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Invited Review

# Reaction pathways and mechanisms of photodegradation of pesticides

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## Abstract

The photodegradation of pesticides is reviewed, with particular reference to the studies that describe the mechanisms of the processes involved, the nature of reactive intermediates and final products. Potential use of photochemical processes in advanced oxidation methods for water treatment is also discussed. Processes considered include direct photolysis leading to homolysis or heterolysis of the pesticide, photosensitized photodegradation by singlet oxygen and a variety of metal complexes, photolysis in heterogeneous media and degradation by reaction with intermediates generated by photolytic or radiolytic means. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Due to the world-wide general application of intensive agricultural methods during the last few decades and to the large-scale development of the agrochemical industry, the variety and quantities of agrochemicals present in continental and marine natural waters has dramatically increased. Most pesticides are resistant to chemical and/or photochemical degradation under typical environmental conditions [1]. In recent years, the scientific community has shown a great concern about the possible adverse effects that the presence of these pesticides in water and food [2] may have for human health and for the equilibrium of ecosystems [3–7]. Such concern, which has recently been highlighted [8,9], is supported by results from major monitoring studies already performed over 20 years ago [10], and confirmed by more recent investigations. Among the possible chronic effects of these compounds are carcinogenesis [11,12], neurotoxicity [13], effects on reproduction [14] and cell development effects, particularly in the early stages of life [15]. With increasing global demand for vegetables, the situation does not look likely to improve. In fact, the current situation might

worsen with the appearance of new and more sophisticated substances.

The critical nature of this environmental problem has prompted the development of faster and more accurate methods for the characterisation and quantification of the pesticides dispersed in the environment. These have generally been very successful. However, until now no completely efficient methods have been developed for remediation of contaminated waters [16].

Advanced oxidation processes (AOPs) are at present considered to have considerable potential in this area and a general survey of these can be found in the review by Legrini et al. [17]. The most efficient of these used nowadays involve the use of UV irradiation with light of an appropriate wavelength [18–21]. The method is based on the ability of UV radiation to attack and damage the DNA of undesirable microorganisms. As a consequence, photochemical processes may take place, in which different transient species are generated:  $e_{aq}^-$  (photoionization), radicals generated by bond homolysis or bond heterolysis, etc, as well as a number of photophysical processes (fluorescence, phosphorescence, etc.) Alternatively, UV-sensitive materials may be added to give rise to photosensitized oxidation, that allow the use of wavelengths that are not absorbed by the pesticides [17]. Hydroxyl radical (HO $\cdot$ ) might also be generated by various different ways, giving rise to induced photodegradation.

The regulations for the control of the quality of water for human use in the European Union clearly establishes

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the maximum admissible values of different substances in solution [22]. Among these, pesticides are identified as toxic, with very low concentrations of them in general being allowed (a maximum permissible concentration for a particular pesticide of 0.1 ppb and of 0.5 ppb for the total load of all plaguicides). In addition, these regulations also establish maximum concentrations for the products of degradation of pesticides [23,22]. No maximum concentration levels have been established in the USA, the regulations depending on the particular compounds, based on the toxicological evidences available for them [24].

The literature reports on pesticide photodegradation products is relatively abundant. However, little information is available on the reaction mechanisms involved in the photolysis of pesticides under typical environmental conditions [1]. The environmental photochemistry of herbicides was reviewed several years ago [25]. Similarly, the kinetics and mechanisms of photodegradation of chlorophenol pesticides have recently been discussed [26].

Considering the environmental relevance and importance of this problem, we review the state-of-the-art situation on the photodegradation of pesticides. These will be classified in terms of the main structural groups, following a chronological order within each group. We shall concentrate on the behaviour in solution and on solid supports. The photochemical decomposition of pesticides and herbicides on plants, on model plant systems and on soil is of fundamental importance to the situation in vivo. Some studies in this area, notably on model plant cuticles, are presented in Section 2. However, much less detailed mechanistic information is available in this case, and we feel, that as a first approximation, it is not unreasonable to extrapolate the behaviour from solution or solid supports to these systems. Most papers reviewed are from the last decade, although some previous articles have also been included to facilitate understanding of mechanistic pathways. Although the production and use of some of the pesticides discussed has been discontinued, we have still considered them, because of their possible persistence in the environment. In identifying products, we report a systematic name in all cases, as some of the common commercial names have changed through the years (CAS names are given in those cases where no systematic name has been found). In addition, we note that several excellent compendia are available compiling the different names and properties of the various different compounds [27–31]. We have chosen to classify the photodegradation studies into four broad categories: direct photodegradation, photosensitized degradation, photocatalyzed degradation and degradation by reaction with hydroxyl radical. Within each group these are discussed in terms of general classes of compounds. However, in some cases these categories overlap. In such situations, we have tried to fit the work to the field that is the authors' main target area. Finally, our aim in this review is to compile and annotate the main reaction types and mechanisms. We do not attempt to

evaluate or authoritatively criticise the cited literature, but hope that this review will stimulate more detailed analyses of the data in each of the particular areas discussed.

## 2. Direct photodegradation

Most pesticides show UV–Vis absorption bands at relatively short UV wavelengths. Since sunlight reaching the Earth's surface (mainly UV-A, with varying amounts of UV-B) contains only a very small amount of short wavelength UV radiation [32,33], the direct photodegradation of pesticides by sunlight is expected to be, in general, of only limited importance. Abundant studies are available, however, with steady state and/or laser-pulsed UV radiation.

Direct irradiation will lead to the promotion of the pesticides to their excited singlet states, which may then intersystem cross to produce triplet states. Such excited states can then undergo, among other processes: (i) homolysis, (ii) heterolysis or (iii) photoionization, as depicted in Scheme 1.

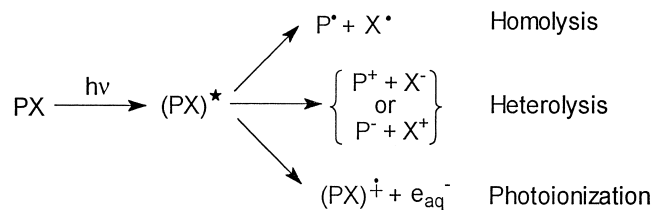
Because of the particular relevance to the photoreactivity of these pesticides under sunlight, relevant references to product identification, kinetics, mechanisms and toxicity of degradation products are summarised in Table 1. More detailed information of photoreactivity under both solar and ultraviolet irradiation is given in the following sections.

### 2.1. Amidinohydrazone insecticides

Adityachaudhury et al. [34] studied the sunlight photodegradation of hydramethylnon {5,5-dimethylperhydro-pyrimidin - 2 - one - 4 - trifluoromethyl -  $\alpha$  - (4 - trifluoromethylstyryl) cinnamylidenehydrazone} and found three products. Transformation took place within 10 h, with the rate of disappearance being only marginally affected by the acidity of the medium.

### 2.2. Anilide herbicides

Tanaka et al. [35] studied the formation of biphenyls upon sunlight photolysis of propanil {3',4'-dichloro-propionanilide}. Coupling of two herbicide molecules took place, leading to formation of a chlorinated biphenyl, with



Scheme 1. Possible chemical events taking place upon direct photolysis.

Table 1  
Studies on pesticides photodegradation under sunlight or simulated sunlight

Compounds	Product identification	Kinetics	Mechanistic studies	Toxicity measurements
Amidinohydrazones	[34]	[34]		
Anilides	[35]	[36–38]		[39]
Avermectins		[40]		
Carbamates	[35,41,42,34,43–46,37]	[47,48]	[49]	
Carboxamides	[50]			
Chloronicotinoids	[51,52]			
Chlorophenols	[53]	[53,54]		
Dicarboximides	[55]			
Dichloroanilines		[53]		
Dinitroanilines	[56]	[57]		
Diphenylethers	[58]			
Halobenzonitriles	[59]			
Mercapto-pyridine- <i>N</i> -oxides				[60]
Methylisocyanate		[61]		
Organophosphorous derivatives	[62–65]	[66,57]	[67]	
Oxadiazoles	[58]	[36]		
Phenols	[68]		[68]	
Phosphorothioates	[69]			
Pyrimidines		[70]		
Sulfonylureas	[71,72]	[73]	[74]	
Thiocarbamates	[75–77]	[78,38]		
Thiones	[79]			
Triazines	[80]	[81,82,38]	[83]	
Triazinones	[84]			
Triazoles		[85]		
Ureas	[86–88,35,89,90]			

very low yield. Probably, the photolability of such a biphenyl would lead to fast degradation, so that they would accumulate only to a very low extent.

The major photoproducts found upon irradiation of alachlor [2-chloro-2',6'-diethyl-*N*-methoxymethylacetanilide] with a medium pressure mercury lamp were hydroxyalachlor and a lactam, plus another three products: norchloralachlor, 2',6'-diethylacetanilide and 2-hydroxy-2',6'-diethyl-*N*-methylacetanilide [91]. The author suggests that the mechanism proceeds via homolytic scission of the C–Cl bond, followed by trapping of the radical so-formed by water or intramolecular hydrogen abstraction.

Albanis and Konstantinou [92] studied the photodegradation of propachlor {2-chloro-*N*-isopropylacetanilide} and propanil {3',4'-dichloropropionanilide} in water and soil, and found the half-lives of the compounds to be  $\approx 1$ –2 months in water and  $\approx 1$  month in soils. The presence of humic substances reduced the photodegradation rate in water but led to an enhancement in soil. The major photoproducts found were the hydroxy and dechlorinated derivatives.

Lin et al. [39] looked into the effect of simulated sunlight on metolachlor {2-chloro-6'-ethyl-*N*-(2-methoxy-1-methylethyl)acet-*o*-toluidine} toxicity in surface waters. They concluded that the toxicity of the herbicide is

reduced, possibly through photodegradation. The observed reduction of toxicity was higher in bay water than in fresh water.

Recently, Mabury and Wilson [37] have investigated the photodegradation of alachlor (vide supra), butachlor {*N*-(butoxymethyl)-2-chloro-2',6'-diethyl-acetanilide}, metolachlor (vide supra) and the model compound 2-chloro-*N*-methylacetanilide in a solar simulator, with the aim of determining the extent of monochloroacetic acid production. The photodegradation followed pseudo-first order kinetics, which was independent of the pH of the medium. Photolysis in synthetic field water reduced the time of photolysis.

Hogenboom et al. [93] used on-line solid-phase extraction liquid chromatography combined with mass spectrometry to screen the products of photodegradation of alachlor (vide supra) and related structures. The structures of ten photodegradation products were proposed, based on the most likely fragmentation MS patterns. Comparison with the results of Hapeman-Somich [91] indicates a rather complicated reaction scheme. However, it is not clear how many of the products resulted from secondary photolysis pathways.

The aqueous photodegradation of butachlor (vide supra) by sunlight takes place with a pseudo-first order rate constant  $0.012 \text{ h}^{-1}$  ( $t_{1/2} = 58.2 \text{ h}$ ) [36].

