2.3
Mercaptans

Mercaptans (alkylthiols) rapidly oxidise to form disulphides on treatment with ozone. Further reaction of the disulphides with ozone results in the production of acidic compounds, probably alkyl sulphonic acids (Faujour et al 1980).

3.5 Oxygen-containing compounds

3.5.1 Chlorination products

3.5.1.1 Carboxylic acids and alcohols

Fatty acids which are commonly present in surface waters (Fielding et al 1981, Lin et al 1981) have been discussed in terms of their reactivity towards chlorine (Carlson and Caple 1978) and degree of incorporation of radio-labelled chlorine (^{36}Cl) into unsaturated fatty acids (Ghanbari et al 1983, 1982). Carlson and Caple (1978) reported the formation of isomeric chlorohydrins on chlorination of oleic acid over a range of pH (2-10). Ghanbari et al concluded that the degree of ^{36}Cl incorporation was directly proportional to the number of double bonds in the molecule and identified a single chlorohydrin derivative (9-chloro-10-hydroxy) of oleic acid using chemical ionisation (isobutane) GC-MS.

Haley et al (1986) and Fielding et al (1987) showed that saturated fatty acids were not consumed by chlorine under typical water treatment conditions. In contrast unsaturated fatty acids were readily consumed. Analysis by GC-MS and FAB-MS showed that the products of these reactions were chlorohydrins, and also confirmed the findings of Ghanbari et al 1983, 1982) that the degree of incorporation of chlorine was proportional to the number of double bonds in the substrate molecule.

Oliver and Carey (1977) examined the effects of chlorination on a range of oxygenated compounds namely ethanol, butanol and benzoic acid in the presence and absence of light. These authors reported that chlorinated and/or oxygenated

derivatives of the starting materials were formed in the presence of light although little or no reaction was observed when these compounds were chlorinated in the dark.

3.5.2 Ozonation products

3.5.2.1 Carboxylic acids and alcohols

Patience (1981) concluded that the reaction of primary alcohols with ozone proceeded via oxidation to aldehydes and then to carboxylic acids. Also, as expected, secondary alcohols were oxidised to ketones and eventually, with cleavage, to carboxylic acids.

Fielding et al (1987) showed that saturated fatty acids did not react with ozone. In contrast, unsaturated acids were readily consumed to form aldehydes and aldehydoacids. Using GC-MS and FAB-MS, these authors showed that the aldehydes and aldehydoacids reacted further with ozone in aqueous solution to form saturated fatty acids and diacids.

The action of ozone on ethanol and 2-propanol was reviewed by Laplanche and Martin (1984). It was noted that when ethanol was present in dilute solutions, acetaldehyde and acetic acid were the only products identified. If, however, a more concentrated solution of ethanol was used other products were found, including peroxide species and condensation products such as polyethylene glycol, ethyl acetate and diethyl acetal. Similarly, after reaction with ozone, propan-2-ol produced acetone, acetic acid, methyl ethyl acetate and in concentrated solution, peroxides. The same alcohols were also studied by Elmghari-Tabib et al (1982) and Chang and Chian (1981) who found similar reaction products. It was observed that the initial oxidation is based on the hetero-atom

undergoing electrophilic attack by ozone. Baker and Taylor (1985) studied the effect of UV light on ozonation of propan-2-ol. Oxidation using just ozone gave only acetone with very little further reaction. However, with UV irradiation the reaction proceeded via a series of sequential reactions: propan-2-ol → acetone → monocarboxylic acids [acetic, 2-oxopropanoic (pyruvic), formic] → oxalic acid → carbon dioxide and water. The authors concluded that the reaction proceeds via the usual free radical mechanism which involves the hydroxyl radical.

3.5.2.2
Aldehydes and ketones

The reactions of aldehydes and ketones with ozone have not been studied since the review by Patience (1981) who concluded that the major difference between the ozonation of aldehydes and ketones was that oxidation of the latter commonly involved C-C bond cleavage whereas the former was a straightforward oxidation of the carbonyl group to the corresponding acid.

3.6 Surfactants

3.6.1 Chlorination products

Several studies have reported the occurrence of surfactants in a range of water samples (Crathorne et al 1984, Levsen et al 1984, Rivera et al 1986). However, few studies have addressed the effect of water treatment chlorination on these compounds. Reinhard and co-workers (1982) extracted waste waters after chlorination and identified a number of alkylphenol ethoxylates and bromoalkylphenol ethoxylates in the extracts. These authors confirmed the identification of the aromatic ring brominated non-ionic surfactants by synthesis of the compounds. Sodium dodecylbenzenesulphonate (Itoh et al 1985) has been shown to react with

chlorine to produce low yields of chloroform. In addition, this study demonstrated that the primary biodegradation products of dodecylbenzenesulphonate produced low yields of chloroform after chlorination.

Rivera et al (1986) used FAB-MS to demonstrate the presence of chloro- and bromo- derivatives of nonyl phenol ethoxylates in extracts of drinking water samples, but not raw water. This suggested that the chlorine and bromine were incorporated into the benzene ring of nonylphenol ethoxylates present in the raw water during chlorination disinfection. Stephanou (1985) showed that ring-halogenated alkylphenol ethoxylates and their biodegradation products were present in secondary sewage effluent which had been chlorinated.

3.6.2 Ozonation products

Rice et al (1980) reviewed the ozonation of surfactants under three classes: linear alkyl sulphonates, linear alkyl benzene sulphonates and aliphatic quaternary amino compounds. The aromatic compounds were reported to be more readily consumed by ozonation than the aliphatic compounds but it was found that the sulphonic group reduced the reactivity of the aromatic ring system towards ozone. Joy et al (1980) used para-toluenesulphonic acid as a model for anionic surfactants. Reaction of ozone with para-toluenesulphonic acid at pH 3 and 12 gave acetic, formic, pyruvic, oxalic and sulphuric acids and hydrogen peroxide as products, the ratio of these products was dependent on pH. In addition lactic acid was produced at pH 12 and a mechanism based on these products was discussed.

3.7
Pesticides

3.7.1
Chlorination products

The effects of chlorine on a range of pesticides have been reviewed by Shevchenko and Taran (1984). Both phosphamide, 0,0-dimethyl-S-[2-methylamino-2-oxoethyl]phosphorodithioate and carbophos, S-1,2-bis(ethoxy-carbonyl)ethyl-0,0-dimethylphosphorodithioate are reported to react with chlorine initially converting the P=S bond into the P=0 analogue. For phosphamide, this reaction is reported to go to completion at chlorine to substrate ratios of 8:1. At higher chlorine ratios (ca 23:1) the P=0 analogue of phosphamide reacts further resulting in cleavage of the remaining phosphorus-sulphur bond.

The effects of chlorine on a range of aryldimethylurea herbicides, for example phenuron, diuron and cotoran (fluometuron), have been reviewed. The initial products of chlorination were reported to be N-chloro derivatives which reacted further to form unspecified products.

3.7.2
Ozonation products

Rice et al (1980) reviewed the ozonation of pesticides and concluded that pesticide reactivity to ozone differs widely. Phosalone and aldrin were both readily oxidised using a small ozone dose while dieldrin, chlordane, lindane, DDT, PCB, PCP and endosulfan showed only slight reactivity under normal ozonation conditions. Legubé et al (1981a, 1981b) and Doré et al (1980b) looked at 2,4-D,MCPA, 2,4,5-T and used phenoxyacetic acid as a reference substance. These pesticides reacted with ozone in a similar way to other aromatic compounds, that is, opening of the ring system was followed by formation of stable reaction intermediates which were highly oxygenated. Degradation was seen even

at low ozone dosage, especially for MCPA. The use of the iodoform test demonstrated the immediate appearance of a compound containing an acetyl group. Reaction products were identified as aliphatic oxygenated compounds such as acids, aldehydes and ketones (Figure 21).

Organophosphorus pesticides were studied by Laplanche et al (1984). Experiments were carried out in organic and aqueous solvents (albeit under conditions atypical of water treatment processes) with representative molecules of various organophosphorus families. The reaction products were identified and three main reaction schemes proposed. However, there are several inconsistencies in the proposed reaction schemes resulting from typographical errors which restrict their usefulness.

4. DISCUSSION AND CONCLUSIONS

The experimental conditions used in the study of products of chlorination and ozonation of organics exert a major influence on the reactions occurring and a summary of experimental conditions used in the studies reviewed herein is therefore presented in Tables 1 (chlorination) and 2 (ozonation). It is clear from these tables that the majority of the studies were carried out using atypically high concentrations (several mg l^{-1}) of individual organic substrates and disinfectants but realistic ratios (1-10 wt/wt) of disinfectant to total organic substrates. In the studies that have used more realistic concentrations of individual substrates, the ratios of disinfectant to organic substrate are frequently very high (>>10). In some part this reflects the problems of monitoring and maintaining the very low concentrations of disinfectant in water which would be required to produce realistic disinfectant to organic substrate

ratios at typical concentrations of individual organic substrates. Most studies were carried out with pH control (ie buffered solutions) see Tables 1 and 2. However, in some cases, especially with ozonation, no pH control was exercised and consequently the ambient pH was strongly influenced by the sample pH and the quantity of disinfectant and substrate added. Overall, the majority of studies reviewed in the text were not carried out under realistic conditions of potable water disinfection since they did not address the following:

(i) realistic concentrations of individual organic substrates,

(ii) modifying reactions of inorganics, eg

$$Br^- + HOCl \rightarrow HOBr + Cl^-$$

The following general observations can be made on the basis of the studies received:

Substituent groups influence both the rate of reaction of aromatic compounds with chlorine and ozone and the site of attack of these oxidants. Electron-donating substituents result in rapid reaction to form ortho- and para-substituted products whereas, electron withdrawing groups lead to slow reaction to form meta-substituted products. Chlorine and ozone react with aromatic compounds to produce hydroxylation, oxidation, condensation and ring cleavage products. With both oxidants, condensation products are favoured by the high substrate concentrations used in some studies, and consequently caution is needed when relating the results to drinking water treatment practice. In the case of chlorination of aromatics, hydroxylation and ring-cleavage reactions are favoured at high pH (>7) whereas chlorine substitution reactions are favoured at lower pH.

Inorganic anions influence the course and rate of reactions between organic compounds and both chlorine and ozone. Bicarbonate anions (HCO_3^-) slow down ozonation reactions by acting as free radical scavengers. In contrast bromide (Br^-) is rapidly converted to hypobromous acid (HOBr) by both ozone and chlorine. Hypobromous acid then reacts with organic substrates (at a faster rate than hypochlorous acid) to form brominated products.

The aromatic heterocyclic compounds studied react with chlorine to form chlorinated, oxygenated and ring-cleavage products. The nitrogen-containing heterocyclic compounds particularly react to form halogenated products. However, only oxygenated products have been observed after chlorination of the sulphur-containing heterocycles studied.

Amino acids react with both chlorine and ozone. Chlorination produces mainly aldehydes and nitriles whereas ozonation results in the formation of hydroxylamines, N-oxides, oximes, amides, acids and aldehydes.

Pesticides and surfactants containing aromatic rings behave like other similarly substituted aromatic compounds towards both chlorine and ozone. Pesticides containing phosphorus-sulphur bonds are susceptible to oxidation which results in formation of phosphorus-oxygen bonds on reaction with both chlorine and ozone. Some of the data reported for chlorination and ozonation of surfactants and pesticides have significant inconsistencies and need to be verified.

Much of the data reviewed relates to experiments carried out under conditions far removed from those typical of water treatment practice, ie high oxidant dose, high substrate concentration, prolonged contact time. For some compound types,

which frequently occur in source waters used for potable water abstraction, little or no information on disinfection by-products exists, eg surfactants, pesticides and esters.

The review indicates that there are areas where there is insufficient knowledge to allow prediction of the products formed during aqueous chlorination and ozonation of organic compounds in source waters. Further research is needed on the effect of chlorination and ozonation on many types of organics which commonly occur in source waters. The conditions used in such studies must be typical of current water treatment practice. The key parameters for study include disinfectant concentration, substrate concentration, contact time, pH and the presence of inorganic anions. Having identified the products formed during laboratory studies it is important to establish the relevance of these findings at drinking water treatment plants. If similar products are shown to be present in potable waters, then an evaluation of the toxicological properties of these compounds will be required.

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Table 1. Summary of conditions used for studies of chlorination products

Reference	Substrate	Substrate concn	Chlorine concn	pH	Contact time	Temp °C
HUMIC SUBSTANCES						
Christman et al (1983)	Fulvic acid	900 mg l^{-1}	* Cl_2:C = 4	7	24 h	Ambient
Quimby et al (1980)	Humic acid Fulvic acid	2000 mg l^{-1} "	10.7 mg l^{-1} "	6.6 "	30 min "	25 "
de Leer et al (1985)	Humic acid	1250 mg l^{-1}	* Cl_2:C = 0.39, 3.35	7.2	24 h	-
	Humic acid	240 mg l^{-1}	* Cl_2:C = 0.12-2.96	7.2	24 h	-
Kringstad et al (1985)	Humic acid	73.5 mg l^{-1}	* Cl_2:C = 4	7.0	2 h	Ambient
Kringstad et al (1983)	Humic acid	73.5 mg l^{-1}	* Cl_2:C = 0.1, 0.5, 1, 2, 4	7.0	2 h	Ambient
Johnson et al (1982)	Humic material	420 mg l^{-1}	* Cl_2:C = 1.5	12	8 h	-
Coleman et al (1984)	Humic acid	1000 mg l^{-1} (%C = 51.5)	* Cl_2:C = 1	2.5-11	90 h	-
McCreary and Snoeyink (1981)	Humic acid	2.5-9.4 mg l^{-1}	2.45-13.3 mg l^{-1}	5.7-7.6	1.9-2.35 min	-
Oliver (1983)	Fulvic acid	1 mg l^{-1}	10 mg l^{-1}	6-8	-	20
AROMATIC COMPOUNDS (excluding hydrocarbons)						
Aizawa et al (1984)	Various aromatics and aliphatics	7.2 mg l^{-1}	28 mg l^{-1} (0.4 x 10^{-3} M)	7	24 h	20
Hasegawa et al (1983)	Alcohols, sugars and aromatics	7.2 mg l^{-1}	28-84 mg l^{-1} (0.4-1.2 x 10^{-3} M)	7	24 h	20

Table 1 (continued)