### 2.3. Bipyridinium herbicides

Different authors [94,95] have shown that photolysis of paraquat [1,1-dimethyl-4,4'-bipyridinium dichloride] yields 4-carboxy-1-methylpyridium ion and methylamine, with the mechanism involving a transient ketone or aldehyde. More recently [96], it has been found that irradiation of paraquat in the presence of oxygen, led to formation of 4,4'-bipyridyl and 4-picolinic acid. In addition, sequential loss of methyl was found to lead to monoquat [1-methyl-4,4'-bipyridinium dichloride] and 4,4'-bipyridyl. The mechanism proposed for formation of 4-picolinic acid involves an oxidative ring cleavage of 4,4'-bipyridyl or demethylation of 4-carboxy-1-methylpyridium ion. If paraquat is irradiated for longer times oxalate, succinate, malate and *N*-formyl glycine are formed.

### 2.4. Carbamate insecticides

Aly and El-Dib [97] investigated the photodecomposition of sevin (carbaryl) {1-naphthyl methylcarbamate}, baygon (propoxur) {2-(1-methylethoxy)phenyl methylcarbamate}, pyrolan {3-methyl-1-phenylpyrazol-5-yl dimethylcarbamate} and dimetilane {pyrazole-1-carboxamide, 3-hydroxy-*N,N*,5-trimethyl-, dimethylcarbamate}. In the case of sevin and baygon the rate of photodegradation increase with the pH of the medium, while no effect was observed for pyrolan and dimetilane. The main photochemical event observed was the bond scission of the ester.  $\alpha$ -Naphthol was identified as the main photoproduct derived from sevin. The order of photostability found was pyrolan > dimetilane > baygon > sevin.

The photodegradation of zectran {4-dimethylamino-3,5-xylyl-*N*-methyl carbamate} was studied in aerated and degassed cyclohexane and ethanol [98]. A photo-Fries rearrangement was proposed as the main reaction pathway.

Kumar et al. [99] studied the 265 nm photodegradation of azak {2,6-di-*tert*-butyl-4-methylphenyl-*N*-methylcarbamates} in aerated or degassed ethanol. A radical mechanism taking place via a photo-Fries rearrangement involving a cyclohexadienone intermediate was proposed.

While studying the photoinduced transformation of ethyl-*N*-phenylcarbamate to ethyl *o*-aminobenzoate, ethyl *p*-amino-benzoate and aniline, Masilamani and Hutchins [100] found an effect of the concentration of the starting material. According to these authors, at high concentrations of carbamate ethyl *o*-aminobenzoate is predominant, while at low concentrations aniline is the only product observed.

A more recent and very detailed study of the UV photodegradation of various alkyl *N*-arylcabamates in ethyl propionate and cyclohexane has been carried out by Herweh and Hoyle [101]. These authors propose a mechanism involving an excited singlet state that undergoes homolytic cleavage of the C–N bond to a radical pair in a solvent cage. This radical pair eventually leads to amines

and photo-Fries rearrangement products, with a low quantum efficiency. In contrast to previous findings, these authors did not observe any effect of the concentration of starting carbamate [100].

Tanaka et al. [35] investigated the generation of biphenyls upon sunlight photolysis of chlorpropham {isopropyl 3-chlorocarbanilate} and PPG-124 {4-chlorophenyl methylcarbamate}. The photoreactions took place via coupling of the two insecticide molecules, leading with very low yield to formation of a chlorinated biphenyl. The high photolability of these biphenyls would lead to their fast degradation, so that they would not accumulate significantly.

A report has been presented of the photochemical degradation of carbaryl (vide supra) and carbofuran {2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate} by the action of sunlight and UV ( $\lambda > 290$  nm) in natural waters of Northern Greece [76]. The major photoproduct observed from degradation of carbofuran was carbofuran-phenol, which further photodegraded. The major photoproduct observed from degradation of carbaryl was  $\alpha$ -naphthol. Continuous irradiation led to almost complete degradation of the pesticide.

The photodegradation of carbetamide {(*R*)-1-(ethylcarbamoyl)ethyl carbanilate} by 290 nm light has been studied in water, ethanol, methanol and a water/1% acetone mixture [41]. The highest quantum yield of photodegradation ( $\approx 9\%$ ) was observed in aqueous acetone. The presence of formulation additives produced, in all cases, a decrease in the photodegradation quantum yield. Aniline and hydroxy phenyl carbamoyloxy 2-*N*-ethyl propionamide were identified as the main photoproducts of aqueous photodegradation.

With relevance to the design and synthesis of light-sensitive urethanes as photoprecursors of amines, Cameron and Fréchet [102] proposed a heterolysis mechanism for the UV photocleavage of carbamates. They subsequently, while studying the photogeneration of organic bases from carbamate derivatives, reported the existence of steric and electronic effects on the quantum efficiency of 254 nm photolysis [103].

The photodegradation of aldicarb {2-methyl-2-(methylthio)propionaldehyde *O*-methylcarbamoyloxime}, carbaryl (vide supra) and carbofuran (vide supra) has been studied using the UV radiation from a high pressure mercury lamp and from a suntest apparatus equipped with a Xe arc lamp in distilled, pond and artificial water, in the absence and presence of humic acids [42]. Aldicarb sulfoxide and 1-naphthol, respectively, were identified as the major photodegradation products from aldicarb and carbaryl. An unidentified major product was produced upon photolysis of carbofuran. Photosensitizing effects, leading to an enhancement of photodegradation were observed with carbaryl and carbofuran when using water containing humic acids.

Adityachaudhury et al. [34] studied the sunlight induced

photodegradation of carbofuran (vide supra). The authors claim they characterized more than twenty photoproducts. Only two of these were, however, confirmed by comparison with authentic samples.

Benítez et al. [104] studied the photooxidation of aqueous solutions of propoxur (vide supra) using the radiation supplied by a low-pressure mercury lamp. This study included the effects of temperature, pH and pesticide concentration, as well as of added O<sub>3</sub> [104]. As a result, a general rate equation for the direct UV photolysis was proposed, with the quantum yield being effectively insensitive to the pH. The process in the presence of O<sub>3</sub> can be divided into a direct reaction with O<sub>3</sub>, a direct photochemical process and a combination of both. An appropriate reaction scheme has been proposed.

The 355 nm laser flash photolysis of *N*-hydroxypyridine-2-thione carbamates yielded dialkylaminyl radicals which, upon protonation, produced the corresponding dialkylaminium radical cations [49]. The kinetics of the reactions undergone by these aminium radical cations have been studied and reported, as well as their acidity constants.

The photodegradation of ethiofencarb {2-[(ethylthio)methyl]phenyl methylcarbamate} by UV light ( $\lambda > 280$  nm) and natural sunlight has been studied in the presence of cyclohexane, cyclohexene and isopropanol, in an attempt to model its photolysis on plant surfaces [44]. The efficiency of the photodegradation was higher in less polar solvents, with the observed half-lives ranging from 75 min to more than 20 h. Different products were obtained depending on the solvent and the light source: ethiofencarb sulfoxide was the main product of irradiation in cyclohexane, while photooxidation, hydrolysis and addition product formation was observed when the photolysis took place in isopropanol.

Benítez et al. [43] studied the photodegradation of aqueous solutions of carbofuran (vide supra) by the polychromatic light supplied by a high-pressure mercury lamp (emitting from 185 nm through to the visible region). The authors claim that the contribution of hydroxyl radicals to the degradation is negligible, since no effect of tert-butyl alcohol was observed on the rate of degradation upon direct photolysis. A simple rate equation is proposed to describe the process and the quantum yield obtained and correlated by an Arrhenius-type expression.

Pirisi et al. [45] have studied the photolysis of pirimicarb {2-dimethylamino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate} in water and in the solid-phase, using three different light sources, a low pressure mercury lamp, high pressure mercury lamps and sunlight, for irradiation. Three photoproducts were observed in solution: 2-[(methylformyl)amino]-5,6-dimethylpyrimidin-4-yl dimethylcarbamate, 2-(dimethylamino)-5,6-dimethyl-1-hydroxypyrimidine and 2-(methylamino)-5,6-dimethylpyrimidin-4-yl dimethylcarbamate. This later product underwent decomposition to yield 2-amino-5,6-di-

methylpyrimidin-4-yl dimethylcarbamate and 2-(formylamino)-5,6-dimethylpyrimidin-4-yl dimethylcarbamate. In the solid-phase 2-[(methylformyl)amino]-5,6-dimethylpyrimidin-4-yl dimethylcarbamate and 2-(methylamino)-5,6-dimethylpyrimidin-4-yl dimethylcarbamate were the observed photoproducts. The different wavelengths used do not seem to change the reaction pathways, but only affect the degradation rate. The mechanism does not seem to be radical-mediated.

A detailed GC–MS study of the products resulting from photolysis of different carbamates by the UV radiation produced by a medium-pressure mercury lamp has been carried out by Climent and Miranda [105,106]. The compounds studied were bendiocarb {2,3-isopropylidenedioxyphenyl methylcarbamate}, isoprocarb {*o*-cumenyl methylcarbamate}, promecarb {3-isopropyl 5-methylphenyl methylcarbamate}, ethiofencarb (vide supra), furathiocarb {butyl 2,3-dihydro-2,2-dimethylbenzofuran-7-yl *N,N'*-dimethyl-*N,N'*-thiodicarbamate}, fenoxycarb {ethyl 2-(4-phenoxyphenoxy)ethylcarbamate} and pirimicarb {2-dimethylamino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate}. In general, photodegradation led to the corresponding phenols as main photoproducts. Photoprocesses such as photo-Fries rearrangements, C–S or N–S bond cleavage or oxidative demethylation were observed, depending on the structures of the compounds.

Mansour et al. [46] studied the photolysis of carbofuran (vide supra) in water and water/soil suspensions using UV light of different wavelengths. The photodegradation was very slow when carbofuran was irradiated with  $\lambda > 290$  nm, but was substantially enhanced in the presence of TiO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> or O<sub>3</sub>.

Albanis and Konstantinou [92] have studied the photodegradation of molinate {*S*-ethyl hexahydro-1*H*-azepine-1 carbothioate} in water and soil. The half-life of the compounds was  $\approx 1$ –2 months in water and  $\approx 1$  month in soils. The presence of humic substances reduced the photodegradation rate in water, but an enhancement was observed in soil. The major photoproduct found was the keto derivative.

The photodecomposition of carbofuran (vide supra) by 254 nm UV light in water follows first-order reaction kinetics [107]. The presence of dissolved organic matter was found to inhibit the photodegradation of carbofuran. The photoproducts were identified by GC–MS and <sup>1</sup>H NMR. A tentative mechanism was proposed for the photodegradation. According to the authors, the carbamate group is cleaved from carbofuran via C–O heterolysis, yielding a phenoxide anion and an acylium cation. The furan moiety of the phenoxide anion then undergoes ring opening in a second step, leading to a substituted catechol moiety with a tert-butyl alcohol substituent. This catechol dehydrates, yielding an alkene.

The photodegradation of the systemic insecticide ethiofencarb (vide supra) has been studied in water, methanol and hexane using a solar simulation unit [47].

The kinetics of photodegradation can be fitted to a first-order rate equation, independent of the nature of the medium, with the reaction rate increasing with the polarity of the medium. The photoproducts depend on the solvents. In water, photocleavage of the C–S bond yields 2-(methyl)phenyl-*N*-methylcarbamate.

Vialaton and Richard [108] carried out a 266-nm laser flash photolysis study of the photolysis of ethiofencarb (vide supra). A quantum yield of 12% was estimated for the photoconversion of ethiofencarb into its sulfoxide, 2-methylphenyl-methylcarbamate and to a further two unidentified products. The homolytic cleavage of the C–S bond was confirmed by spectroscopic detection of benzyl radicals. The authors suggest that the mechanism of generation of the sulfoxide may result from an electron transfer from the triplet excited state to oxygen, yielding a radical cation which then recombines with the superoxide ion, to produce an intermediate peroxy sulfoxide, eventually leading to the sulfoxide.

A study of the direct photolysis of propoxur (vide supra) in water, using 266 nm laser flash photolysis showed almost complete disappearance of propoxur, with formation of the corresponding photo-Fries rearrangement products [109]. According to the authors, the process can be rationalized on the basis of an initial homolytic C(O)–O scission of the carbamate moiety from the singlet excited state of propoxur, with generation of 2-isopropoxyphenoxy-carbamoyl radical pair. Radical recombination or escape out of the cage would produce the observed photoproducts. No oxygen quenching was observed.

Ibarz et al. [48] studied the aqueous photodegradation of carbendazim {methyl-2-benzimidazole carbamate} at various pH values, using the radiation supplied by a mercury lamp emitting between 250 and 750 nm. The process followed a first-order rate equation, and the rate of photodegradation increased with pH and O<sub>2</sub> concentrations. The quantum yields for photodegradation at different pH values were in all cases very low (less than 1%).

Detailed studies of the initial stages of photodegradation of a variety of carbamates using laser flash photolysis combined with pulse radiolysis showed the photodegradation is a biphotonic process when 308, 266 and 248 nm light is used for excitation, and monophotonic if 193 nm light is used. Photoionization is observed in all cases, with very low quantum yields, as well as formation of the corresponding phenoxy radicals. The observed photoproducts, detected using GC–MS and HPLC, and checked in some cases against authentic commercial samples, were the corresponding phenols and photo-Fries products. The rate constants for one-electron oxidation of the carbamates by SO<sub>4</sub><sup>•-</sup>, one-electron reduction by e<sub>aq</sub><sup>-</sup>, and for HO<sup>•</sup> addition were obtained. Structure–reactivity correlations have been established in order to predict the reactivity of other carbamates upon direct photolysis [110].

However, it is worth noting that in aqueous solutions, hydrolysis of carbamates may efficiently compete with

photodegradation, and in some cases may even be the dominant pathway.

### 2.5. Carboxamide fungicides

In the presence of humic acid the half-life of photodegradation of carboxin {5,6-dihydro-2-methyl-*N*-phenyl-1,4-oxathiin-3-carboxamide} was reduced by 25%. Oxy-carboxin {5,6-dihydro-2-methyl-*N*-phenyl-1,4-oxathiin-3-carboxamide 4,4,-dioxide} photodegradation after 8 h increased from 10 to 25% [111,112].

UV irradiation ( $\lambda > 290$  nm) of prochloraz {*N*-propyl-*N*-[2-(2,4,6-trichlorophenoxy)-ethyl]imidazole-1-carboxamide} in soil led to prochloraz-formylurea, which subsequently hydrolysed to prochloraz-urea [50].

### 2.6. Chloronicotinoid insecticides

Irradiation of imidacloprid {1-(6-chloro-3-pyridin-3-yl-methyl)-*N*-nitroimidazolidin-2-ylidenamine} in aqueous solution with 290 nm light resulted in 90% degradation after 4 h [51]. The main photoproducts were identified as 6-chloronicotininaldehyde, *N*-methylnicotinamide, 1-(6-chloronicotinyl)imidazolidone and 6-chloro-3-pyridylmethyl-ethylendiamine. Some minor products were also formed, but not identified.

The sunlight induced photolysis of the insecticide imidacloprid (vide supra) in aqueous solution was studied on the surface of tomato leaves [52]. The photodegradation was rapid, and five photoproducts were found, four of which could be identified.

Kole et al. [56] studied the UV photolysis (240–260 nm) of imidacloprid (vide supra) in 10% acetonitrile/water. Three photoproducts were observed, and were suggested to be formed by N–NO<sub>2</sub> bond cleavage, hydroxylation of the imidazolidine ring and oxidative cleavage of the methylene bridge. The authors sketch a possible mechanism for the process.

An additional study of the photodegradation of imidacloprid (vide supra) has been reported in HPLC grade water and as the formulated product Confidor in tap water [113]. Several degradation products have been identified, with 1-(6-chloro-3-pyridinyl)-methyl-2-imidazolidinone as the main one. The photodegradation followed a first-order rate equation.

### 2.7. Chlorophenol pesticides

Miille and Crosby [53] studied the photodegradation of pentachlorophenol by simulated sunlight in seawater. The photolysis reaction was slower in seawater, which was attributed to the photonucleophilic interaction of the substrate with chloride ions. Photooxidation, photonucleophilic substitution and photoreduction reactions were observed. The amount of photoreduction products was higher than in distilled water, and the unstable tetrachloro-

muconic acid was isolated and identified as an intermediate ring-fission photoproduct.

The photodegradation of MCPA {4-chloro-2-methylphenoxy acetic acid} was studied in distilled water and river (Thames) water, using low intensity 300–450 nm UV light and sunlight [54]. Upon UV irradiation, MCPA photodegradation was almost negligible in distilled water, while in river water it accelerated. Early autumn sunlight photolysis took place with a pseudo first-order rate constant  $k_{\text{exp}} = 0.009 \text{ h}^{-1}$  ( $t_{1/2} = 168 \text{ h}$ ).

## 2.8. Cyclodiene insecticides

Mukerjee et al. [114] reported an amine-induced stereoselective method of photodehalogenation of aldrin {(1*R*,4*S*,4*aS*,5*S*,8*R*,8*aR*)-1,2,3,4,10,10-hexachloro-1,4,4*a*,5,8,8*a*-hexahydro-1,4:5,8-dimethanonaphthalene}, in which they obtain a mixture of two photoproducts in the proportion 9:1 upon irradiation with a high pressure Hg lamp.

## 2.9. Dicarboximide fungicides

Schwack et al. [115] examined the photodegradation of vinclozolin {3-(3,5-dichlorophenyl)-5-methyl-5-vinyl-1,3-oxazolidine-2,4-dione} in various organic solvents, in an attempt to simulate the plant cuticle environment, using a high-pressure Hg lamp. Different photoproducts were observed depending on the solvent, indicating that the formation of bound residues in plant cuticles is possible, with the solvent molecules in the model reactions being replaced by constituents of plant waxes and the cutin polymer. A similar study was carried out with iprodione {3-(3,5-dichlorophenyl)-*N*-(1-methylethyl)-2,4-dioxo-1-imidazolidinecarboxamide} [116].

Schwack et al. [55] analysed the potential of procymidone {3-(3,5-dichlorophenyl)-1,5-dimethyl-3-azabicyclo[3.1.0]hexane-2,4-dione} to undergo photoinduced processes in the presence of different organic groups. Their objectives were to seek explanations for the possible formation of bound residues in plant cuticles where solvent, waxes and cutin polymer molecules are present. A high pressure mercury lamp was used for irradiation ( $\lambda > 280 \text{ nm}$ ). Photodegradation in isopropanol or cyclohexane led to photodehalogenation and substitution by solvent molecules. Photodegradation in cyclohexene led to substitution of Cl by a solvent molecule, the monodehalogenated procymidone resulting as photoproduct.

Hustert and Moza [117] studied the photochemical degradation of procymidone (vide supra) and vinclozolin (vide supra) using a mercury lamp in the presence of soil constituents in water. The photodegradation rate in the presence of humic and fulvic acids increased relative to the situation in which they are absent.  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  photocatalyzed the disappearance of both compounds. Dechlorination and isomerization are the major photodegradation pathways.

Recently, Moza et al. [118] have revisited the photolysis of vinclozolin in water and methanol–water. Irradiation for 10 min at 254 nm resulted in  $\approx 90$ –95% degradation, while photolysis for 8 h at 290 nm resulted in 10% degradation, and irradiation for 8 h under artificial sunlight led to 55% degradation. The main photoproducts were 3,5-dichlorophenyl isocyanate and 3,5-dichloroaniline, generated by ring opening of the 2,4-oxazolidine-dione.

## 2.10. Dinitroaniline pesticides

$^{19}\text{F}$  NMR was suggested as a possible analytical tool for monitoring the sunlight photodegradation of trifluralin { $\alpha,\alpha,\alpha$ -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine} without extraction, cleanup, concentration or chromatographic separation procedures [119]. The major photodegradation products, identified by comparison with authentic samples were  $\alpha,\alpha,\alpha$ -trifluoro-2,6-dinitro-*N*-propyl-*p*-toluidine,  $\alpha,\alpha,\alpha$ -trifluoro-2,6-dinitro-*p*-toluidine and 2-ethyl-7-nitro-5-(trifluoromethyl)benzimidazole. Different unidentified NMR peaks were attributed to labile intermediates not generally observed with other analytical techniques.

Adityachaudhury et al. [34] investigated the transformation of the herbicide pendimethalin {*N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine using UV light of  $\lambda \geq 250 \text{ nm}$ . They found that the main processes taking place are *N*-dealkylation, arylmethyl oxidation, nitro group elimination and cyclization.

Mansour et al. [46] studying the photolysis of pendimethalin (vide supra) by UV light of different wavelengths in water and water/soil suspensions, found various conversion products, depending on the wavelength used for photolysis.

UV and sunlight induced photolysis of fluchloralin {*N*-(2-chloroethyl)-2,6-dinitro-*N*-propyl-4-(trifluoromethyl)-aniline} in aqueous methanol (80%) yielded four photoproducts, that the authors attribute to result from *N*-dealkylation, nitroreduction and cyclization pathways [56].

A theoretical framework has been presented to understand the combined effects of direct photolysis, layer thickness and transport processes on the photodegradation of organic pollutants on soil surfaces under environmental conditions, using a xenon long arc lamp, equipped with filters cutting out wavelengths below 280 nm and the IR [120]. The model has been used to explain the behaviour of trifluralin (vide supra) on kaolinite layers of variable thickness. The use of the appropriate experimental setup and a mathematical model allowed the authors to determine the rate constant for direct photolysis of trifluralin as  $k = 1.6 \text{ h}^{-1}$ . From this, it was shown that 20% of the initial amount of trifluralin was degraded without transport.

Miller et al. [57] developed a method based on a solid-phase microextraction technique to determine the rate of sunlight (simulated) photodegradation of trifluralin (vide supra) in the gas phase at high temperatures. The gas phase photolysis of trifluralin took place with half-lives of 22–24

min. The photodegradation rate was not affected by changing the temperature from 60 to 80 °C.

### 2.11. Diphenylether herbicides

In a study of the photodegradation of methanolic solutions of oxyfluorfen {2-chloro-1-(3-ethoxy-4-nitro-phenoxy)-4-(trifluoromethyl)benzene}, Adityachaudhury et al. [34] found 13 photoproducts.

Ying and Williams [58] studied the sunlight photodegradation of the oxyfluorfen {vide supra} in detail on soil and in water. The photoproducts detected showed that loss of the nitro group, dechlorination and cyclisation were the main processes taking place. The photodegradation was faster in water than in soil.