Reference	Substrate	Substrate concn	Chlorine concn	pH	Contact time	Temp °C
Jenkins et al (1978)	Aniline	26.6 and 5.3 mg l^{-1} (0.28 and 0.06 x 10^{-3} M)	20 mg l^{-1} (0.28 x 10^{-3} M)	6.5-7.5	20 min	-
	Dimethylaniline	3.4-33.8 mg l^{-1} (0.028-0.28 x 10^{-3} M)	20 mg l^{-1} (0.28 x 10^{-3} M)	6.5-7.5	20 min	-
	Benzidine	51.5 mg l^{-1} (0.28 x 10^{-3} M)	20 mg l^{-1} (0.28 x 10^{-3} M)	6.5-7.5	20 min	-
Nazar et al (1981)	Catechol	0.44 and 0.88 g l^{-1} (4 and 8 x 10^{-3} M)	0-18 g l^{-1}	2	30 min	-
Onodera et al (1985)	Phenylphenols	0.1 g l^{-1} (0.6 x 10^{-3} M)	852 mg l^{-1} (12 x 10^{-3} M)	7	24 h	20
Onodera et al (1982)	α-and β-Naphthol	4 mg l^{-1} (0.027 x 10^{-3} M)	0-20 mg l^{-1} (0-0.28 x 10^{-3} M)	7 7 4-10	24 h 1 h 1 h	20 20 20
HYDROCARBONS						
Smith et al (1977)	Biphenyl	500 mg l^{-1} (3.2 x 10^{-3} M)	5 g l^{-1} (71 x 10^{-3} M)	2-7	16 h	Ambient
	Naphthalene	500 mg l^{-1} (3.9 x 10^{-3} M)	5 g l^{-1} (71 x 10^{-3} M)	3-6	16 h	Ambient
	Naphthalene	10 mg l^{-1} (78 x 10^{-6} M)	30 mg l^{-1} (0.42 x 10^{-3} M)	3-6	16 h	Ambient
Lin et al (1984)	Biphenyl	108-308 µg l^{-1} (7-20 x 10^{-7} M)	19 mg l^{-1} (2.7 x 10^{-4} M)	4.5-7.5	24 and 48 h	24

Table 1 (continued)

Reference	Substrate	Substrate concn	Chlorine concn	pH	Contact time	Temp °C
	Naphthalene	90–256 µg l^{-1} ($7–20 \times 10^{-7}$ M)	19 mg l^{-1} (2.7×10^{-4} M)	4.5–7.5	24 and 48 h	24
Harrison et al (1976)	Fluoranthene	0.22–0.86 µg l^{-1} ($1.1–4.2 \times 10^{-9}$ M)	0.44–13.2 mg l^{-1}	4.5–7.6	5–25 min	5–20
	Pyrene	0.16–0.57 µg l^{-1} ($0.79–2.8 \times 10^{-9}$ M)				
	Benzo[a]anthracene	0.13–0.52 µg l^{-1} ($0.57–2.3 \times 10^{-9}$ M)				
	Benzo[k]fluoranthene	0.06–0.22 µg l^{-1} ($0.2–0.87 \times 10^{-9}$ M)				
	Benzo[a]pyrene	0.06–0.22 µg l^{-1} ($0.19–0.83 \times 10^{-9}$ M)				
	Perylene	0.06–0.22 µg l^{-1} ($0.2–0.87 \times 10^{-9}$ M)				
	Indeno[1,2,3-cd] pyrene	0.03–0.13 µg l^{-1} ($0.12–0.47 \times 10^{-9}$ M)				
	Benzo[ghi]perylene	0.04–0.14 µg l^{-1} ($0.14–0.5 \times 10^{-9}$ M)				
Oyler et al (1982)	Methylnaphthalene	2.84 mg l^{-1} (2×10^{-5} M)	71 mg l^{-1} (1×10^{-3} M)	3 and 8	1–96 h	-
	Fluorene	0.229 mg l^{-1} (1.38×10^{-6} M)	29.5 mg l^{-1} ($0.4–0.42 \times 10^{-3}$ M)	3 and 7.7	6 h – 7 days	-
	Dibenzofuran	3.36 mg l^{-1} (2×10^{-5} M)	71 mg l^{-1} (1×10^{-3} M)	3 and 8	4 h – 7 days	-

Table 1 (continued)

Reference	Substrate	Substrate concn	Chlorine concn	pH	Contact time	Temp °C
	Anthracene	0.35 mg l^{-1} (1.99×10^{-6} M)	71 mg l^{-1} (1×10^{-3} M)	3 and 8	30 min	-
	Phenanthrene	0.117-0.147 mg l^{-1} ($6.6-8.25 \times 10^{-7}$ M)	31-54 mg l^{-1} ($0.45-0.77 \times 10^{-3}$ M)	3 and 8	20-90 min	-
	1-Methylphenanthrene	2.7 mg l^{-1} (1.39×10^{-5} M)	71 mg l^{-1} (1.0×10^{-3} M)	3 and 8	1-23 h	-
	Fluoranthrene	0.067-0.26 mg l^{-1} ($3.32-12.9 \times 10^{-7}$ M)	21-127 mg l^{-1} ($0.3-1.82 \times 10^{-3}$ M)	3 and 8	4-19 h	-
Oyler et al (1982)	Pyrene	1.3-1.4 mg l^{-1} ($6.6-7.1 \times 10^{-6}$ M)	77-84 mg l^{-1} ($1.1-1.2 \times 10^{-3}$ M)	3 and 8	30-90 min	-
Oyler et al (1978)	1-Methylnaphthalene	336-531 ng l^{-1} ($2.4-3.7 \times 10^{-9}$ M)	20-24 mg l^{-1} ($0.28-0.34 \times 10^{-3}$ M)	3.8-4.1	3 h	-
	Fluorene	333-819 ng l^{-1} ($2.0-4.9 \times 10^{-9}$ M)	1.2-21.3 mg l^{-1} ($0.017-0.3 \times 10^{-3}$ M)	3.35-7	0.5-3 h	-
	Anthracene	552-1042 ng l^{-1} ($3.1-5.9 \times 10^{-9}$ M)	0-12.9 mg l^{-1} ($0-0.18 \times 10^{-3}$ M)	6-7.1	0.08-4 h	-
	Phenanthrene	118-820 ng l^{-1} ($0.66-4.6 \times 10^{-9}$ M)	3.2-26 mg l^{-1} ($0.05-0.37 \times 10^{-3}$ M)	4-7.1	0.5-3 h	-
	1-Methylphenanthrene	178-994 ng l^{-1} ($0.93-5.2 \times 10^{-9}$ M)	3.1-25.6 mg l^{-1} ($0.04-0.37 \times 10^{-3}$ M)	4-6.9	0.5-3 h	-
	Fluoranthrene	239-824 ng l^{-1} ($1.2-4.1 \times 10^{-9}$ M)	3.4-23.9 mg l^{-1} ($0.05-0.34 \times 10^{-3}$ M)	4-6.8	0.5-3 h	-

Table 1 (continued)

Reference	Substrate	Substrate concn	Chlorine concn	pH	Contact time	Temp °C
Fielding *et al* (1987)	Toluene	10 µg l^{-1} (1.08×10^{-7} M)	1 and 10 µg l^{-1} (1.4×10^{-5} and 1.4×10^{-4} M)	7	4 h	20
	o, *m* & *p* Xylene	10 µg l^{-1} (9.4×10^{-8} M)				
	Naphthalene	10 µg l^{-1} (7.8×10^{-8} M)				
	Fluorene	10 µg l^{-1} (6.0×10^{-8} M)				
	Phenanthrene	10 µg l^{-1} (5.6×10^{-8} M)				
	Fluoranthrene	10 µg l^{-1} (5×10^{-8} M)				
	Pyrene	10 µg and 100 µg l^{-1} (5×10^{-8} and 5×10^{-7} M)				
NITROGEN AND/OR SULPHUR-CONTAINING COMPOUNDS						
Gould and Hay (1982)	Uracil	11.2 mg l^{-1} (100×10^{-6} M)	7.1 mg l^{-1} (100×10^{-6} M)	8.5, 10.4	0-250 mins	Ambient
	Cytosine	5.7 mg l^{-1} (52×10^{-6} M)	5.0 mg l^{-1} (71×10^{-6} M)	6.5	0-60 h	Ambient
	Caffeine	19.4-97 mg l^{-1} ($100-500 \times 10^{-6}$ M)	21.3-92.3 mg l^{-1} ($300-1300 \times 10^{-6}$ M)	5, 7 and 9	0-140 min	Ambient

Table 1 (continued)

Reference	Substrate	Substrate concn	Chlorine concn	pH	Contact time	Temp °C
Gould and Richards (1984)	Caffeine	ca 38.8 mg l^{-1} (ca 200 x 10^{-6} M)	ca 19.5 mg l^{-1} (ca 275 x 10^{-6} M)	5, 7 and 9	0-24 h	-
Gould et al (1984a)	Uracil	ca 112-118 mg l^{-1} (ca 100-105 x 10^{-6} M)	3.8-75 mg l^{-1} (55-1075 x 10^{-6} M)	5-9	0-100 mins	20-25
Gould et al (1984b)	Cytosine	11.1 and 27.8 mg l^{-1} (200 and 500 x 10^{-6} M)	106 mg l^{-1} (1500 x 10^{-6} M)	5-9	0-300 mins	-
	5-Methylcytosine	25 and 62.5 mg l^{-1} (200 and 500 x 10^{-6} M)	106 mg l^{-1} (1500 x 10^{-6} M)	5-9	0-300 mins	-
Lin and Carlson (1984)	Heterocyclics (16)	1 mg l^{-1} (1 x 10^{-6} - 1 x 10^{-5} M)	15.6-17.8 mg l^{-1} (2.2-2.5 x 10^{-4} M)	5.3 and 7.0	15 mins-24 h	24
Le Cloirec and Martin (1985)	Alanine	4-22.3 mg l^{-1} (0.45-2.5 x 10^{-4} M)	1-10 mg l^{-1} (1.5-15 x 10^{-5} M)	5, 7 and 9	2 h-24h	18
	Phenylalanine	5 mg l^{-1} (0.3 x 10^{-4} M)	1-10 mg l^{-1} (1.5-15 x 10^{-5} M)	5, 7 and 9	2 h-24h	18
	Tyrosine	5 mg l^{-1} (0.28 x 10^{-4} M)	1-10 mg l^{-1} (1.5-15 x 10^{-5} M)	5, 7 and 9	2 h-24h	18
Glaze et al (1982)	Serine	1050 mg l^{-1} (10 x 10^{-3} M)	1000 mg l^{-1} (14 x 10^{-3} M)	1-2	30 min	Ambient
	Threonine	1190 mg l^{-1} (10 x 10^{-3} M)	1000 mg l^{-1} (14 x 10^{-3} M)	1-2	30 min	Ambient
	Alanine	890 mg l^{-1} (10 x 10^{-3} M)	1000 mg l^{-1} (14 x 10^{-3} M)	1-2	30 min	Ambient

Table 1 (continued)

Reference	Substrate	Substrate concn	Chlorine concn	pH	Contact time	Temp °C
	Valine	1170 mg l^{-1} (10×10^{-3} M)	1000 mg l^{-1} (14×10^{-3} M)	1-2	30 min	Ambient
	Tyrosine	1810 mg l^{-1} (10×10^{-3} M)	1000 mg l^{-1} (14×10^{-3} M)	1-2	30 min	Ambient
Fielding and Horth (1986)	Methionine	3.73 mg l^{-1} (25×10^{-6} M)	3 to 15 mg l^{-1} (4.2×10^{-5} to 2.1×10^{-4} M)	6.2	24 h	Ambient
	Tryptophan	5.1 mg l^{-1} (25×10^{-6} M)				
	Phenylalanine	4.1 mg l^{-1} (25×10^{-6} M)				
OXYGEN-CONTAINING COMPOUNDS						
Carlson and Caple (1978)	Oleic acid	-	-	2-10	-	-
Ghanbari et al (1983)	Oleic acid	1000 mg l^{-1} (3.5×10^{-3} M)	180 mg l^{-1} (5×10^{-3} M)	6	1 h	25
Oliver and Carey (1977)	Ethanol	460 mg l^{-1} (1×10^{-2} M)	7.1 g l^{-1} (0.1 M)	4, 7 and 10	0-60 min	-
	n-Butanol	740 mg l^{-1} (1×10^{-2} M)	7.1 g l^{-1} (0.1 M)	4, 7 and 10	0-60 min	-
	Benzoic acid	1.22 mg l^{-1} (1×10^{-2} M)	7.1 g l^{-1} (0.1 M)	4, 7 and 10	0-60 min	-
de Leer et al (1985)	3,5-Dihydroxy-benzoic acid	308 mg l^{-1} (2×10^{-3} M)	1400 mg l^{-1} (20×10^{-3} M)	7.2	2 h	-

Table 1 (continued)

Reference	Substrate	Substrate concn	Chlorine concn	pH	Contact time	Temp °C
Haley et al (1986)	Decanoic acid	10 µg l^{-1} (5.8×10^{-8} M)	1 and 10 µg l^{-1} (1.4×10^{-5} and 1.4×10^{-4} M)	7	4 h	20
	Dodecanoic acid	10 and 500 mg l^{-1} (5×10^{-8} and 2.5×10^{-6} M)				
	Tetradecanoic acid	10 µg l^{-1} (4.4×10^{-8} M)				
	Hexadecanoic acid	10 µg l^{-1} (3.9×10^{-8} M)				
	Hexadec-9-enoic acid	10 and 500 µg l^{-1} (3.9×10^{-8} and 2.0×10^{-6} M)				
	Heptadecanoic acid	10 µg l^{-1} (3.7×10^{-8} M)				
	Octadecanoic acid	10 µg l^{-1} (3.5×10^{-8} M)				
	Octadec-9,12-dienoic acid	10 and 500 µg l^{-1} (3.6×10^{-8} and 1.8×10^{-6} M)				
SURFACTANTS						
Itoh et al (1985)	Surfactants	6.2 mg l^{-1}	3-20 mg l^{-1}	7	24 h	20

* = Chlorine:carbon ratio
- = not specified

Table 2. Summary of conditions used for studies of ozonation products

Reference	Substrate	Substrate concn	Ozone concn	pH	Contact time	Temp °C
HUMIC SUBSTANCES						
Lawrence et al (1980)	Fulvic acid	500 mg l^{-1}	(0.2 g h^{-1}; 0.3-1.0 mg O_3 per mg fulvic)	-	15-60 min	Ambient
Gilbert (1983)	Humic acid	67 mg l^{-1}	-	3.7	70 min	-
Rechow and Singer (1984)+	Fulvic acid	ca 4.0 mg l^{-1} TOC	9 mg l^{-1}	7.0	0-60 min	21
Legubé et al (1985)+	Fulvic acid	5 and 10 mg l^{-1}	0.3-4 mg l^{-1}	7.5 and 7.0	120 min or more	20
Watts (1985)	Humic acid	ca 35 and 200 mg l^{-1}	ca 125 mg l^{-1}	6 and 7	60 min	Ambient
	Fulvic acid	ca 25 and 200 mg l^{-1}	ca 125 mg l^{-1}	6 and 7	30 min and 60 min	Ambient
	Natural water	11 and 13 mg l^{-1}	3.5-4 mg O_3 per mg Org C	6 and 7	20 min	Ambient
Doré et al (1987)	Fulvic acid	5 mg l^{-1}	1 mg mg^{-1} (COD)	7.5	120 min	20
AROMATIC COMPOUNDS (excluding hydrocarbons)						
Doré et al (1980a)	Phenol	18.8 mg l^{-1} (2×10^{-4} M)	* 5 (200 mg h^{-1})	-	0-40 min	-
	Catechol	22 mg l^{-1} (2×10^{-4} M)	* 5 (200 mg h^{-1})	-	0-40 min	-
	Phenol	0.9 mg l^{-1} (10^{-5} M)	* ca 70	-	0-10 min	-