### 2.12. Halobenzonitrile pesticides

Kochany [59] studied the photodegradation of bromoxynil {3,5-dibromo-4-hydroxyphenyl cyanide} in aqueous solutions in the presence of carbonate and bicarbonate ions using from a mercury–xenon lamp ( $\lambda > 300$  nm). A quenching effect by carbonate was observed, as well as a smaller quenching by bicarbonate. The main photoproducts found were 3-bromo-4-hydroxybenzoxynitrile and 4-hydroxybenzoxynitrile. Small amounts of other unstable or unidentified products were detected. The results suggest that carbonate may be involved in the photodegradation of bromoxynil, although the nature of the processes involved is not clear.

The photodegradation has been studied of bromoxynil (vide supra), chlorothalonil {tetrachloroisophthalonitrile}, chloroxynil {3,5-dichloro-4-hydroxybenzoxynitrile}, dichlobenil {2,6-dichlorobenzoxynitrile} and ioxynil {4-hydroxy-3,5-diodobenzoxynitrile} in aqueous, pH-buffered and organic solutions, using the radiation supplied by a xenon lamp [121]. The quantum yields for photolysis were, respectively, 0.0093, 0.0001, 0.0060, 0.0000 and 0.0024. Dichlobenil did not undergo photoreactions under the conditions used. Results indicate that the photoreactivity is influenced by the presence of both substituted halogen groups and hydroxy substituents.

The main processes involved in the UV photolysis ( $\lambda \geq 250$  nm) of the fungicide chlorothalonil (vide supra) in ethanolic and methanolic aqueous solutions seems to be the homolytic cleavage of 4-C–Cl bond followed by alkylation of the  $\alpha$ -radicals derived from the alcohols [56]. 4,5,7-trichloro-6-cyano-3-methyl-1(3*H*)-isobenzofuranone was identified as photoproduct in ethanolic solution and 4,5,7-trichloro-6-cyano-3,3-dihydro-1-isobenzofuranone in methanolic solution.

### 2.13. Organophosphorus pesticides

The UV-induced photoreactions of the fungicides IBP {*S*-benzyl *O,O*-di-isopropyl phosphorothioate}, edifenphos

{*O*-aqueous solutions, thin films and *n*-hexane have been known for some time [62]. Photoisomerization by light of  $\lambda > 350$  nm was observed in the *S*-benzyl esters IBP and inezin, but not for the *S*-phenyl ester edifenphos. The photoisomerization of IBP led to a reverse  $P=O \leftrightarrow P=S$  isomerization. The  $P=O$  derivatives of IBP and inezin underwent photooxidation to yield the corresponding *O*-benzyl esters. Cleavage of the P–S bond was observed, leading to formation of phenylthio radicals, which subsequently yielded benzoic acid or sulphuric acid via disulphides and sulfonic acids. Reductive cleavage, photohydrolysis and transesterification via radicals were also observed.

Mansour et al. [67] studied the sunlight induced photodegradation of parathion {*O,O*-diethyl *O*-4-nitrophenyl phosphorothioate} in deaerated water, methanol, 2-propanol and aqueous mixtures of these. The authors suggest that two main processes take place: a free-radical mechanism in apolar solvents and a ionic breakdown in aqueous solvents. The quantum yield for generation of photoproducts was  $\approx 0.1\%$ . The half-life time for photodegradation in water was  $\approx 65$  h at pH 7.8.

Wamhoff et al. [122] studied the photodegradation of azinphos-ethyl {*O,O*-diethyl-*S*-3,4-dihydro-4-oxobenzo[*d*][1,2,3]triazine-3-yl-methyl}phosphorodithioate} in chloroform and methanol solution using the radiation supplied by a high-pressure mercury lamp. 3,4-dihydro-3-methyl-4-oxobenzo[*d*][1,2,3]triazine-3,4-dihydro-4-oxo-benzo[*d*]-[1,2,3]triazine, *O,O*-diethyl-*o*-(3-methylbenzo[*d*][1,2,3]triazine-4-yl)phosphate, *N*-methyl-anthranilic acid and sulfur were found as photoproducts. The authors propose a reaction mechanism to explain the formation of the observed products, starting either with a C–S or C–N bond homolysis or with desulfuration by simultaneous C–S and P–S bond cleavages. The intermediate radicals or other species have, however, not been detected.

Photolysis of coumaphos {*o,o*-diethyl-*o*-(3-chloro-4-methyl-coumarin-7-yl)-thiophosphate} by radiation of  $\lambda > 313$  nm in chloroform led to head-to-tail [2+2] regioselective photodimerization to yield the anti-dimer. The reaction was not affected by singlet oxygen [63]. The authors established the structure of the compound by single crystal X-ray diffraction, and concluded that the photoreactive part of the molecule is the coumarin ring, with the thiophosphoryl group being relatively stable toward UV irradiation.

Esplugas et al. [123] studied the aqueous photodegradation of parathion (vide supra) using the UV radiation supplied by a mercury lamp. The rate of the process followed first-order kinetics, with the rate increasing with the pH of the medium. Very low quantum yields of less than 1% were obtained, depending on the pH. Coloured compounds were obtained. The authors recommend carrying out the photodegradation in alkaline medium, in order to improve the degradation yield.

The photochemistry of the herbicide butamifos {*O*-ethyl



*O*-5-methyl-2-nitrophenyl *sec*-butylphosphoramidothioate} has been studied using a 500-W xenon arc lamp [65]. An intramolecular oxygen transfer from the nitro group to the P=S moiety was observed. The nitroso-oxon derivative formed was photodegraded to various polar compounds. The photodegradation of butamifos and its photoproducts was found to be rapid and efficient.

The photodegradation of chlorpyrifos {*O,O*-diethyl *O*-3,5,6-trichloro-2-pyridyl phosphorothioate} and fenamiphos {ethyl 4-methylthio-*m*-tolyl isopropylphosphoramidate} by simulated sunlight in water/methanol (2–4%) has been studied [64]. Fenamiphos degraded more readily than chlorpyrifos. The major photoproducts were 3,5,6-trichloro-2-pyridinol and fenamiphos sulphoxide, respectively. Under the same conditions, the extent of photodegradation of vamidothion {*O,O*-dimethyl *S*-2-(1-methylcarbamoylthio)ethyl phosphorothioate} after 6 h of irradiation was only 2%.

Barceló et al. [83] studied the photodegradation of the insecticide fenitrothion {phosphorothioic acid *O,O*-dimethyl-*O*-(3-methyl-4-nitro-phenyl) ester} in a 20% methanolic solution, using a high-pressure mercury lamp. Attempts were made to use a suntest apparatus for the photolysis, but the photodegradation rate was too slow. Oxidation of the P=S group to trimethyl phosphate was the main photolytic pathway, although products of solvolysis and isomerization (*O,O,S*-trimethyl phosphorothioate and the *S*-methyl isomer of fenitrothion) were also observed. A further tentative photodegradation mechanism was proposed. These authors subsequently revisited the photodegradation of fenitrothion under similar conditions [124], and identified 21 photoproducts, arising from oxidation, isomerization, denitration and solvolysis. A tentative photodegradation scheme was proposed.

Mok et al. [66] carried out a comparative study of the quantum yields of direct photolysis of 16 different organophosphorus pesticides and their phenolic derivatives in aqueous solution. The solutions were irradiated at 254 and 313 nm, and a significant correlation was found between both sets of quantum yields. Similarly, a significant correlation was found between the quantum yields of the studied organophosphorus pesticides and those of their phenolic derivatives.

Niessner et al. [125] studied the aqueous photodegradation of parathion-methyl {*O,O*-dimethyl *O*-(4-nitrophenyl)phosphorothioate} by UV light at a pilot plant for drinking water treatment in the presence of O<sub>2</sub> and using a combination of O<sub>2</sub>/O<sub>3</sub>. The photodegradation rate increased when using this latter combination with respect to O<sub>2</sub>.

In two separate papers, Mabury and co-workers [126,127] have recently described the role of the CO<sub>3</sub><sup>•-</sup> radical anion in the sunlight induced degradation of fenthion {*O,O*-dimethyl *O*-[3-methyl-4-(methylthio)phenyl] phosphorothioate} in natural waters. The major degradation pathway was through fenthion sulfoxide,

possibly by one-electron abstraction on the sulfur atom to form a radical cation which would subsequently react with oxygen. 3-Methyl 4-methyl thiophenol was also formed by P–O bond cleavage. The photodegradation in carbonate/bicarbonate radical matrixes took place faster than by direct photolysis.

Miller et al. [57] developed a method based on the analytical technique of solid-phase microextraction to determine the rate of sunlight (simulated) photodegradation of chlorpyrifos (vide supra) in gas phase at high temperatures.

The effect of visible and UV(A–C) light on fenthion (vide supra) and disulfoton {*o,o*-diethyl *S*-2-ethylthioethyl phosphorodithioate} was studied. Visible light did not induce photodegradation, that took place with UV light. The photodegradation process was faster in aqueous solution than in solid-phase, probably due to the presence of the dissolved oxygen in the former. Under the same conditions, fenthion (vide supra) is more readily degraded than disulfoton (vide supra). The corresponding sulfoxides were identified as photolysis products, which are photostable in environmental conditions [128].

Recently a general review on the photochemical transformations of organophosphorus insecticides has been published, focusing on environmental problems and covering from the late 1960s to 2000 [129].

#### 2.14. Oxadiazole herbicides

Ying and Williams [58] studied the sunlight photodegradation of the oxadiazone {3-[2,4-dichloro-5-(1-methylethoxy)phenyl]-5-(1,1-dimethylethyl)-1,3,4-oxadiazol-2-(3*H*)-one} on soil and water. Three photoproducts were isolated and identified, showing that loss of chlorine was the main process taking place. The photodegradation was faster in water than in soil.

The aqueous photodegradation of oxadiazone (ronstar) {5-*tert*-butyl-3-(2,4-dichloro-5-isopropoxyphenyl)-1,3,4-oxadiazol-2(3*H*)-one} by sunlight takes place with a pseudo-first order rate constant 0.0245 h<sup>-1</sup> (*t*<sub>1/2</sub> = 28.5 h) [36].

#### 2.15. Phenol-based pesticides

The aqueous photodegradation of mecoprop {(*R,S*)-2-(4-chloro-*o*-tolylloxy)propionic acid} by 254 nm and polychromatic light was studied. The main products were found to be 2-methyl-phenol, 2-methyl-cyclohexadie-2,5-ene-1,4-dione, 2-methyl-methoxybenzene, 2-methyl-1,4-dihydroxybenzene and 2-methyl-4-chlorophenol [130], suggesting a radical-mediated mechanism.

A fast photodegradation of aqueous solutions of 2,4-D {2,4-dichlorophenoxyacetic acid} by UV radiation has been observed, with more than 99% of the starting material decomposing within the first hour of treatment [131]. The authors suggest that the main processes taking place

involve C–Cl and C–O bond homolysis, with a subsequent cascade of various free radical reactions. However, none of these radical intermediates were detected.