Table 2 (continued)

Reference	Substrate	Substrate concn	Ozone concn	pH	Contact time	Temp °C
	Catechol	1.1 mg l^{-1} (10^{-5} M)	* ca 70	-	0-10 min	-
Brunet et al (1980)	Phenols	2 x 10^{-4} M	ca 150 mg h^{-1}	-	30 min	Ambient
Chrostowski et al (1983)	Phenols	10-50 mg l^{-1}	1.5 mg min^{-1}	3.0-11.2	0-60 min	Ambient
Gilbert (1980)	trans,trans-muconic acid	142 mg l^{-1} (10^{-3} M)	10 mg $min^{-1}.l^{-1}$	3	0-180 min	Ambient
Decoret et al (1984)	Phenol	235-470 µg l^{-1} (2.5 to 5.0 x 10^{-6} M)	2 x 10^{-5} M l^{-1} - consumed	4 and 6	0-90 min	1 and ambient
	Benzaldehyde	265-530 µg l^{-1} (2.5 to 5.0 x 10^{-6} M)	-	4 and 6	0-90 min	1 and ambient
	Acetophenone	300-600 µg l^{-1} (2.5 to 5.0 x 10^{-6} M)	-	4 and 6	0-90 min	1 and ambient
El Dine et al (1984)	Phthalic acid	80 mg l^{-1} (0.48 x 10^{-3} M)	0.75 mg min^{-1}	Natural	60 min	Ambient
Caprio et al (1984)	Nitrobenzene	307 mg l^{-1} (2.5 x 10^{-3} M)	max 20 x 10^{-3} M l^{-1}		0-150 min	20
Legubé et al (1981a)	Phenol	38-2820 mg l^{-1} (0.4-30 x 10^{-3} M)	-	Natural	-	Ambient
	Aniline	930-27 000 mg l^{-1} (10-300 x 10^{-3} M)	-	Natural	-	Ambient
	Phenoxyacetic acid	760 mg l^{-1} (5 x 10^{-3} M)	-	Natural	-	Ambient

Table 2 (continued)

Reference	Substrate	Substrate concn	Ozone concn	pH	Contact time	Temp °C
	p-Cresol	1080 mg l^{-1} (10×10^{-3} M)	-	Natural	-	Ambient
	2-Methyl-4-chlorophenoxy-acetic acid (MCPA)	500 mg l^{-1} (2.5×10^{-3} M)	-	Natural	-	Ambient
Legubé et al (1981b)	Phenol	18.8 mg l^{-1} (2×10^{-4} M)	56.4 mg l^{-1} (3.6 l h^{-1})	-	0-120 min	Ambient
	Hydroquinone	22 mg l^{-1} (2×10^{-4} M)	62.7 mg l^{-1} (3.7 l h^{-1})	-	0-120 min	Ambient
	Aniline	18.6 mg l^{-1} (2×10^{-4} M)	49.4 mg l^{-1} (3.5 l h^{-1})	-	0-120 min	Ambient
	2,4-Dichloro-phenoxyacetic acid	22.1 mg l^{-1} (1×10^{-4} M)	61.8 mg l^{-1} (3.4 l h^{-1})	-	0-120 min	Ambient
	MCPA	30 mg l^{-1} (1.5×10^{-4} M)	61.8 mg l^{-1} (3.4 l h^{-1})	-	0-120 min	Ambient
Legubé et al (1983)	Styrene	11.4 mg l^{-1} (1.1×10^{-4} M)	197 mg h^{-1} (12.8 l h^{-1})	5.0	ca 10 min	-
	Benzaldehyde	22.4 mg l^{-1} (2.11×10^{-4} M)	238 mg h^{-1} (12 l h^{-1})	4.2	60 min	-
	Naphthalene	32.4 mg l^{-1} (2.53×10^{-4} M)	212 mg h^{-1} (12.8 l h^{-1})	5.9	ca 30 min	-
	Diethylphthalate	35.5 mg l^{-1} (1.6×10^{-4} M)	251 mg h^{-1} (12 l h^{-1})	6.3	150 min	-

Table 2 (continued)

Reference	Substrate	Substrate concn	Ozone concn	pH	Contact time	Temp °C
	Ethylbenzene	20.5 mg l^{-1} (1.93×10^{-4} M)	197 mg h^{-1} (13.3 l h^{-1})	6.3	120 min	-
	Chlorobenzene	18.5 mg l^{-1} (1.65×10^{-4} M)	142 mg h^{-1} (13.3 l h^{-1})	6.3	150 min	-
Gilbert and Zinecker (1980)	4-Aminobenzene sulphonic acid	173 mg l^{-1} (1×10^{-3} M)	10 mg min^{-1} (24 l h^{-1})	-	15-20 min	-
	4-Aminobenzoic acid	137 mg l^{-1} (1×10^{-3} M)	10 mg min^{-1} (24 l h^{-1})	-	15-20 min	-
	4-Amino-2-nitrophenol	154 mg l^{-1} (1×10^{-3} M)	10 mg min^{-1} (24 l h^{-1})	-	15-20 min	-
	4-Chloro-aniline	127 mg l^{-1} (1×10^{-3} M)	10 mg min^{-1}	-	15-20 min	-
	2-Aminophenol	109 mg l^{-1} (1×10^{-3} M)	10 mg min^{-1}	-	15-20 min	-
	4-Amino-5-hydroxy naphthalene-sulphonic acid mono-sodium salt	262 mg l^{-1} (1×10^{-3} M)	10 mg min^{-1}	-	15-20 min	-
Gilbert (1983)	Aniline	93 mg l^{-1} (1×10^{-3} M)	10 mg min^{-1}	6.3	15 min	-
	Benzenesulphonic acid	158 mg l^{-1} (1×10^{-3} M)	10 mg min^{-1}	5.5	60 min	-
	4-Chloro-o-cresol	142 mg l^{-1} (1×10^{-3} M)	10 mg min^{-1}	5.5	40 min	-

Table 2 (continued)

Reference	Substrate	Substrate concn	Ozone concn	pH	Contact time	Temp °C
	2-Nitro-p-cresol	153 mg l^{-1} (1×10^{-3} M)	10 mg min^{-1}	5.9	50 min	-
HYDROCARBONS						
Butkovic et al (1983)	Pyrene	50.5 µg l^{-1} (2.5×10^{-7} M)	10^{-4} M	7	less than 5 mins	25
	Phenanthrene	279 µg l^{-1} (1.57×10^{-6} M)	10^{-4} M	7	less than 5 mins	25
	Benzo[a]pyrene	176 µg l^{-1} (7×10^{-7} M)	10^{-4} M	7	less than 5 mins	25
Helleur et al (1979)	Fluorene	1.2 mg l^{-1} (7.2×10^{-6} M)	* 2-4	5-8	0-20 mins	-
	Fluoren-9-one	6.0 mg l^{-1} (33.3×10^{-6} M)	* 2-4	5-8	0-20 mins	-
Fielding et al (1987)	Toluene	10 µg l^{-1} (1.08×10^{-7} M)	5 mg l^{-1}	Ambient	30 mins	10
	o, m, p-Xylene	10 µg l^{-1} (9.4×10^{-8} M)				
	Naphthalene	10 µg and 1 mg l^{-1} (7.8×10^{-8} and 7.8×10^{-6} M)				
	Fluorene	10 µg and 1 mg l^{-1} (6.0×10^{-8} and $6.0\ 10^{-6}$ M)				

Table 2 (continued)

Reference	Substrate	Substrate concn	Ozone concn	pH	Contact time	Temp °C
	Phenanthrene	10 µg and 1 mg l^{-1} (5.6×10^{-8} and 5.6×10^{-6} M)	5 mg l^{-1}	Ambient	30 mins	10
	Fluoranthrene	10 and 200 µg l^{-1} (5×10^{-8} and 1×10^{-6} M)				
	Pyrene	10 and 200 µg l^{-1} (5×10^{-8} and 1×10^{-6}M)				
NITROGEN AND/OR SULPHUR-CONTAINING COMPOUNDS						
Faujour et al (1980)	Ethylamine	1.4 g l^{-1} (31×10^{-3} M)	3.6 g h^{-1}	Basic	0-60 min	-
	Dimethylamine	1.4 g l^{-1} (31×10^{-3} M)	3.6 g h^{-1}	Basic	0-60 min	-
	Trimethylamine	1.4 g l^{-1} (24×10^{-3} M)	3.6 g h^{-1}	Basic	0-60 min	-
	Ethylmercaptan	50 mg l^{-1} (0.8×10^{-3} M)	3.6 g h^{-1}	-	0-120 min	-
	n-Butylmercaptan	50 mg l^{-1} (0.56×10^{-3} M)	3.6 g h^{-1}	-	0-120 min	-
	n-Propylmercaptan	50 mg l^{-1} (0.66×10^{-3} M)	3.6 g h^{-1}	-	0-120 min	-
Elmghari-Tabib et al (1982)	Methylamine	70 g l^{-1} (2.26 M)	2.6 g h^{-1}	Basic	0-40 min	-

Table 2 (continued)

Reference	Substrate	Substrate concn	Ozone concn	pH	Contact time	Temp °C
	Ethylamine	70 g l^{-1} and 14 mg l^{-1} (1.56 M and 0.3 x 10^{-3} M)	2.6 g h^{-1}	Basic	0-40 min	-
	Propylamine	70 g l^{-1} (1.2 M)	2.6 g h^{-1}	Basic	0-40 min	-
	Cyclohexylamine	70 g l^{-1} (0.71 M)	2.6 g h^{-1}	Basic	0-40 min	-
	Dimethylamine	70 g l^{-1} (1.56 M)	2.6 g h^{-1}	Basic	0-40 min	-
	N-Methylbutylamine	70 g l^{-1} (0.8 M)	2.6 g h^{-1}	Basic	0-40 min	-
	Trimethylamine	70 g l^{-1} and 64 mg l^{-1} (1.2 M and 1.1 x 10^{-3} M)	2.6 g h^{-1}	Basic	0-40 min	-
	Triethylamine	70 g l^{-1} and 70 mg l^{-1} (0.69 M and 0.7 x 10^{-3} M)	2.6 g h^{-1}	Basic	0-40 min	-
Duguet et al (1980)+	Glycine	150 mg l^{-1} (2 x 10^{-3} M)	ca 30 mg min^{-1}	6.1 - 10.7	0-180 min	20
Yamada and Somiya (1980)	Glycine	100 mg l^{-1} (1.3 x 10^{-3} M)	14-140 mg min^{-1}	4, 7 and 10	20-80 min	20
	Leucine	100 mg l^{-1} (0.76 x 10^{-3} M)	14-140 mg min^{-1}	4, 7 and 10	20-80 min	20

Table 2 (continued)

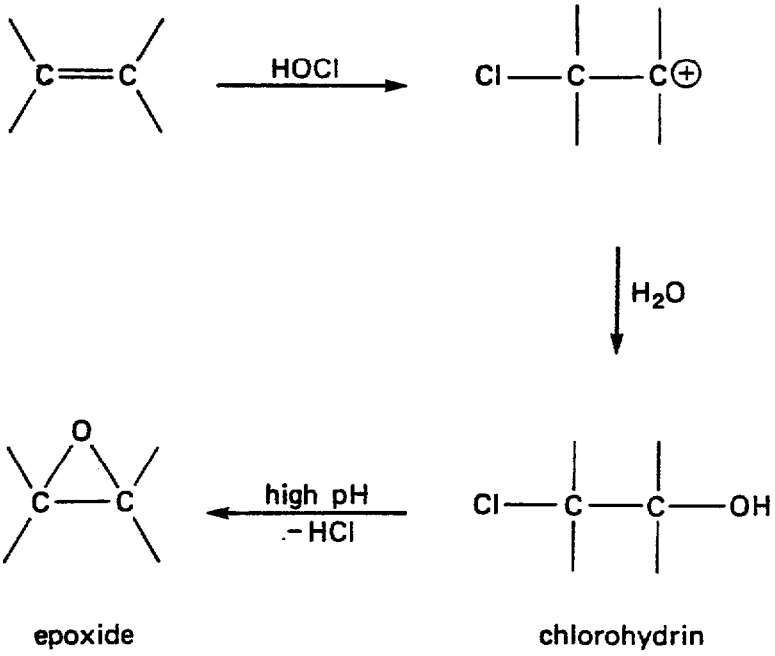
Reference	Substrate	Substrate concn	Ozone concn	pH	Contact time	Temp °C
	Phenol	100 mg l^{-1} (1.06×10^{-3} M)	14-140 mg min^{-1}	4, 7 and 10	20-80 min	20
	Glucose	100 mg l^{-1} (0.55×10^{-3} M)	14-140 mg min^{-1}	4, 7 and 10	20-80 min	20
OXYGEN-CONTAINING COMPOUNDS						
Lutton et al (1979)+	EDTA	29.2-146 g l^{-1} (0.1 - 0.5 M)	54 mg min^{-1}	-	6 h	25 and 60
Chang and Chian (1981)	Methanol	15-35 mg l^{-1} ($0.47-1.1 \times 10^{-3}$ M)	13 mg l^{-1} (gas phase)	9	-	21-25
Fielding et al (1987)	Decanoic acid	10 µg l^{-1} (5.8×10^{-8} M)	5 mg l^{-1}	Ambient	30 min	10
	Dodecanoic acid	10 and 500 µg l^{-1} (5×10^{-8} and 2.5×10^{-6} M				
	Tetradecanoic acid	10 µg l^{-1} (4.4×10^{-8} M)				
	Hexadecanoic acid	10 µg l^{-1} (3.9×10^{-8} M)				
	Hexadec-9-enoic acid	10 and 500 µg l^{-1} (3.9×10^{-8} and 2.0×10^{-6} M)				
	Heptadecanoic acid	10 µg l^{-1} (3.7×10^{-8} M)				

Table 2 (continued)

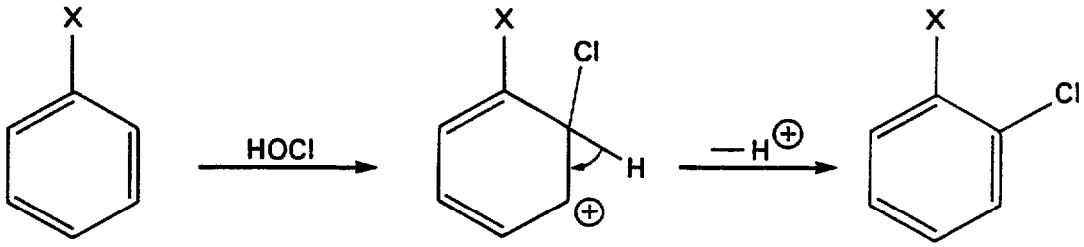
Reference	Substrate	Substrate concn	Ozone concn	pH	Contact time	Temp °C
	Octadecanoic acid	10 μg l^{-1} (3.5×10^{-8} M)	5 mg l^{-1}	Ambient	30 min	10
	Octadec-9,12-dienoic acid	10 and 500 μg l^{-1} (3.6×10^{-8} and 1.8×10^{-6} M)				
SURFACTANTS						
Joy et al (1980)	p-Toluene sulphonic acid	172 mg l^{-1} (1×10^{-3} M)	24 and 11 mg min^{-1}	3 and 12	0-180 min	25
PESTICIDES						
Legubé et al (1981)	2,4-D and MCPA	see aromatics section				
Doré et al (1980b)	2,4-D	22 mg l^{-1} (1.0×10^{-4} M)	200-220 mg h^{-1}	-	0-120 min	-
	MCPA	22 mg l^{-1} (1.5×10^{-4} M)	200-220 mg h^{-1}	-	0-120 min	-
	Phenoxyacetic acid	30 mg l^{-1} (1.5×10^{-4} M)	200-220 mg h^{-1}	-	0-120 min	-

- = not specified
* = ozone to substrate ratio (moles per mole)
+ = the effects of the presence of some inorganics were studied

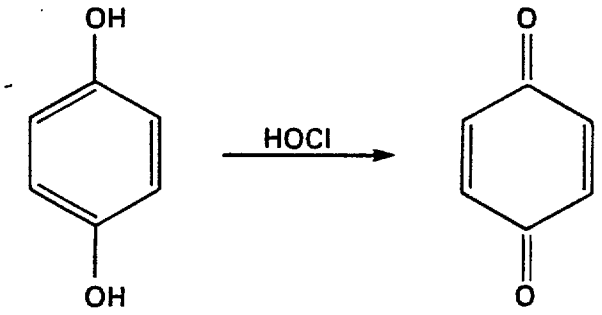
Figure 1. Typical reactions of chlorine with organics.



Addition Reaction



Substitution Reaction



Oxidation Reaction

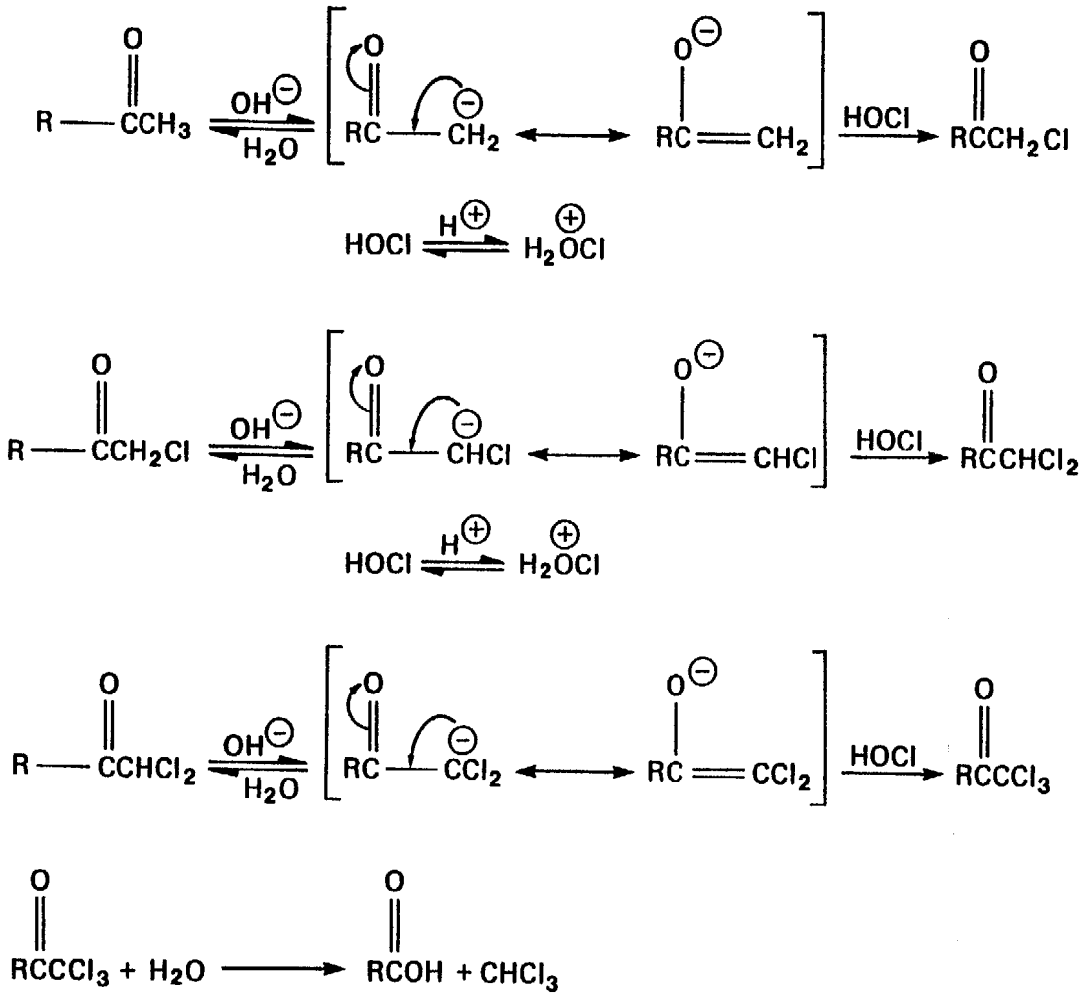


Figure 2. Scheme for haloform reaction.

(Glaze et al., 1982)

Figure 3. Reaction scheme for 1, 3 - dipolar cyclo - addition.
(Doré , 1985).

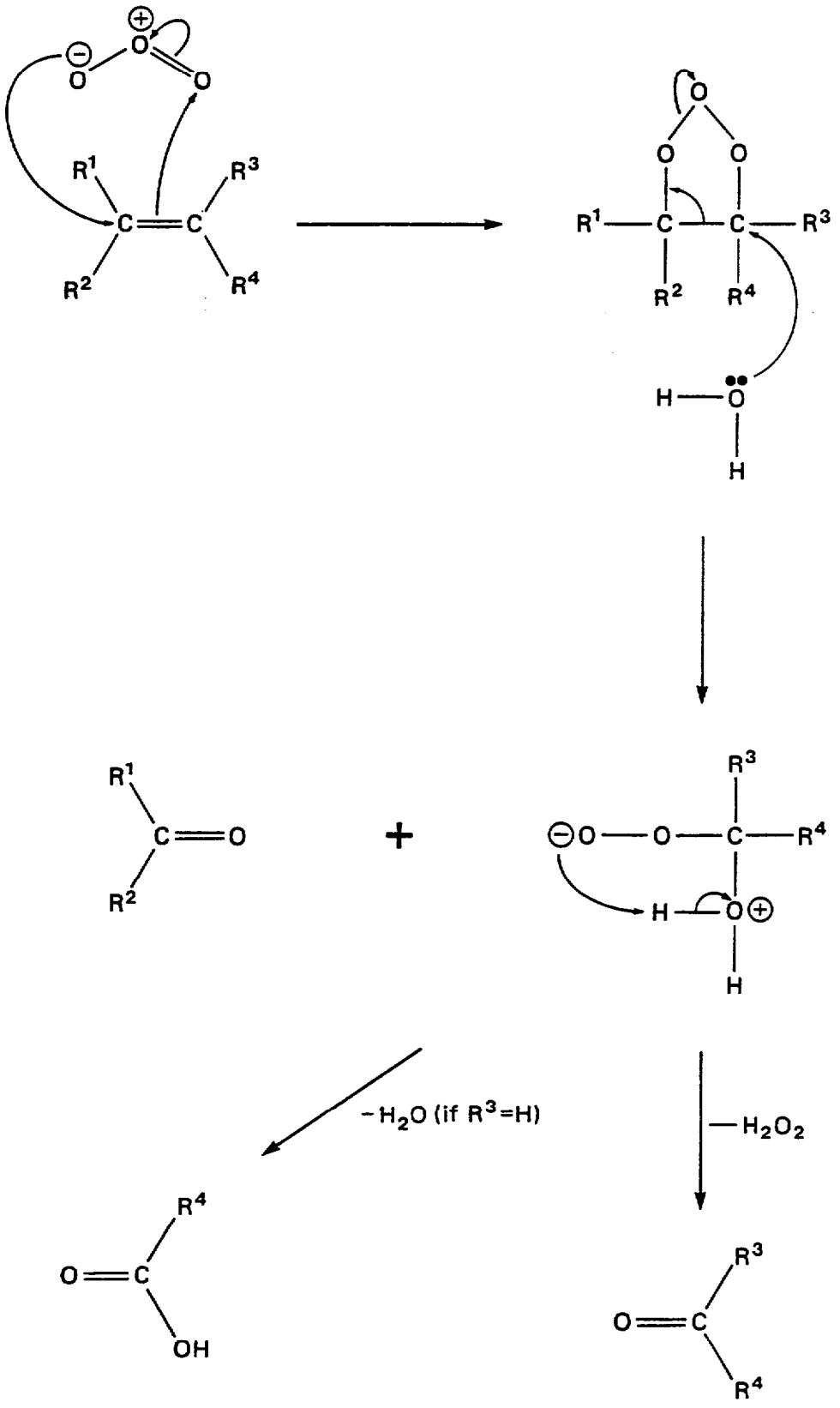


Figure 4. Reaction scheme for electrophilic attack.
(Doré , 1985).

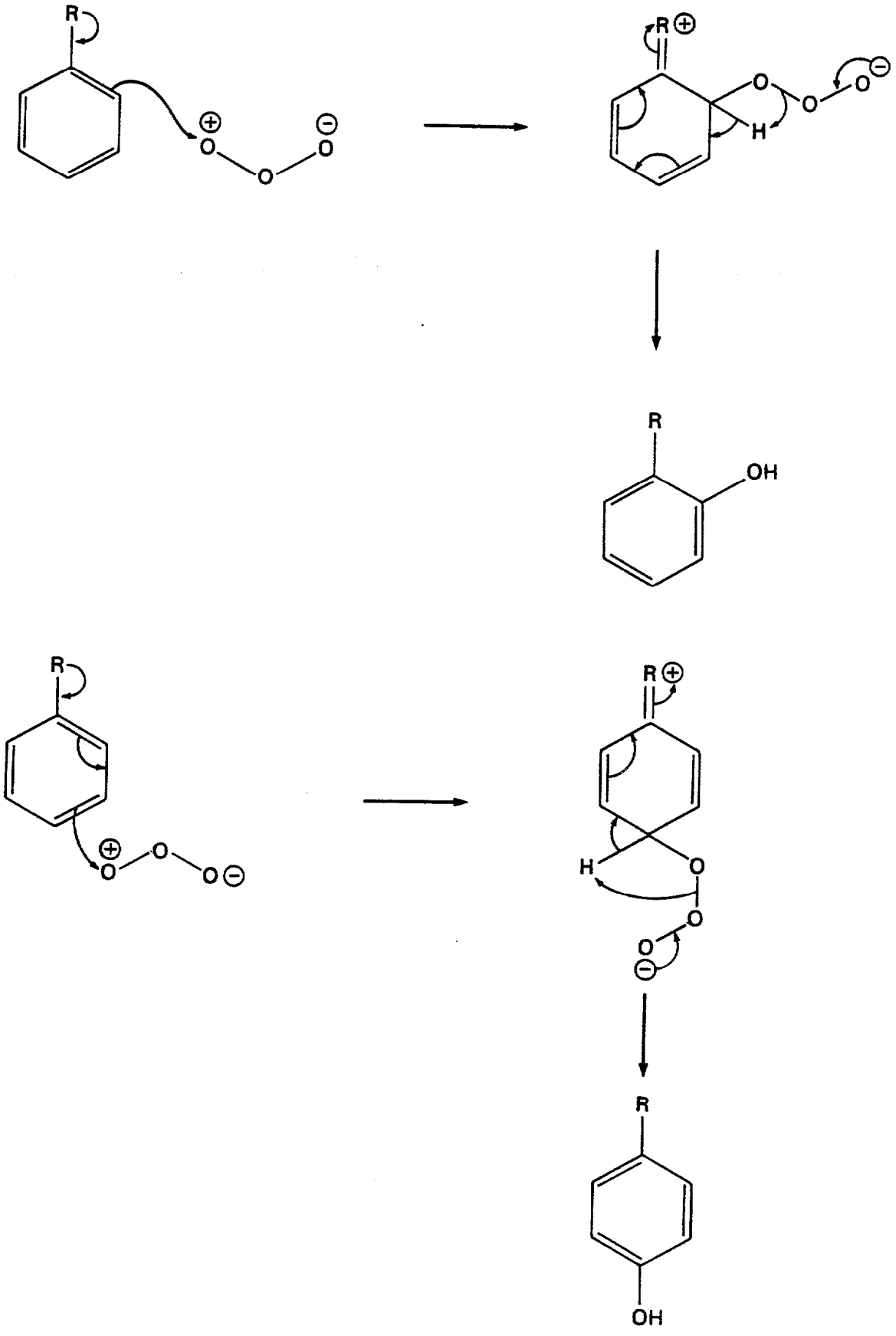


Figure 5. Reaction scheme for nucleophilic attack.
(Doré, 1985)

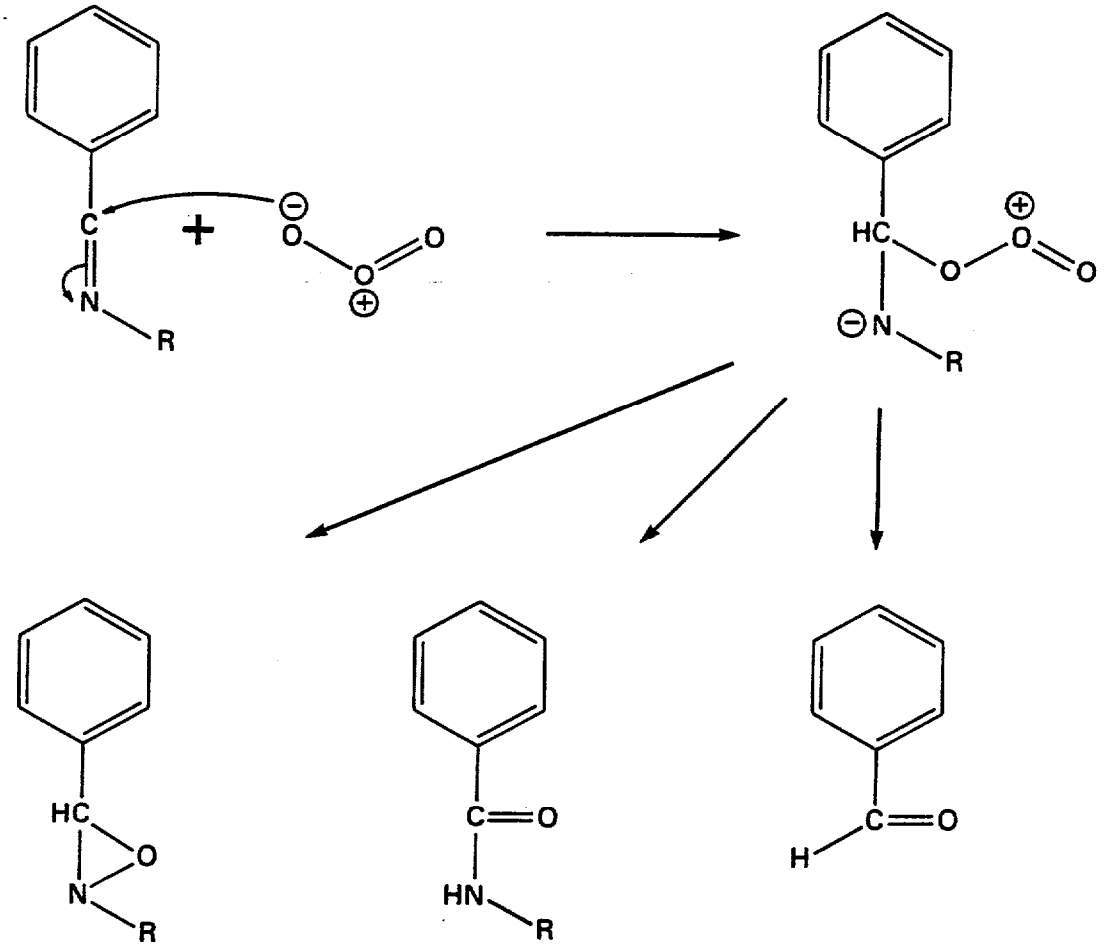


Figure 6. Indirect reaction (action of $OH^{\bullet}$ on phenol)