Climent and Miranda [132] studied by GC–MS and GC–FTIR the aqueous photodegradation of dichlorprop {2-(2,4-dichlorophenoxy)propionic acid} and 2-naphtoxyacetic acid, using a medium-pressure mercury lamp. Photolysis of dichlorprop under oxygen led to 2-chlorophenol, 2,4-dichlorophenol, 4-chlorophenol, 2,4-dichlorophenyl acetate, 2-(4-chloro-2-hydroxyphenoxy)propionic acid and 2-(2-chlorophenoxy)propionic acid. Under Ar, the first three of these products and the last one were also obtained, plus 2,4-dichlorophenyl ethyl ether. In the case of 2-naphtoxyacetic acid under oxygen atmosphere,  $\beta$ -naphthol and minor amounts of 2-hydroxy-1-naphthaldehyde and naphtho-[2,1-*b*]furan-2(1*H*)-one were the observed products, while only the first and last were observed under Ar atmosphere.

A mechanistic study of the photodegradation of the lampricide (3-trifluoromethyl-4-nitrophenol) was carried out, with irradiation at 365 nm [68]. The main photoproduct found was trifluoroacetic acid. The mechanistic study was extended to various trifluoromethylated phenols, and it was shown that the nature of the substituents, the substitution pattern and the acidity of the medium strongly affected the photodegradation process. The half-life times found for photodegradation were 22 and 91.7 h, at pH values of 9 and 7, respectively, with corresponding yields of trifluoroacetic acid of 5.1 and 17.8%. Photodegradation of trifluoromethylquinone led quantitatively to trifluoroacetic acid.

#### 2.16. Phenylamide pesticides

The photolysis of the fungicides metalaxyl (vide supra), benalaxyl {methyl *N*-phenylacetyl-*N*-(2,6-xylyl)-DL-alaninate} and furalaxyl {methyl *N*-(2-furoyl)-*N*-(2,6-xylyl)-DL-alaninate} in water was studied with different UV lamps emitting between 254 and 290 nm [45]. The authors propose a relatively complex mechanism involving two C–N bond scissions taking place via consecutive or parallel/consecutive processes. The bond cleavage is proposed to take place homolytically, leading to neutral nitrogen-centered radicals, that have not been detected.

The metalaxyl {methyl *N*-(2-methoxyacetyl)-*N*-(2,6-xylyl)-DL-alaninate} photodegradation after 8 h was observed to increase by 6–20% [111,112].

#### 2.17. Phosphorothioate insecticides

Mansour et al. [46] studied the photolysis of diazinon {*O,O*-diethyl *O*-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate} by UV light of different wavelengths in water and water/soil suspensions. Diazinon degraded faster in river water than in distilled water, and this rate enhancement was higher upon exposure to sun-

light. The effect of added humic acids was lower than that of river water components.

The photoreactions of potasan {*O,O*-diethyl-*O*-(4-methyl-2-oxo-2*H*-1-benzopyran-7-yl)-phosphorothioate} have been studied upon UV irradiation by light of  $\lambda > 313$  nm in chloroform and/or methanol alone and under conditions where singlet oxygen may be present [69]. The main photoproducts found were 2-oxo-2*H*-1-benzopyran-phosphate, 7-ethoxy-4-methyl-2-oxo-*sH*-1-benzopyran and a 3,3'-bipotasan dehydromer. The authors propose a mechanism involving homolytic cleavage of the 7-*O*–P bond to generate intermediate radicals which further react.

#### 2.18. Pyrazole insecticides

The photodegradation of fipronil {(±)-5-amino-1-(2,6-dichloro- $\alpha, \alpha, \alpha$ -trifluoro-*p*-tolyl)-4-trifluoromethyl-sulfinylpyrazole-3-carbonitrile} has been studied in acidic aqueous solution and on the surface of Niger and Mediterranean soils by the radiation supplied by a xenon lamp [133]. The degradation in aqueous solution followed first-order kinetics, and the observed photoproducts were 5-amino-4-cyano-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-phenylpyrazole and 5-amino-3-cyano-1-(2,6-dichloro-4-(trifluoromethyl)-phenyl)pyrazole-4-sulfonic acid, corresponding to desulfinylation and oxidation processes, respectively. The authors suggest that the mechanism is probably radical in nature, the primary photoproduct is the corresponding sulfone and from there those products are formed by simultaneous reactions. The mechanism was not elucidated, however. The photodegradation in soils led to the formation of 4-(trifluoromethyl)pyrazole, with the degree of photodegradation being inversely proportional to fipronil adsorption.

Crosby et al. [134] studied the photolysis of fipronil (vide supra) in aqueous solution to produce desthio-fipronil. The need for a sulfone intermediate has not been clarified, and the products of photodegradation not identified. Desthio-fipronil was formed directly and underwent photodechlorination, substitution of chlorine by trifluoromethyl, and pyrazole ring cleavage.

#### 2.19. Pyrimidine pesticides

Mateus et al. [135] investigated the photophysics and photochemistry of the fungicide fenarimol { $\alpha$ -(2-chlorophenyl)- $\alpha$ -(4-chlorophenyl)-5-pyrimidine methanol}. The photophysical studies suggest that the lowest excited singlet state has predominantly  $n, \pi^*$  character, and a small singlet–triplet splitting. Halides were found to quench fenarimol fluorescence. The photodegradation of fenarimol seems not to involve dechlorination. More recently, the same authors studied the kinetics and mechanism of photodegradation of fenarimol in natural water and the effect of salt solutions, using both sunlight and light of 313 nm [70]. The rate of photodegradation was found to

decrease with increasing salinity. Fluorescence quenching studies with halide and non-halide salts were carried out, and the correlation of the so-obtained rates with halide ion oxidation potentials suggests involvement of an electron transfer mechanism. This may be used to improve/reduce the fungicide photodegradability.

Adityachaudhury et al. [56] studied the UV (240–260 nm) and sunlight photolysis of fenarimol (vide supra) in aqueous methanol and isopropanol solutions. Upon 24 h of UV photolysis of methanolic solution, 2,4'-dichlorobenzil and *p*-chlorobenzoic acid were identified as photoproducts, while *p*-chlorobenzoic acid, 2,4'-dichlorobenzophenone and *o*-chlorobenzoic acid were the photoproducts found in aqueous isopropanol. Two additional unidentified photoproducts were formed upon sunlight photolysis. The authors suggest a mechanism for the process.

Recently, Bhattacharyya et al. [72] revisited the aqueous alcoholic photodegradation of fenarimol (vide supra) by light with  $\lambda \geq 250$  nm. Irradiation in an aqueous methanolic solution for a day yielded 2,4'-dichlorobenzil and *p*-chlorobenzoic acid, while in an aqueous isopropanol solution *p*-chlorobenzoic acid, 2,4'-dichlorobenzophenone and *o*-chlorobenzoic acid were found. The authors hypothesize possible mechanisms for these transformations, involving different C–C bond homolysis processes.

## 2.20. Sulfone herbicides

Ming and Wamhoff [136] studied the photolysis of dimethipin {2,3-dihydro-5,6-dimethyl-1,4-dithi-ine 1,1,4,4-tetraoxide} by 254 nm UV radiation in acetonitrile and methanol containing a small amount of water ( $\approx 0.5\%$ ). The disodium salt of ethane-1,2-disulfonic acid was identified as photoproduct resulting from  $\alpha, \alpha'$ -cleavage following  $n \rightarrow \pi^*$  excitation of both sulfonyl groups. 2-Butyne, the other fragment which should be produced from such fragmentation could not be identified, possibly, according to the authors, due to its volatility and/or rapid polymerization. Photolysis in acetone with longer wavelengths ( $\lambda > 313$  nm) led to the same photoproduct.

## 2.21. Sulfonylurea herbicides

The photodegradation of chlorimuron-ethyl {ethyl 2-(4-chloro-6-methoxy-pyrimidin-2-yl-carbamoylsulfamoyl)-benzoate} by sunlight and UV light has been studied on a soil surface [71]. The major photoproducts arise from cleavage of the sulfonylurea bridge, but some others are formed by dechlorination, hydrolysis and cyclization. The photodegradation follows first-order kinetics, with the process being much faster upon UV irradiation than upon sunlight irradiation.

The environmental fate of flupyr-sulfuron-methyl {methyl 2-(4,6-dimethoxy-pyrimidin-2-yl-carbomoylsulfamoyl)-6-trifluoro-methylnicotinate monosodium salt} was investi-

gated [137]. Photodegradation products were clearly identified, although hydrolysis was faster than photolysis.

Chowdhury and co-workers [56,138] studied the UV-induced photodegradation of metsulfuron {2-(4-methoxy-6-methyl-1,3,5-triazin-2-yl-carbamoylsulfamoyl)benzoic acid in water. They found that  $\approx 50\%$  of the herbicide was degraded within 15 h. They detected three photoproducts and proposed a mechanism involving hydrolytic cleavage of the sulfonylurea bridge to form the corresponding phenyl sulfonyl carbamic acid and *s*-triazine, with the carbamic acid subsequently decarboxylating to form a phenyl sulfonamide and a cyclic derivative.

The aqueous photodegradation of tribenuron-methyl {methyl 2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl-(methyl-amino)carbonyl]benzoate} both by sunlight and by the radiation supplied by a medium-pressure mercury lamp was found to take place readily [72]. The main photoproducts detected were *N*-methyl-4-methoxy-6-methyl-1,3,5-triazine-2-amine, methyl 2-(aminosulfonyl) benzoate, *o*-benzoic sulfimide, *N*-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-*N*-methyl urea and *N*-(2-carbomethoxyphenyl)-*N*-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-*N'*-methyl urea. The photodegradation process followed first-order kinetics and the reaction rate increased with pH and with the concentration of dissolved inorganic substances. The authors claim that the main processes taking place are cleavage of the sulfonylurea bridge, scission of the  $\text{SO}_2\text{-NH}$  bond and de-esterification and contraction of the sulfonylurea bridge.

Bufo et al. [73] studied the photolysis of rimsulfuron {1-(4,6-dimethoxypyrimidin-2-yl)-3-(3-ethylsulfonyl-2-pyridylfulfonyl)urea} and of its commercial formulation both in water and in organic solvents, using a high-pressure mercury lamp and solar simulator. The photolysis of the commercial formulation in organic solvents was faster than for pure rimsulfuron. The half-life for sunlight photodegradation in water ranged from 1 day at pH 5 to 9 days at pH 9. The authors report that the rate of hydrolysis is comparable to that of photolysis. The observed reaction products are, therefore, a mixture of hydrolysis and photolysis products.

Aqueous photodegradation of triasulfuron {1-[2-(2-chloroethoxy)phenylsulfonyl]-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea} by 254 nm radiation followed first order kinetics [74]. The observed photoproducts were 2-chloroethoxybenzene and (4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea. Upon sunlight photolysis the reaction was slower, yielding the same photoproducts plus 2-amino-4-methoxy-6-methyltriazine and 2-(2-chloroethoxy)benzenesulfonamide. The authors suggest a mechanism to account for the observed photoproducts.

## 2.22. Thiocarbamate herbicides

The photodegradation of EPTC {*S*-ethyl dipropylthiocarbamate}, PEBC {*S*-propyl butyl(ethyl)thiocarbamate} and cycloate {*S*-ethyl cyclohexyl(ethyl)-

thiocarbamate} by UV light supplied by a medium pressure mercury lamp in hexane has been studied [139]. The observed photoproducts were the corresponding formamide, dialkylamine, mercaptan and disulfide. The authors hypothesise a mechanism taking place via C–S bond homolysis, with subsequent recombination and H abstraction from the solvent to yield, respectively, a disulfide and a formamide. The observed disulfides could result from the combination of two sulfur-centered radicals. The dialkylamines found are probably due to the photolysis of the formamides, with loss of CO, and not to the direct cleavage of the thiocarbamates. No effects of the concentration of herbicide or temperature were observed. The authors note the increased biotoxicity of the photoproducts, relative to the starting herbicides.

Photolysis of thiobencarb {*S*-4-chlorobenzyl diethylthiocarbamate} at 300 nm in aqueous solution or in the form of a thin film led to 30 photoproducts, the most abundant of which were thiobencarb sulfoxide, *N*-desethyl thiobencarb, *N*-acetyl thiobencarb, 4-chlorobenzyl diethylcarbamate, *N*-(4-chlorobenzyl)diethylamine and 4-chlorobenzaldehyde [75]. The authors propose a mechanism involving photocleavage of the C–S bond to generate the 4-chlorobenzyl radical, which leads to 4-chlorotoluene in the presence of hydrogen donors. These authors also studied the photodegradation of diallate {*S*-2,3-dichloroallyl diisopropyl thiocarbamate}, finding it to be more photostable than thiobencarb, reacting mainly by *cis*–*trans* isomerization and via radicals formed at the *N*-alkyl and *S*-dichloroallyl moieties.

The photochemical degradation of thiram {tetramethylthiuram disulfide} by the action of sunlight and UV ( $\lambda > 290$  nm) was studied in natural waters of Northern Greece [76]. Two photoproducts were detected, but could not be identified. However, and in contrast with a previous report [140], it was shown that these were not ethylenethiourea or ethylenethioammonium.

The photodegradation of captan {*N*-(trichloromethylthio)cyclohex-4-ene-1,2-dicarboximide} by the UV radiation ( $\lambda > 280$  nm) supplied by a high-pressure mercury lamp was shown to be more efficient in cyclohexene and isopropanol than in cyclohexane [77]. The photolysis process takes place via C–Cl bond homolysis. If sufficient hydrogen donors are present *N*-(dichloromethylthio)-*cis*-4-cyclohexene-1,2-dicarboximide is formed, and then photodecomposes, losing thiophosgene to yield tetrahydrophthalimide.

The UV photolysis of sodium diethyldithiocarbamate, thiram (vide supra), captan (vide supra), captafol {*N*-(1,1,2,3-tetrachloroethylthio)cyclohex-4-ene-1,2-dicarboximide} and folpet {*N*-[(trichloromethylthio)phthalimide]} has been studied under N<sub>2</sub> atmosphere, photo-oxidation in the presence of oxygen, and by photosensitized oxidation using a 100-W tungsten lamp, also under oxygen atmosphere [141]. Various photoproducts have been identified, including SH<sub>2</sub>, S<sub>8</sub>, SO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>, CS<sub>2</sub>, amines, hydrazines,

thioamides and thioureas. Mechanisms involving radicals derived from C–S, S–S– and S–H bond homolysis have been put forward.

Thiobencarb (vide supra) photodegrades readily upon sunlight or UV (254 nm) photolysis [78]. The photodegradation by UV light takes places much faster. It has also been observed that the photodegradation is faster in aqueous solution ( $t_{1/2} = 1.5$  h with UV light, 3 days under sunlight) or on glass ( $t_{1/2} = 1$  h) or silica gel surfaces ( $t_{1/2} = 2$  h) than on a soil surface ( $t_{1/2} = 20$  h). The major photoproducts found were 4-chlorobenzyl alcohol, 4-chlorobenzaldehyde and 4-chlorobenzoic acid. A tentative mechanistic scheme is proposed, including a C–S bond cleavage process to form a 4-chlorobenzyl radical that further oxidizes successively to 4-chlorobenzyl alcohol, 4-chlorobenzaldehyde and 4-chlorobenzoic acid. Oxidation at the S atom would yield thiobencarb sulfoxide and thiobencarb sulfone, which further decompose to the corresponding sulfinic and sulfonic acids, leading eventually to 4-chlorobenzoic acid.

Vialaton and Richard [108] carried out a 266-nm laser flash photolysis study of the photolysis of thiobencarb (vide supra). A quantum yield of 14% was estimated for the photoconversion of thiobencarb into 4-chlorobenzaldehyde, 4-chlorobenzylalcohol and 2-methylphenylmethylcarbamate, with the first one being formed by homolytic C–S bond cleavage, and the last two by heterolytic C–S bond cleavage. The authors suggest the mechanisms involved electron transfer from a triplet excited state to oxygen, yielding a radical cation, which then cleaves to yield the benzaldehyde derivative.

### 2.23. Triazine pesticides

Pape and Zabik [142] studied the 254-nm photolysis of atrazine {6-chloro-*N*<sup>2</sup>-ethyl,*N*<sup>4</sup>-isopropyl-1,3,5-triazine-2,4-diamine}, propazine {6-chloro-*N*<sup>2</sup>,*N*<sup>4</sup>-di-isopropyl-1,3,5-triazine-2,4-diamine}, simazine {6-chloro-*N,N'*-diethyl-1,3,5-triazine-2,4-diamine}, atraton {2-ethylamino-4-isopropylamino-6-methoxy-*s*-triazine}, prometon {*N*<sup>2</sup>,*N*<sup>4</sup>-di-isopropyl-6-methoxy-1,3,5-triazine-2,4-diamine}, simeton {*N,N'*-diethyl-6-methoxy-1,3,5-triazine-2,4-diamine}, ametryn {2-ethylamino-4-isopropylamino-6-methylthio-*s*-triazine}, prometyrn {*N*<sup>2</sup>,*N*<sup>4</sup>-di-isopropyl-6-methylthio-1,3,5-triazine-2,4-diamine} and symetryrn {*N,N'*-diethyl-6-methylthio-1,3,5-triazine-2,4-diamine} in water and in the solvents: methanol, ethanol, *n*-butanol and benzene. The aqueous photolysis led to the corresponding 2-hydroxy-triazines, the photolysis in methanol to the 2-methoxy-triazines, etc. The yields observed were high ( $\approx 85$ – $90\%$ ). Exceptions to this were atraton, prometon and simeton, which did not undergo photolysis in methanol, ethanol or water. No photochemical reactions were observed at wavelengths longer than 300 nm. In a subsequent paper, these authors studied the photolysis of 2-fluoro- and, 2-

bromo-4,6-bis(ethylamino)-*s*-triazine, 2-iodo-triazine analogues of atrazine, propazine and simazine and 2-azido-4-ethylamino-6-methylthio-*s*-triazine in water, methanol, ethanol and *n*-butanol [143]. From considerations of thermal, photochemical and spectroscopic data, the authors suggest the involvement of a Chugaev-type cyclic transition state in the dealkylation of *s*-triazines.

Atrazine (vide supra) has been showed to photo-dehalogenate in aqueous solution, with subsequent photo-dealkylation of the hydroxylated compounds to the mono- and nonalkylated species [144].

Mamaev et al. [145] found that nitro-1,3,5-triazines may be obtained by photooxidation of azido-1,3,5-triazines by atmospheric oxygen.

A laser microprobe analysis, using 266 nm laser light, was applied to study the photodegradation of atrazine (vide supra), propazine (vide supra) and simazine (vide supra) [146]. The photoproducts were detected using time-of-flight mass spectrometry, and the results showed that the main process is ring-opening, with or without chlorine expulsion.

Doré et al. [130] studied the aqueous phototransformations of atrazine by 254 nm and polychromatic light. The main photoproducts found upon UV photodegradation, identified by their mass spectra, were hydroxy atrazine, 6-chloro-*N*-isopropyl-2,4-diamino-1,3,5-triazine, 6-chloro-*N*-ethyl-2,4-diamino-1,3,5-triazine, 6-hydroxy-amino-1,3,5-triazine, ammeline, (*N,N'*)-isopropyl-2,4-diamino-1,3,5-triazine, 6-chloro-2,4-diamino-1,3,5-triazine and 6-hydroxy-*N*-ethyl-2,4-diamino-1,3,5-triazine. The authors propose a complex mechanism including oxidations, dealkylations and hydrolyses. The authors also suggest a significant involvement of radicals in these processes.

Recently, using a medium pressure mercury lamp, Héquet et al. [147] estimated the half-life of atrazine around 5 min, the corresponding 2-hydroxy-atrazine being the major photoproduct.

Barceló et al. [83] studied the photodegradation of the herbicide propazine (vide supra) in aqueous solution, using a suntest apparatus. According to the authors, the main photodegradation pathways correspond to dealkylation, hydroxylation and dehalogenation, leading to deisopropylpropazine (deethylatrazine), hydroxypropazine and 2-H analogues. A tentative photodegradation mechanism is proposed.

The photodegradation of cyanazine {2-(4-chloro-6-ethylamino-1,3,5-triazin-2-yl-amino)-2-methylpropionitrile} was studied in an aqueous solution bubbled with an oxygen stream, using a low pressure mercury lamp emitting monochromatically at 254 nm [148]. The observed photodegradation quantum yields ranged from 0.05 to 0.10%, at temperatures between 10 and 40 °C. The authors hypothesize the existence of a free-radical chain reaction mechanism for the photodegradation process.

The use of an industrial-scale UV chamber to reduce the amount of atrazine in a drinking water supply has been

discussed [149]. The efficiency of atrazine removal depended only on the UV radiation input. Addition of H<sub>2</sub>O<sub>2</sub> improved the efficiency of photodegradation, but required higher UV doses. The main photoproduct identified was hydroxyatrazine.

Niessner et al. [125] studied the aqueous photodegradation of atrazine (vide supra) by UV light in the presence of O<sub>2</sub> and using a combination of O<sub>2</sub>/O<sub>3</sub> at a pilot plant for drinking water treatment. The photodegradation rate was not enhanced by the last combination with respect to O<sub>2</sub>. However, in experiments carried out at large scale in field conditions the degradation of atrazine and desethylatrazine improved with increasing O<sub>3</sub> dose and increasing radiant power.

Similarly, Lai et al. [150] studied the photooxidation of simazine (vide supra) by UV radiation in the presence and absence of O<sub>3</sub>. Simazine disappearance increased with UV intensity, yielding dechlorination byproducts. In contrast, the combination of UV radiation with O<sub>3</sub> led to the generation of dealkylation, deamination and dechlorination byproducts.

The UV photolysis of two products of photodegradation of atrazine (vide supra), namely deethylatrazine and deisopropylatrazine was studied [151]. Significant reductions in the rate of photodegradation were observed in surface waters, which the authors attribute to the presence of natural radical scavengers. No attempts were made to identify by-products of these photolysis reactions.