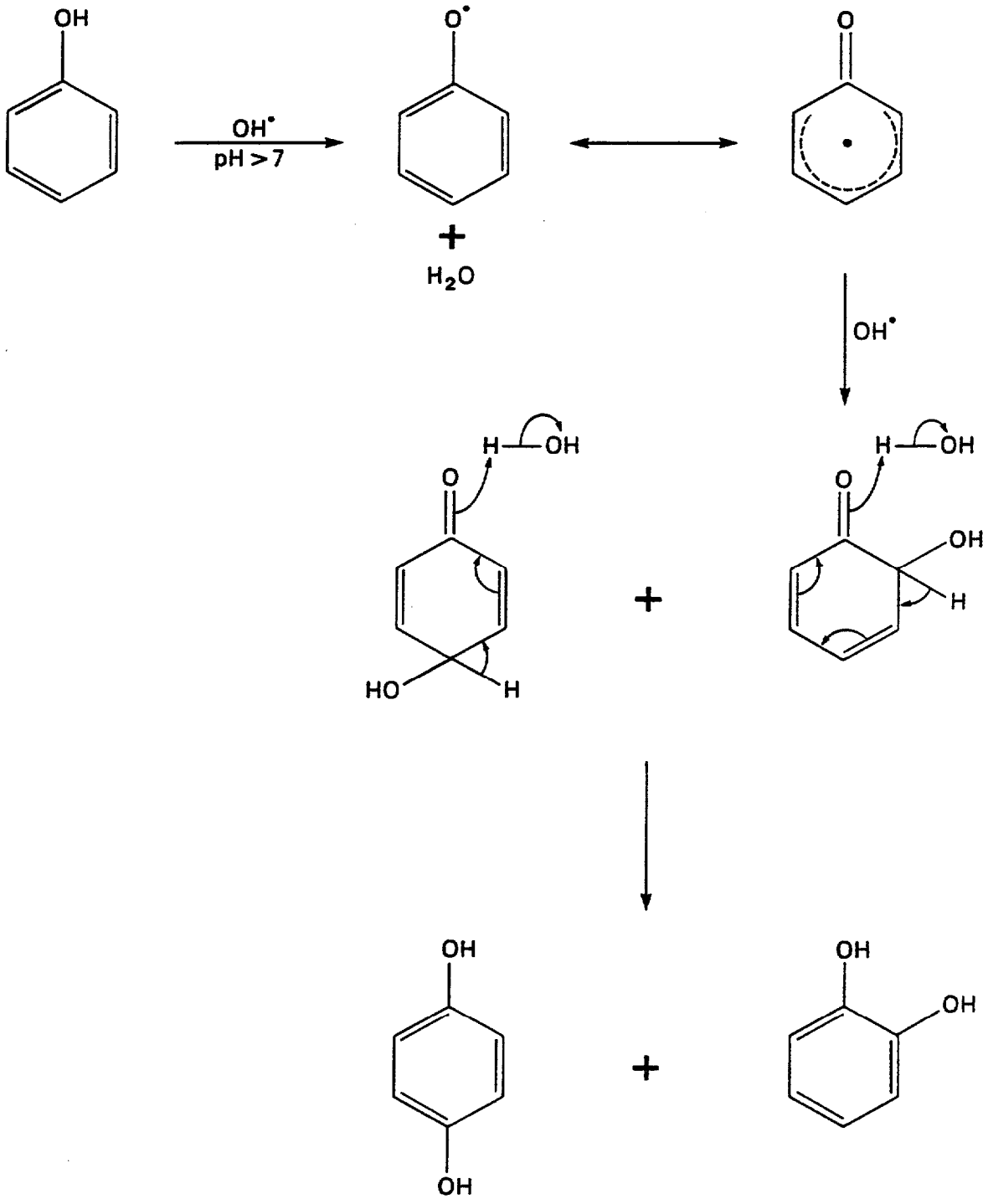


Figure 7. Reaction scheme for chlorination of aniline.
(Jenkins et al., 1978)

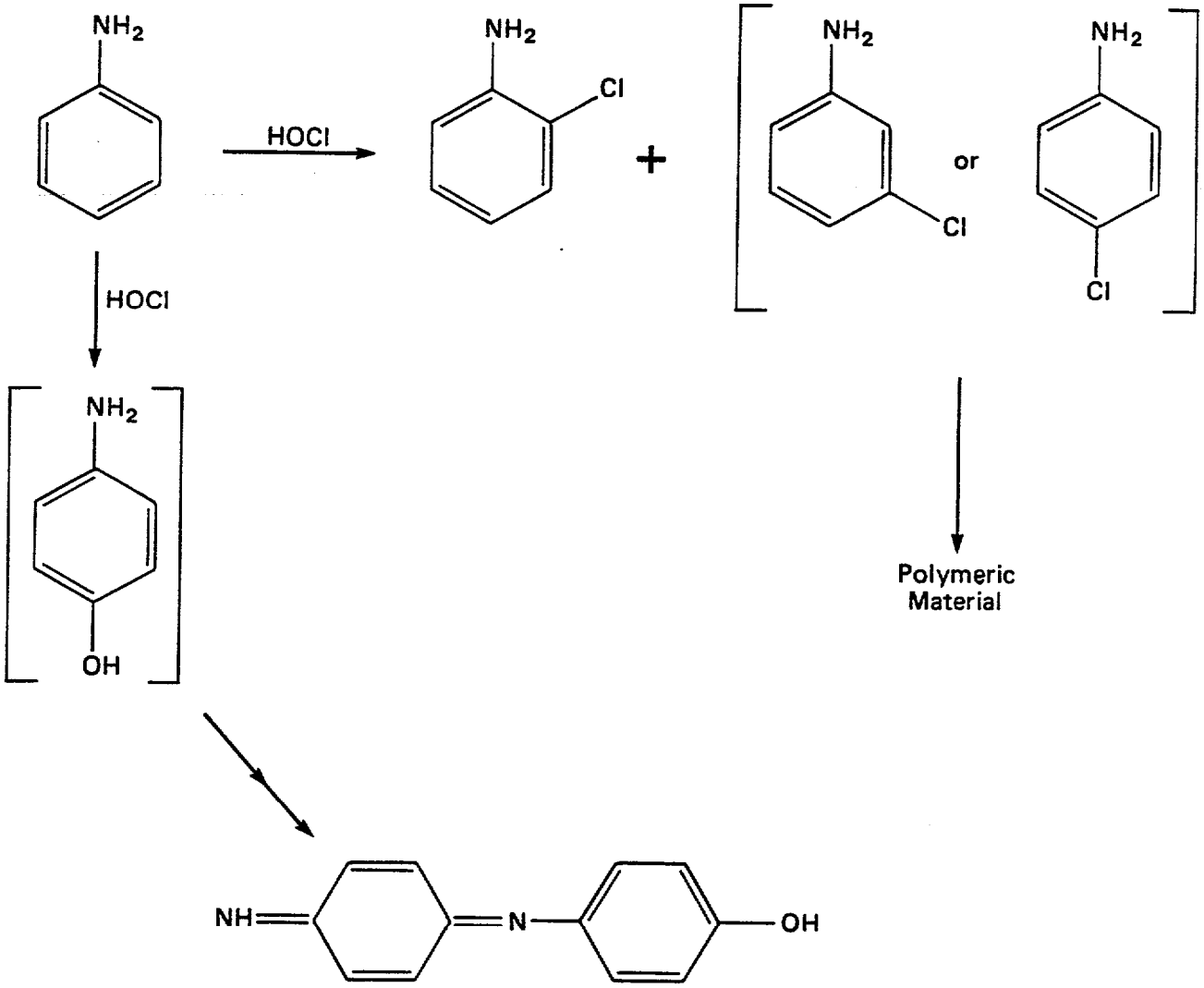
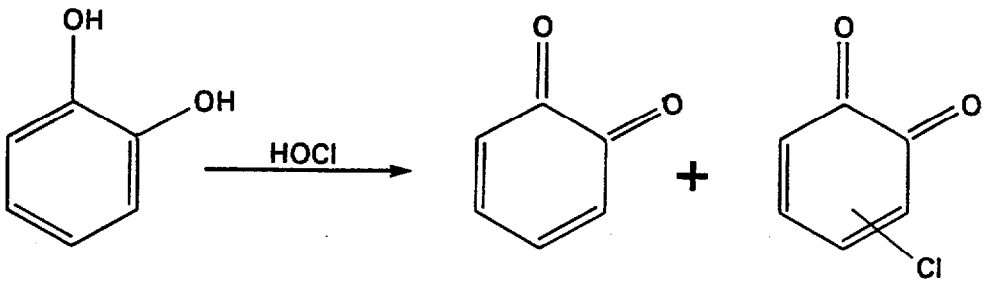


Figure 8. Reaction scheme for chlorination of catechol.
(Nazar et al., 1981).



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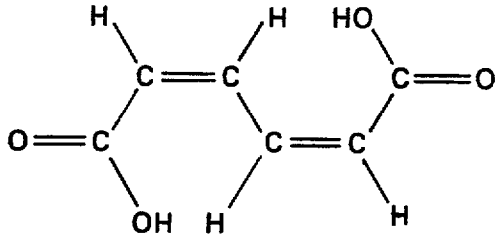


Cis, Cis – muconic acid

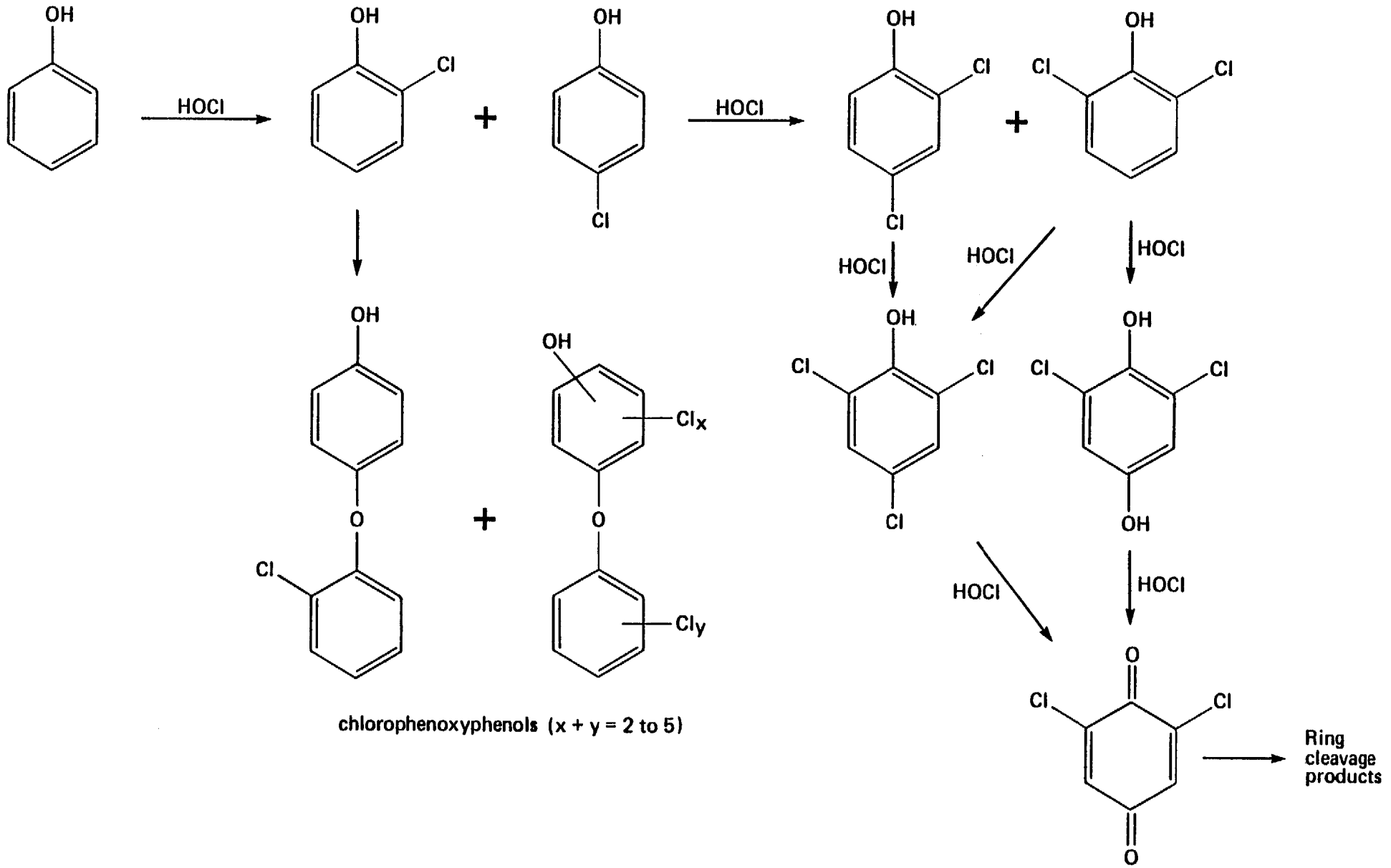
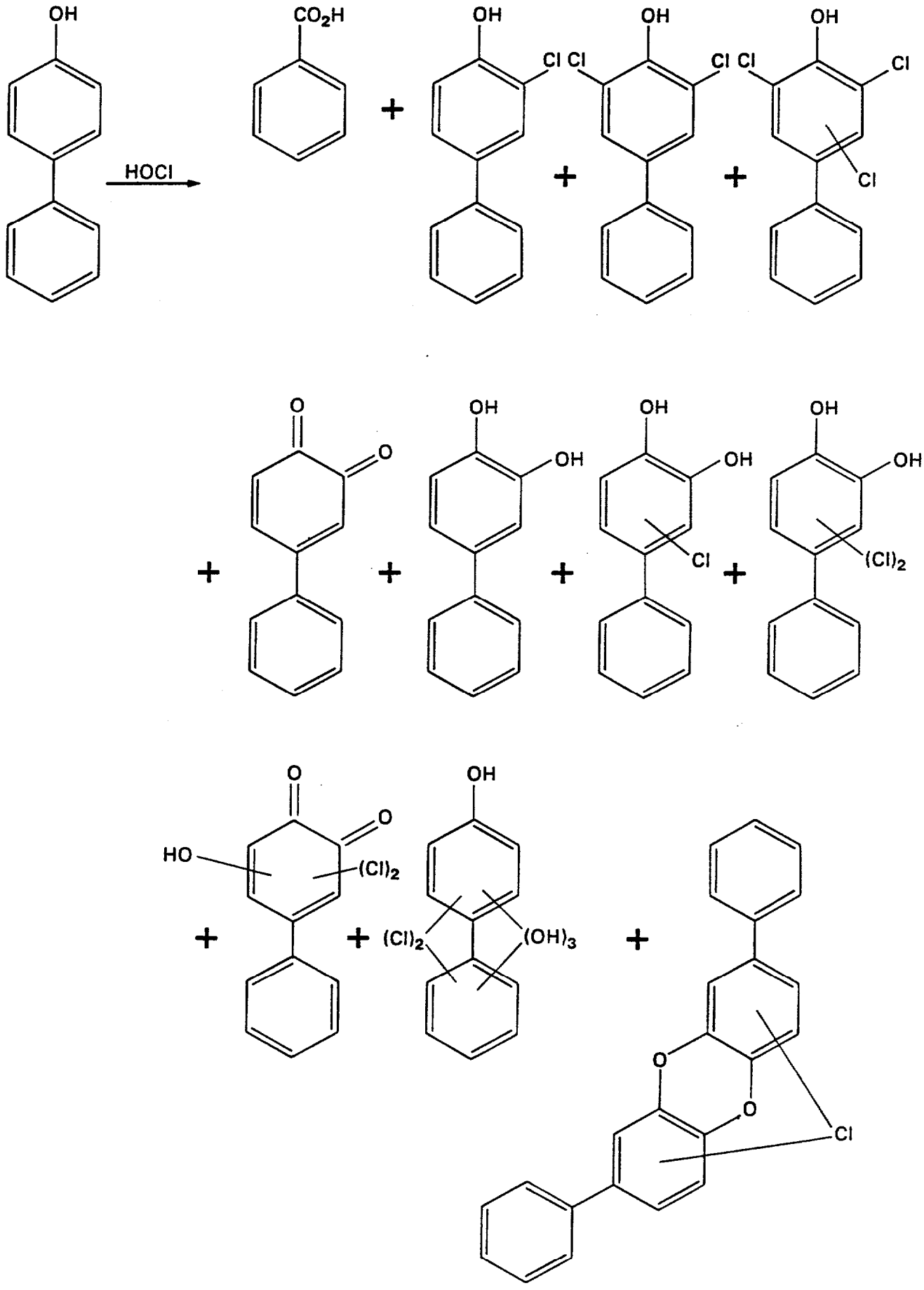