The photodegradation of ametryn (vide supra), atraton (vide supra), atrazine (vide supra), propazine (vide supra), simazine (vide supra) and terbuthylazine {2-chloro,4-tert-butylamino,6-ethylamino,(1,3,5)-triazine} by the radiation supplied by a xenon lamp were investigated in aqueous and buffered solutions (pH 7–9) containing a small percentage of acetonitrile [152]. The quantum yields for photodegradation were measured, and comparable values (≈5%) found. A temperature dependence was observed for the photodegradation of terbuthylazine, which allows the estimation of an activation energy ≈13 kJ mol<sup>-1</sup>. Atraton showed a very low photodegradation quantum yield, ≈0.2%, which shows that it can be considered not to be significantly photodegradable under the conditions used. The photodegradation quantum yields in acetonitrile and hexane for terbuthylazine are about one half of the values observed in water. From the observed data, half-lives for these pesticides under sunlight can be estimated, ranging from 39 h to 3 months.

The photodegradation of terbuthylazine (vide supra) at 254 nm and with simulated sunlight ( $\lambda > 290$  nm) has been studied [153]. The corresponding 2-hydroxylated derivative is generated in a few minutes, and then undergoes a slow dealkylation to ameline {2-hydroxy,(4,6)-diamino,(1,3,5)-triazine}.

Mansour et al. [46] studied the photolysis of metamitron {4-amino-3-methyl-6-phenyl-1,2,4-triazine-5(4*H*)-one} and terbuthylazine (vide supra) by UV light of different

wavelengths in water and water/soil suspensions. Metamitron degraded rapidly, yielding desaminometamitron, which was much more stable. In the case of terbutylazine, an important enhancing effect was observed for humic acids, leading to products of oxidation of side chains, such as deethylterbutylazine.

The photodegradation of five non-commercial unsaturated triazines with pesticide activity was investigated in water, using a mercury lamp [154]. It was observed that the photodegradation efficiency was enhanced by the presence of unsaturated substituents.

Albanis and Konstatinou [92], when studying the photodegradation of atrazine (vide supra), propazine (vide supra) and prometryn {*N,N'*-bis(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine}, found the half-life of the compounds to be  $\approx 1$ –2 months in water and  $\approx 1$  month in soils. The presence of humic substances produced a reduction of the photodegradation rate in water and an enhancement in soil. The major photoproducts found were the hydroxy and dealkylated derivatives.

The photodegradation of metribuzin {4-amino-6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one} in water was studied using a low pressure mercury lamp [155]. Desaminometribuzin, diketometribuzin and desaminodiketometribuzin were identified as photoproducts, plus six other unknown metabolites resulting from side-chain degradation, some of which were very stable toward photolysis. Inorganic and organic ions, such as monocarboxylic, dicarboxylic and ketocarboxylic acids were also formed by side-chain degradation and ring cleavage.

Mansour et al. [81] studied the photodegradation of terbutylazine (vide supra) in distilled water and in soil using simulated sunlight ( $\lambda \geq 290$  nm), in the presence and absence of humic acids. The half-life time in water, without and with humic acids added were, respectively,  $\approx 23$  and 8 h. The photodegradation process followed pseudo-first kinetics. Dealkylation was the main degradation pathway, the main photoproducts being desethylterbutylazine and desisobutylterbutylazine.

The photodecomposition of 4-amino-1,2,4-triazin-3,5-diones and 4-amino-1,2,4-triazin-thiones in oxygenated aqueous solutions at different pH values were studied by Raschke et al. [156]. Deamination, decarboxylation and dealkylation reactions were observed. Dealkylation was a slow and non-selective process. The details of the proposed mechanisms were discussed.

A laser flash photolysis study of the photodegradation of *s*-triazine, ametryn (vide supra), desmetryn {2-isopropylamino-4-methylamino-6-methylthio-*s*-triazine}, prometryn (vide supra) and terbutryn {2-tert-butylamino-4-ethylamino-6-methylthio-*s*-triazine} by 193 nm UV light showed all the compounds underwent monophotonic photoionization, with yields less than 10%. No significant photoionization was observed when using longer wavelengths [157].

Comber [82] studied the photolysis of atrazine (vide

supra) and simazine (vide supra) in river water at different pH values and contents of dissolved organic carbon, also with buffered samples, under the artificial light supplied by fluorescent tubes ( $300 < \lambda < 400$  nm), and upon sunlight photolysis. Photodegradation was initiated by a wide range or wavelengths at pH 4, but only wavelengths lower than 300 nm were able to initiate it in near-neutral media. On this basis, and considering the rates of hydrolysis of these pesticides at different pH values, the author estimates the half-life of the studied pesticides in acidic upland waters as nearly a week, some months for lowland river and years for groundwaters.

The antifouling agent Irgarol {2-methylthio-4-tert-butylamino-6-cyclopropylamino-*s*-triazine} is rather stable toward hydrolysis, but undergoes sunlight photodegradation in aqueous solution [80], the process being much faster in natural waters. Three main photoproducts were observed, with two of them being stable even after 6 months irradiation.

Lin et al. [39] studied the effect of simulated sunlight on atrazine (vide supra) toxicity of surface waters, concluding that the toxicity of the herbicide is reduced, possibly through photodegradation. The observed reduction of toxicity was higher in bay water than in fresh water.

Breithaupt and Schwack [158] studied the photoinduced addition of the fungicide anilazine {4,6-dichloro-*N*-(2-chlorophenyl)-1,3,5-triazin-2-amine} to cyclohexene and methyl oleate upon irradiation with a metal halogen lamp. Both olefinic compounds were used as models for plant cuticle components. Extensive reaction of anilazine with the *cis*-double bond of both olefins was observed. The addition is considered to be radical-mediated, the initial step being suggested as C–Cl bond cleavage. The conclusion is drawn that photochemical reactions within the plant cuticle can lead to the formation of bound-residues of anilazine with unsaturated biomolecules.

Detailed studies of the first stages of photodegradation of a variety of triazines using laser flash photolysis combined with pulse radiolysis showed the photodegradation is monophotonic when 193 nm light is used for excitation. It was not possible to observe the generation of intermediates in the nanosecond time-scale using higher wavelengths (222, 248, 266 nm). The photodegradation, however, certainly takes place and has been observed when samples were exposed to 254 nm steady-state photolysis, and the some major photoproducts identified by HPLC, comparing them with authentic samples. Photoionization was observed for all compounds when photolysis was carried out at 193 nm, with very low quantum yields. The rate constants for the one-electron oxidation of the triazines with  $\text{SO}_4^{\cdot-}$ , one-electron reduction with  $e_{\text{aq}}^-$  and  $\text{HO}^\cdot$  addition were obtained, using both the laser flash photolysis and the pulse radiolysis techniques. The fact that  $\text{HO}^\cdot$  undergoes addition to the aromatic ring, and not one-electron oxidation, has been proved by experiments performed with conductance detection. The one- $e^-$  reduction

with  $e_{\text{aq}}^-$  has also been studied, and the corresponding rate constants obtained. Triazines have been shown to quench the fluorescence of excited  $\text{UO}_2^{2+}$ . The rate of decay of the laser flash photolysis generated uranyl in the presence and absence of triazines has been measured. All these results allow to confine the one-electron reduction potential of triazines to the interval  $2.4 < E^\circ(T^{++}/T) < 2.7$  V vs. NHE. The observed photoproducts, detected using HPLC, have been studied upon irradiation at 254 nm, obtaining mainly the 2-hydroxy derivative and, in minor amounts, photoproducts dealkylated in the side chains bind to the amino groups. Structure–reactivity correlations have been established in order to predict the reactivity of other triazines upon direct photolysis [157,110,159–161].

#### 2.24. Triazinone herbicides

The aqueous photodegradation of metamitron {4-amino-3-methyl-6-phenyl-1,2,4-triazin-5(4H)-one} by UV radiation from a xenon lamp and by sunlight has been studied [84]. The study included UV and phosphorescence spectroscopy, determination of quantum yields at different pH values and determination of the photoproducts. No reaction was observed in methanol, acetonitrile and hexane, or in water in the dark. The photodegradation products found in aqueous solution were deamino metamitron and an unidentified compound. The triplet energy was obtained by phosphorescence spectroscopy ( $E_T \approx 245$  kJ mol<sup>-1</sup>, to be compared with  $E_S \approx 325$  kJ mol<sup>-1</sup>). This does not allow to discard a possible reaction involving the triplet state. In view of its  $\text{p}K_a$  and the fact that the photodegradation quantum yields at pH 4 and 9 were comparable ( $\approx 1.6\%$ ), the participation of the hydroperoxyl radical ( $\text{HO}_2^\cdot$ ) cannot explain the photodegradation of metamitron. The photodegradation quantum yield at pH 7 was a factor of 2 higher, which the authors attributed to the influence of the phosphate buffer used. The photodegradation of metamitron is strongly dependent on the presence of oxygen. The mechanism of generation of the photoproducts is unclear.

#### 2.25. Triazole fungicides

In the presence of humic acid the photodegradation of triadimefon {1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)butan-2-one} changed only from 87 to 91% after 4 h [111,112].

The photodegradation of folicur {1-(4-chlorophenyl)-4,4-dimethyl-3-(1H-1,2,4-triazole-1-yl)methyl)-pentan-3-ol} by UV radiation has been studied in benzene, ether, methylene chloride, methanol [162]. Two photoproducts have been observed and identified by chromatography/spectroscopy and direct comparison with authentic samples.

The photodegradation of triadimefon (vide supra) by 254 nm light on glass and soil surfaces led to 1-(4-chloro-

phenoxy)methyl)-1,2,4-triazole, 1-(4-chlorophenoxy)-2,2-dimethyl-1-(1,2,4-triazol-1-yl)propane, 1-(1,2,4-triazol-1-yl)-3,3-dimethylbutan-2-one and 1-(4-chlorophenoxy-3,3-dimethyl-1-(1,2,4-triazol-1-yl)butan-2-ol [163]. The observed reactions followed first order kinetics. The authors suggest the main processes taking place upon photolysis are C1 to C2 and C1 to triazole bond cleavage, hydrolysis, reduction and extrusion of C=O.

Murthy et al. [85] studied the photodegradation of triadimefon (vide supra) and epoxiconazol {[(2RS,3SR)-1-[3-(2-chlorophenyl)-2,3-epoxy-2-(4-fluorophenyl)-propyl]-1H-1,2,4-triazole]} under simulated sunlight, using a xenon suntest lamp. Triadimefon degraded to 21% in 72 h, and epoxiconazol to 12% in 120 h. When the same pesticides were photolyzed in soil containing 6% moisture the observed levels of photodegradation were, respectively, 37 and 56% in 72 h. *p*-Chlorophenol was identified as photoproduct upon photodegradation of triadimefon.

The photophysics and photochemistry of triadimefon {1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)butan-2-one} and triadimenol {1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)butan-2-ol} in solution have been studied. 4-Chlorophenol and 1,2,4-triazole were identified in both cases as major photodegradation products. The photodegradation quantum yield of triadimefon in cyclohexane at 313 nm is 0.022, whereas triadimenol is reported as photostable under the same conditions. Flash photolysis experiments showed the presence of 4-chlorophenoxy radicals, pointing to a mechanism via homolytic cleavage of the C–O bond of the asymmetric carbon [164].

#### 2.26. Urea-based herbicides

Metobromuron {3-(*p*-bromophenyl)-1-methoxy-1-methylurea} was used as a model compound to study the sunlight photodegradation of urea-based herbicides [86]. Upon exposure to sunlight for 17 days, the major photoproduct found was 3-(*p*-hydroxyphenyl)-1-methoxy-1-methylurea. Minor products were 3-(*p*-bromophenyl)-1-methylurea and *p*-bromophenylurea, with experimental evidence for the existence of a dimerization product.