Figure 9. Reaction scheme for chlorination of phenol
(Pierce, 1978 and Onodera et al., 1984)

Figure 10. Reaction products from chlorination of p - phenylphenol.
(Onodera et al., 1983, 1985).



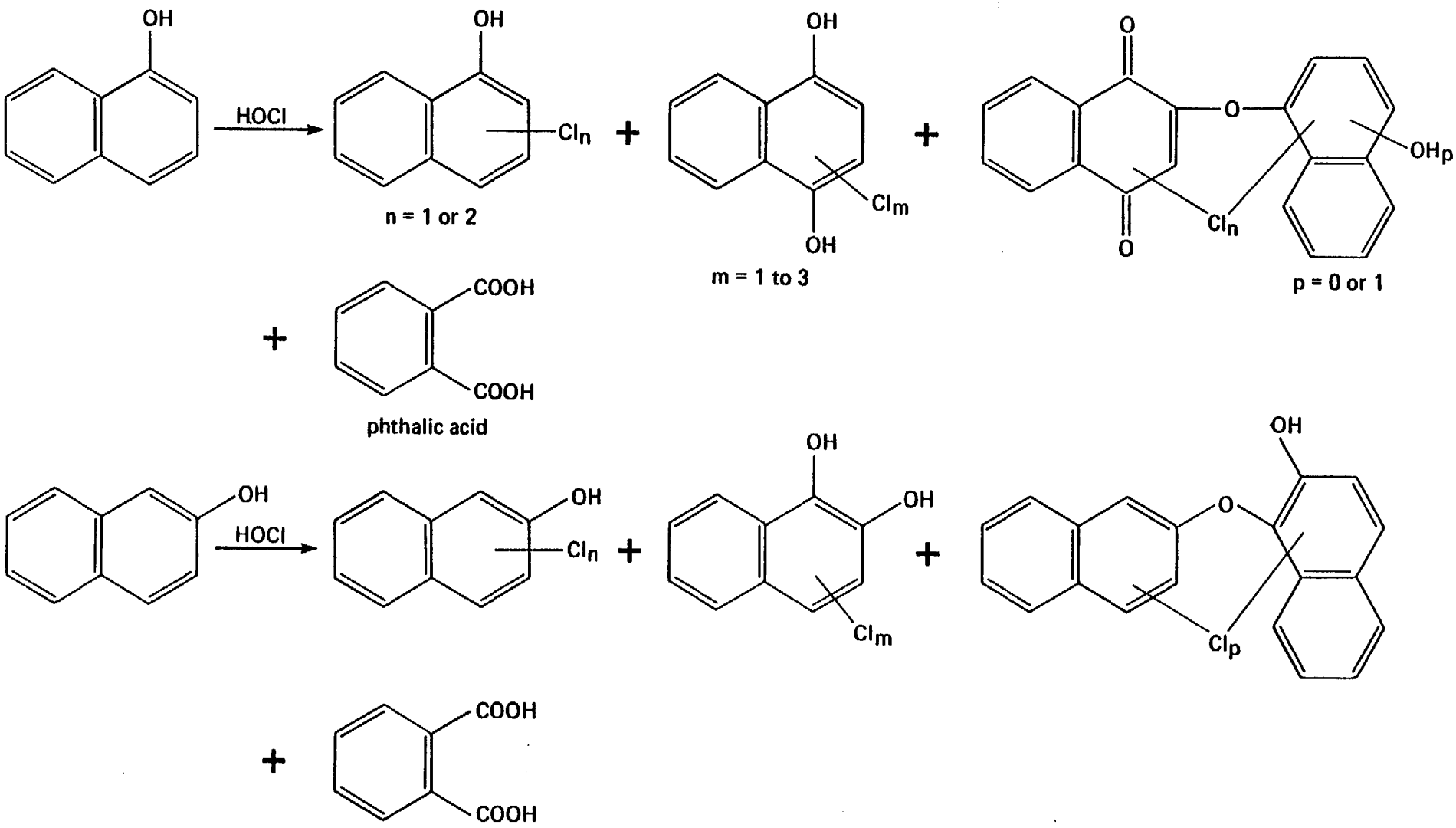
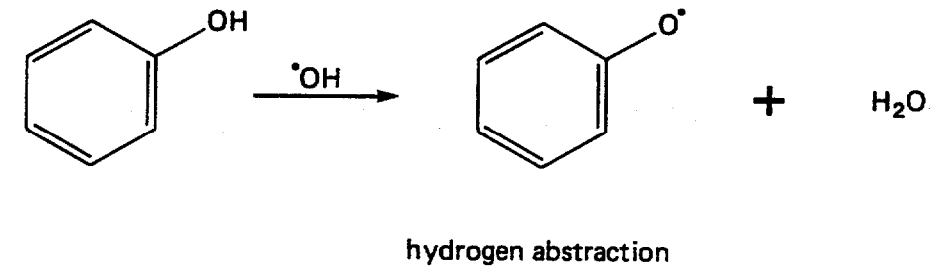
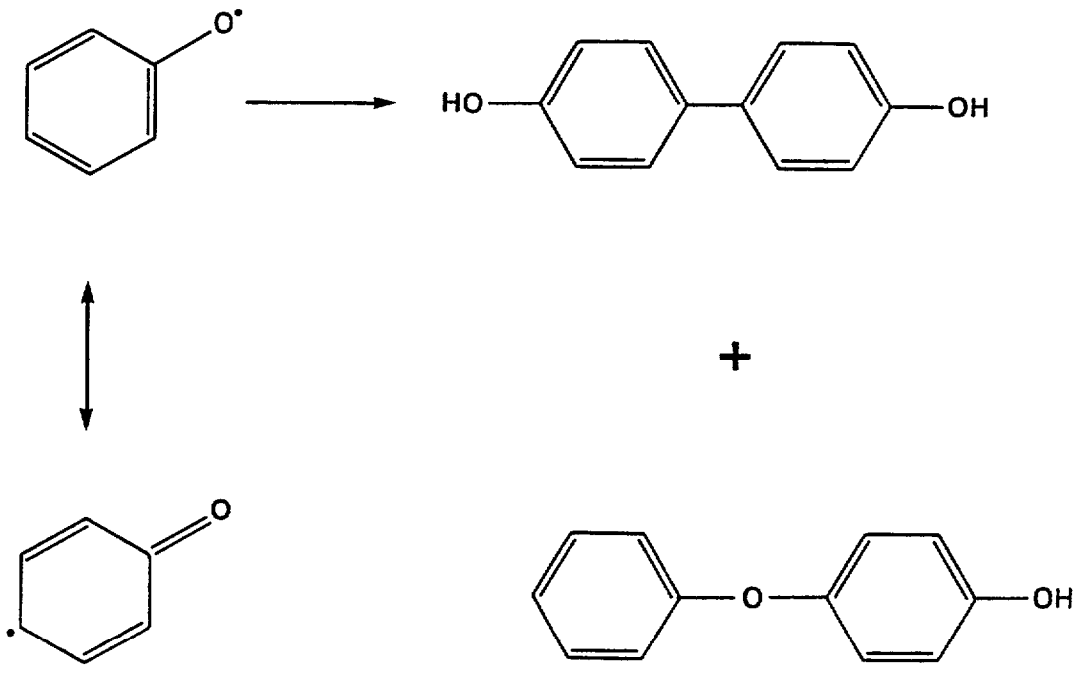


Figure 11. Reaction products from chlorination of naphthols.
(Onodera, et al., 1982).

Figure 12. Reaction scheme for oxidative coupling of phenol.
(Chrostowski et al., 1983)



hydrogen abstraction



oxidative coupling

Figure 13. Reaction scheme for ozonation of 4 – phenylazo – 1 – naphthol. (Matsui et al., 1981).

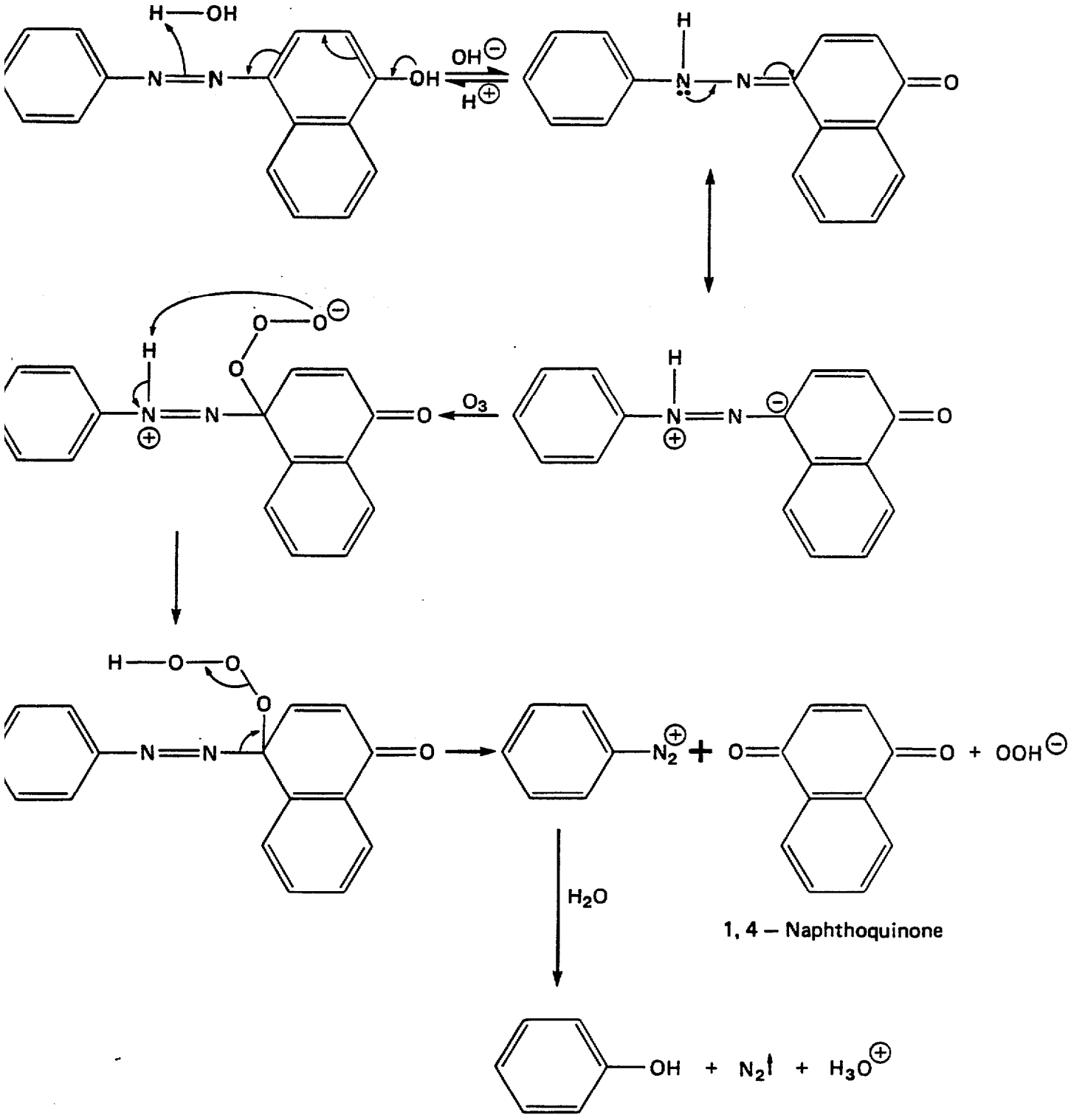
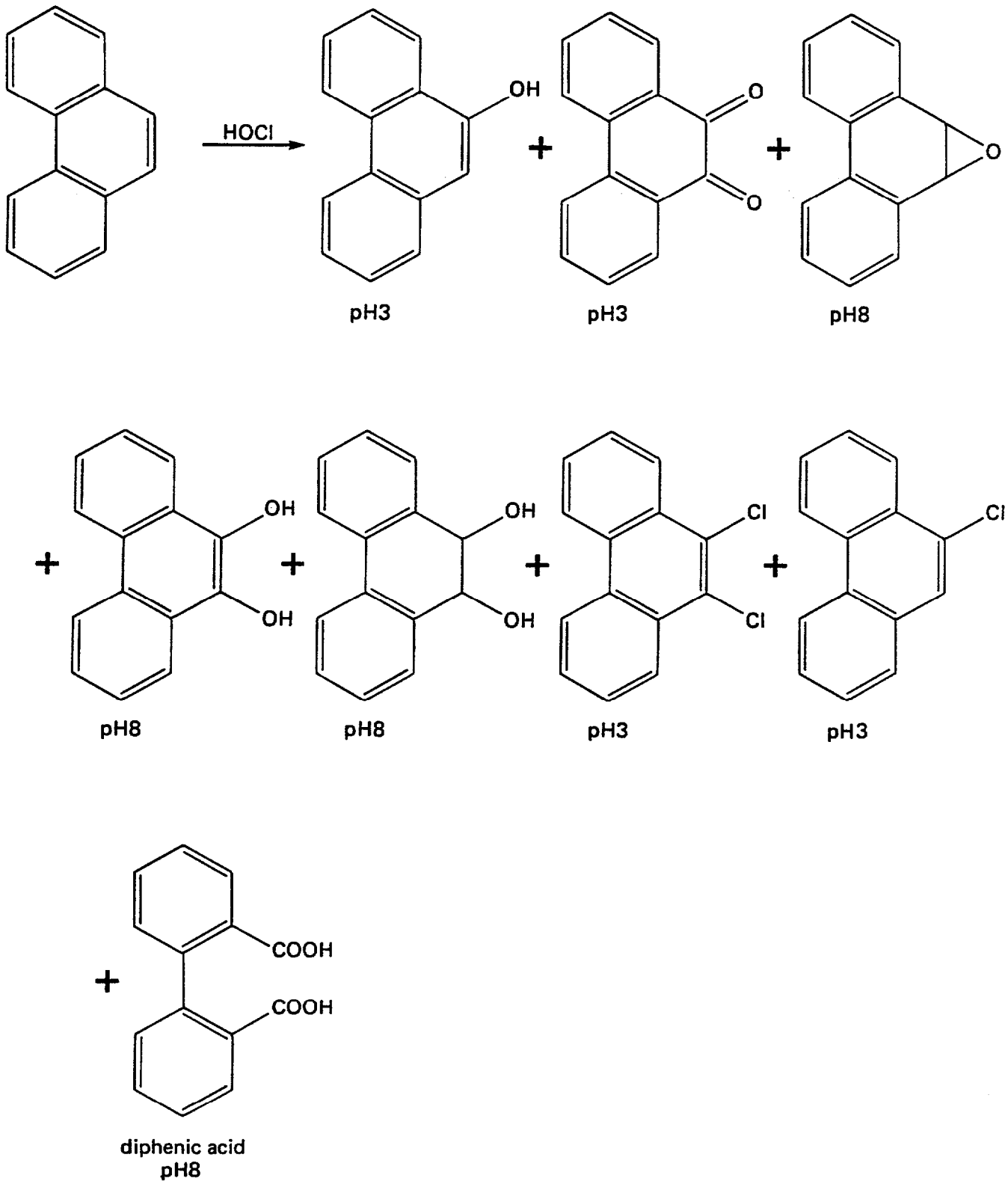


Figure 14. Reaction products from chlorination of phenanthrene at different pH's. (Oyler et al., 1982).



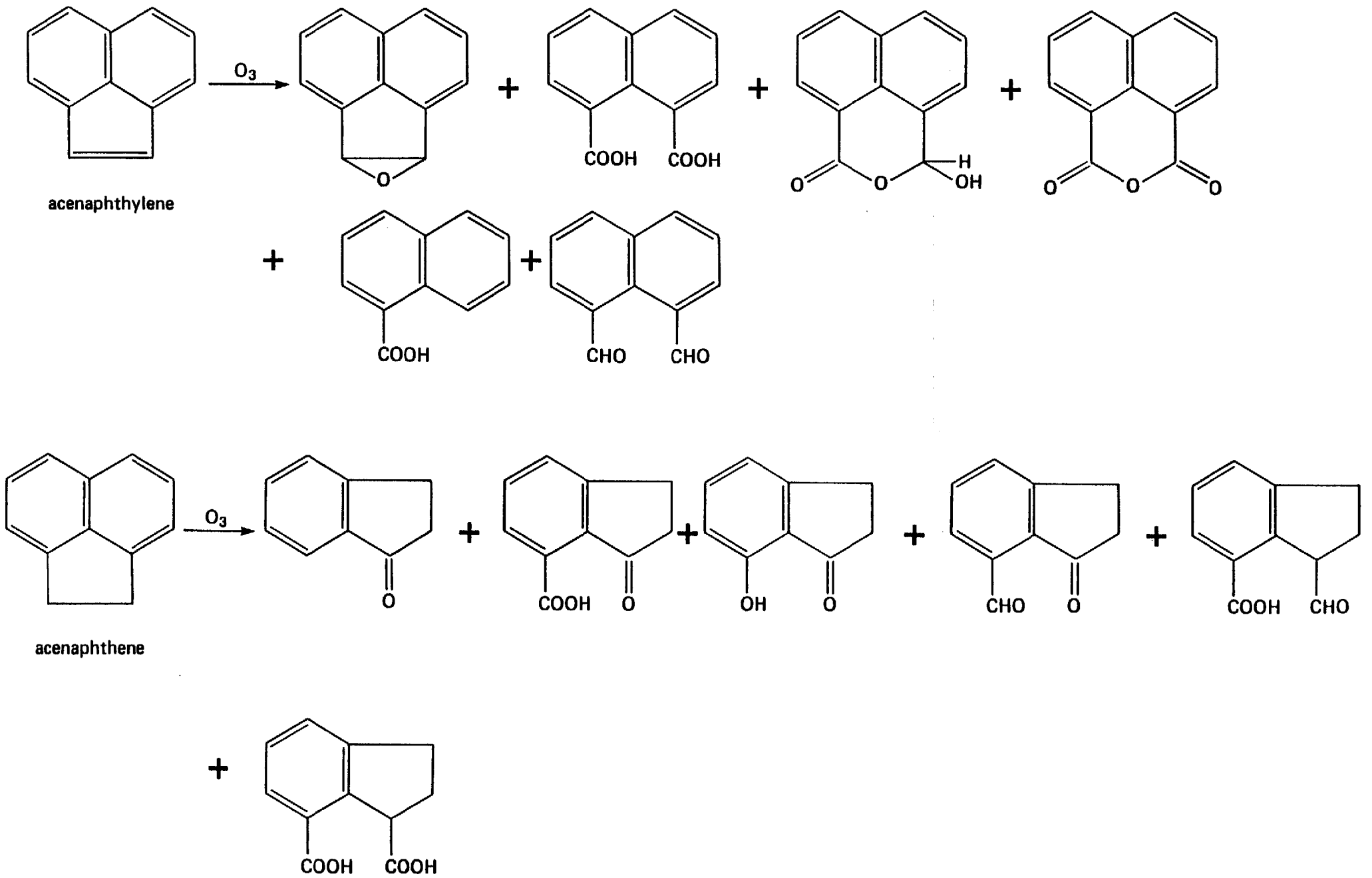


Figure 15. Reaction products from ozonation of acenaphthylene and acenaphthene in methanol and hexane. (Chen et al., 1979).

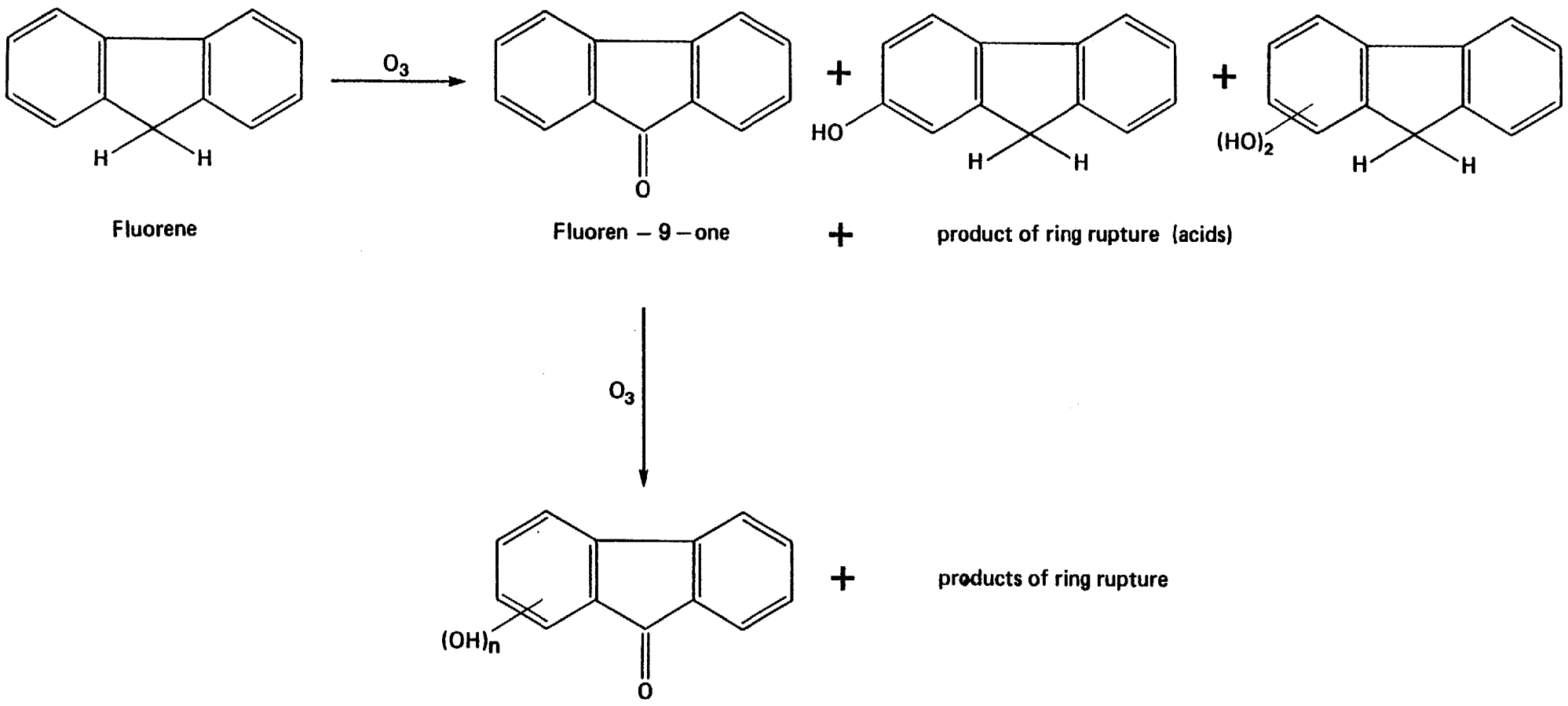
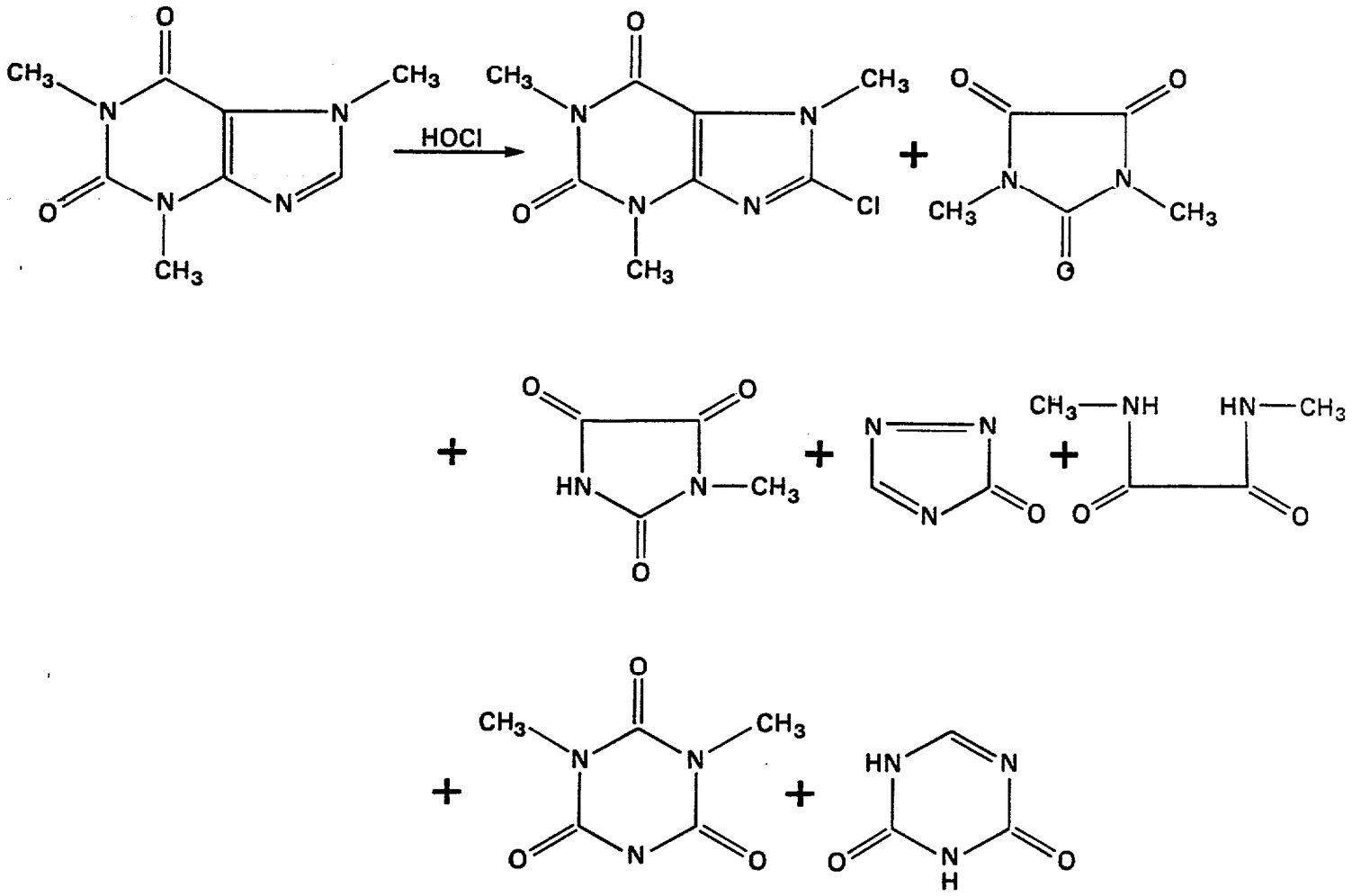


Figure 16. Reaction scheme for ozonation of fluorene and fluoren – 9 – one. (Helleur et al., 1979).

Figure 17. Reaction products from chlorination of caffeine.
(Gould et al., 1982, 1984).



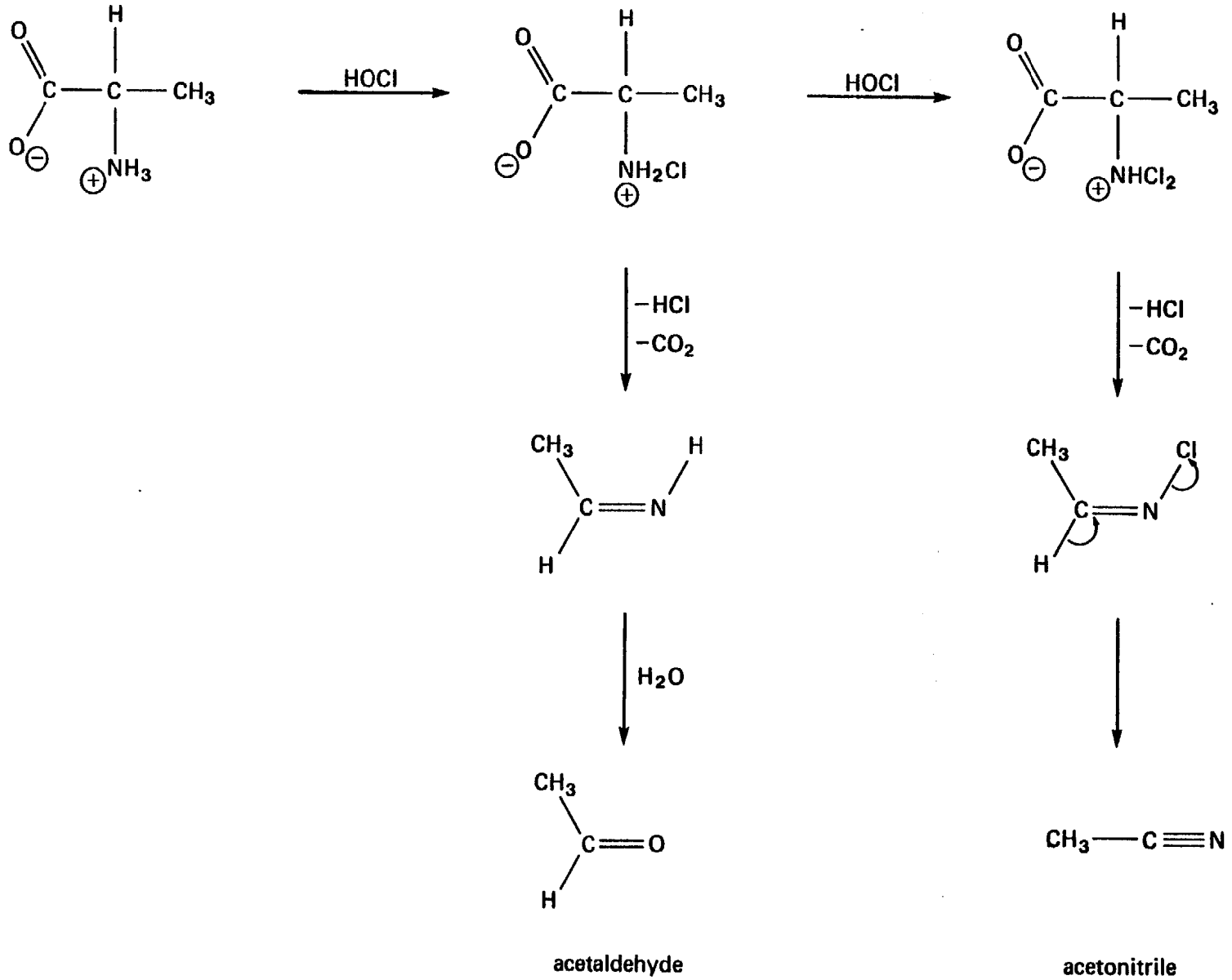


Figure 18. Reaction scheme for chlorination of alanine (Le Cloirec et al., 1985).

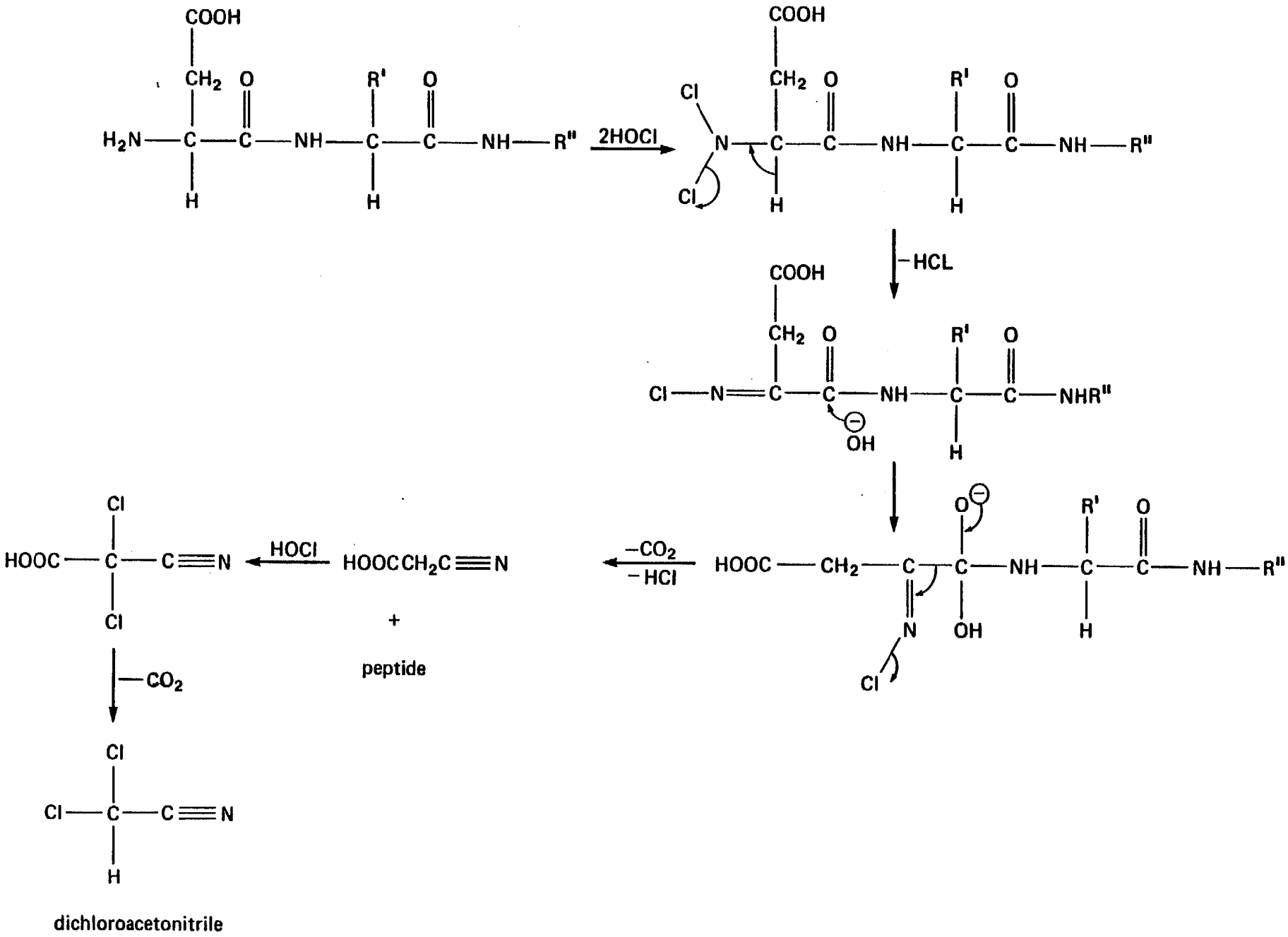
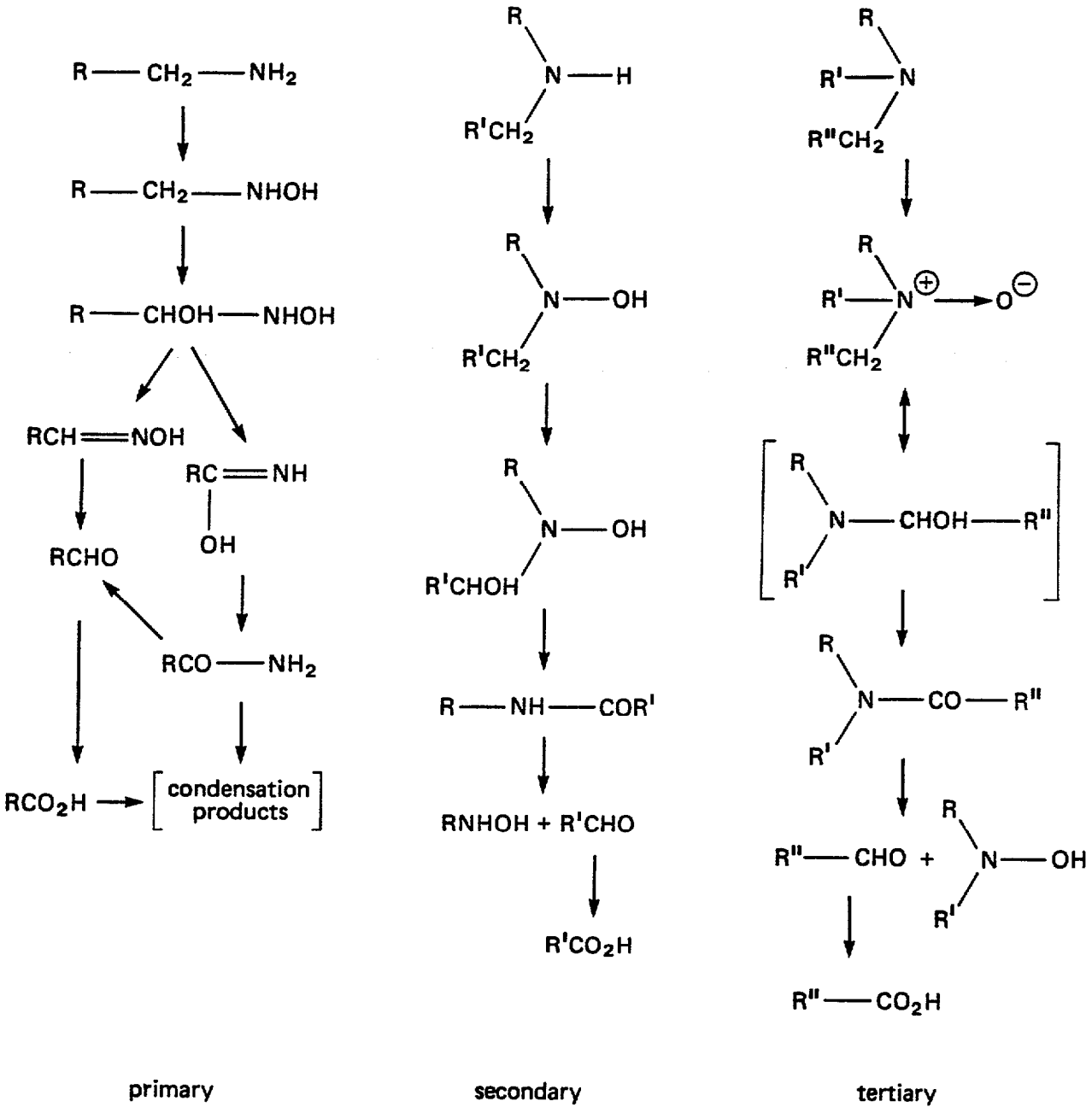


Figure 19. Reaction scheme for chlorination of peptides and proteins. (Bieber and Trehy, 1983).

Figure 20. Reaction schemes for ozonation of amines.
(Elmghari – Tabib et al., 1982).



primary secondary tertiary

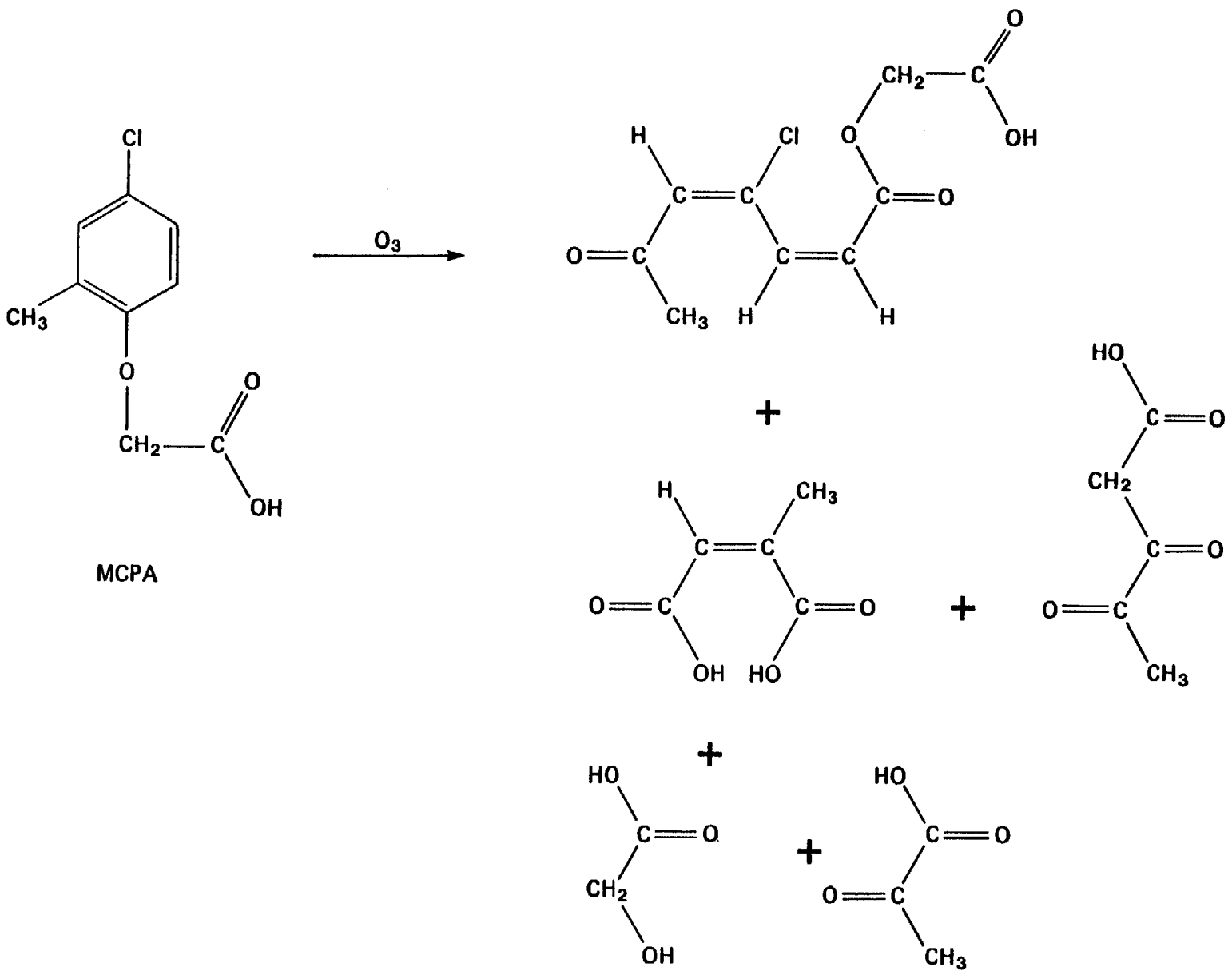


Figure 21. Reaction products from ozonation of MCPA (4-chloro-2-methylphenoxyacetic acid: Legubé et al., 1981).