The sunlight photolysis of linuron {3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea} and monuron {3-(4-chlorophenyl)-1,1-dimethylurea} was studied [87]. After 2 months exposure, linuron yielded 13% 3-(3-chloro-4-hydroxyphenyl)-1-methoxy-1-methylurea, 10% 3,4-dichlorophenylurea and 2% 3-(3,4-dichlorophenyl)-1-methylurea. Upon photolysis of monuron, 3-(*p*-hydroxyphenyl)-1,1-dimethylurea was identified as photoproduct.

Kotzias and Korte [88] reviewed the photochemistry of phenylurea herbicides and their environmental reactions. The authors conclude that substituted phenylurea herbicides are degraded by UV and sunlight, the degradation being influenced by the presence of oxygen. H abstraction is the main process in methanol, phenols are the main

photoproducts in water, while C–C bond scission takes place in benzene.

Tanaka et al. [35] studied the generation of biphenyls upon sunlight photolysis of monuron (vide supra), diuron {3-(3,4-dichlorophenyl)-1,1-dimethylurea}, linuron (vide supra) and metobromuron {3-(4-bromophenyl)-1-methoxy-1-methylurea}. The photoreactions proceeded via coupling of two herbicide molecules, leading to a chlorinated biphenyl. The yields of biphenyls observed were very low, suggesting a high photolability that would lead to their fast degradation, such that they would only accumulate to a very low extent.

The photodegradation of 1,3-dimethyl-1-(2-(3-fluorobenzylthio)-1,3,4-thiadiazol-5-yl)urea has been studied in methylene chloride using the UV radiation provided by a mercury lamp has been studied in a thin film and in solution [165]. Two photoproducts were found and characterized. The rearrangements involved an *S* to *N* benzyl migration, followed by a sulfur–oxygen substitution.

Tanaka et al. [89] also studied the photolysis of diuron {3-(3,4-dichlorophenyl)-1,1-dimethylurea} using UV lamps and natural sunlight. Seven photoproducts, with similar yields, were identified in both cases.

A study of the photodegradation of diuron {3-(3,4-dichlorophenyl)-1,1-dimethylurea} has been reported using simulated sunlight in distilled water and artificial seawater containing humic acids [166]. The main photoproduct was monuron {3-(4-chlorophenyl)-1,1-dimethylurea}, a product of dechlorination. A quenching effect was observed by the chloride ions present in seawater, leading to retardation of the photodegradation.

The photoreduction of 1-(2-chlorobenzoyl)-3-(4-chlorophenyl)urea in methanol was studied using a Xe lamp [167]. The observed process followed in all cases first-order kinetics, with rate constants in O<sub>2</sub> atmosphere greater than in N<sub>2</sub> atmosphere. The main photoproducts found were 2-chlorobenzamide, *N*-phenylmethylcarbamate, *N*-(4-chlorophenyl)methylcarbamate and 4-chlorophenyl urea.

Doré et al. [130] studied the aqueous photodegradation of isoproturon {3-(4-isopropylphenyl)-1,1-dimethylurea} by 254 nm and polychromatic light, and found *N*-(4-isopropyl-hydroxyphenyl)-*N'*-methylurea, *N*-(4-isopropylphenyl)-*N'*-dimethylurea and *N*-(4-isopropylphenyl)-*N'*-acetamide as main photoproducts. The authors propose a complex mechanism involving hydroxylation, demethylation and deamination reactions, possibly with participation or radical intermediates.

The photochemical degradation of nine different urea-based herbicides in aqueous solution by UV light supplied by a low pressure mercury lamp was studied, and the main photoproducts identified [168]. The quantum yields for photodegradation ranged from 0.5% for fenuron {3-phenyl-1,1-dimethylurea} to 13% for monuron (vide supra). The observed photoproducts were formed through three different pathways: (i) cleavage of the N–O bond in the case of pesticides containing an *N*-methoxy moiety, such as linuron (vide supra), with formation of formaldehyde, (ii)

replacement of halogen substituents by OH groups, (iii) replacement of halogen substituents by H atoms.

Jirkovský et al. [90] studied the photolysis of diuron {3-(3,4-dichlorophenyl)-1,1-dimethylurea} using various different wavelengths between 254 and 350 nm. According to their results, the major photoproducts resulted from a photoheterolysis process followed by substitution of Cl by OH. Different photoproducts were observed depending on the wavelength used during the photolysis: 3-(4-chloro-3-hydroxyphenyl)-1,1-dimethylurea was the major product when photolysing with 254 nm, while 3-(3-chloro-4-hydroxyphenyl)-1,1-dimethylurea was the main one when using 365 nm light.

Mansour et al. [46] investigated the photolysis of isoproturon (vide supra) by UV light of different wavelengths in water and water/soil suspensions. Irradiation of isoproturon in the presence of organic matter shows that photolysis in inert atmosphere is faster, suggesting that molecular oxygen might act as a quencher.

The photolysis of chlorotoluron {3-(3-chloro-*p*-tolyl)-1,1-dimethylurea} in acetonitrile, hexane and aqueous solutions buffered to pH 4, 7 and 9, and of isoproturon (vide supra) in aqueous and buffered solutions by the radiation supplied by a Xe lamp were investigated [169]. Both herbicides were degradable by  $\lambda < 240$  nm, but photostable when  $\lambda > 240$  nm. In the case of chlorotoluron in aqueous solution, the main photoproduct found was 3-(3-hydroxy-4-methyl-phenyl)-1,1-dimethylurea, while the quantum yields for photodegradation were  $\approx 0.07$  in aqueous and buffered solutions,  $\approx 0.035$  in acetonitrile, and 0.70 in hexane. In the case of isoproturon the quantum yield obtained for photodegradation was  $\approx 0.004$  in all solutions.

The photodegradation of hexaflumuron {1-[3,5-dichloro-4-(1,1,2,2,-tetrafluoroethoxy)phenyl]-3-(2,6-difluorobenzoyl)urea}, teflubenzuron {1-(3,5-dichloro-2,4-difluorophenyl)-3-(2,6-difluorobenzoyl)urea} and diflubenzuron {*N*-[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide} in river water buffered to pH 9.0 was studied [170]. Hexaflumuron was the most rapidly degraded, with a half-life of 8.6 and 5.0 h at pH 7 and 9, respectively. Diflubenzuron was the slowest to degrade, with half-life times of 17 and 8 h at pH 7 and 9. Dark controls showed no loss of the parent compounds over similar time periods.

The initial stages of photodegradation of various urea-based herbicides has been studied using laser-flash photolysis and pulse radiolysis. Radical cations are generated immediately after the laser pulse, and deprotonate to yield neutral radicals. The quantum yield of 193 nm photoionization are  $\approx 10\%$ . Pulse-radiolytic one-*e*<sup>-</sup> oxidation with SO<sub>4</sub><sup>-</sup> also yields the radical cation and, after deprotonation, the neutral radical. Semiempirical simulations of UV–Vis spectra support the experimental observations. A bathochromic displacement of the bands of the radical cation is observed as the number of *e*<sup>-</sup>-withdrawing ring substituents increases. The extinction coefficients of the radical cation and neutral radical are, respectively,  $\approx 3000$



and  $\approx 2000 \text{ M}^{-1} \text{ cm}^{-1}$ . The  $\text{p}K_{\text{a}}$  for deprotonation of the radical cation is  $\approx 0$ . The reaction with hydroxyl radical has also been studied, both by laser flash photolysis and pulse radiolysis, and the rate constants obtained. The photoproducts observed by GC–MS and HPLC, and in some cases checked against authentic samples, are the corresponding anilines and the photo-Fries products. Furthermore, the rate constants for one-electron reduction with  $e_{\text{aq}}^-$  and for  $\text{HO}^\cdot$  addition have been obtained. Structure–reactivity correlations have been established in order to predict the reactivity of other ureas upon direct photolysis [171,110,172,173].

### 2.27. Miscellaneous

Neihof et al. [60] evaluated the sunlight photodegradation of the biocides mercaptopyridine-*N*-oxide, sodium-2-mercaptopyridine-*N*-oxide, 2-(tert-butylamine)-mercaptopyridine-*N*-oxide and 2,2'-dithio-bis-(pyridine-*N*-oxide) in artificial seawater and in aged natural seawater sterilized by autoclaving. The biocide activity dramatically reduced after 5–10 h of exposure to sunlight. UV spectral measurements showed that pyridine-*N*-oxide-2-sulfonic acid was an early photoproduct. An unidentified insoluble photoproduct was also observed. According to the authors, temperature, pH and salinity were not relevant variables. The rates of loss of toxicity were lower in the presence of oxygen.

The photodegradation of the fungicide isoprothiolane {diisopropyl 1,3-dithiolan-2-ylidnemalonate} by 254 nm UV light on solid particles yielded oxalic acid, dithiolanylidnemalonic acid, dithiolanylideneacetic acid, 2,4-bis[bis(isopropoxycarbonyl)methylene]-1,3-dithietane, 3,5-bis[bis(isopropoxy-carbonyl)methylene]-1,2,4-trithiolane and sulfur [174]. Photolysis of the methyl and ethyl analogues yielded the corresponding photoproducts. Based on product analysis, the authors propose the involvement of dithiolane ring cleavage, ester hydrolysis, decarboxylation, dithietane and trithiolane formation and sulfur liberation. A surface effect was observed, the photodegradation being much more rapid on sand than on a glass plate. The authors observed the same phenomena also with other sulfur-containing pesticides.

Badr et al. [175] studied the photolysis of phenylacetamide, *N*-benzylphenylacetamide and phenylacetanilide in air using a mercury lamp. The photoproducts obtained from phenylacetamide were benzaldehyde, toluene, bibenzyl, stilbene and phenanthrene. In addition to these, benzylamine was found upon photolysis of *N*-benzylphenylacetamide, and aniline, *N*-benzylaniline, *o*-aminodiphenylmethane and *p*-aminodiphenylmethane following photolysis of phenylacetanilide. The authors suggest the mechanism proceeds via C–N bond homolysis to yield phenylacetyl and aminyl radicals, that would lead to the observed photoproducts.

Miille and Crosby [53] studied the photodegradation of 3,4-dichloroaniline by simulated sunlight in seawater. The

photolysis reaction took place at about the same rate in seawater and in distilled water. Photooxidation, photonucleophilic substitution and photoreduction reactions are observed. The amount of photoreduction products was higher than in distilled water.

The photolysis of the fungicide and bactericide 2-mercaptobenzothiazole, and of the  $\pi$ -isoelectronic 2-mercaptobenzimidazole by UV radiation in benzene, toluene, methanol, ethanol and acetonitrile by UV radiation has been studied [176]. The thiazole derivative yielded bis-(2-benzothiazolyl)disulfide in benzene and toluene and bis-(2-benzothiazolyl)disulfone and eventually benzothiazole sulphate when methanol, ethanol and acetonitrile were the solvents. The imidazole led to bis-(2-benzimidazolyl)disulfone and benzimidazole sulfate when methanol, ethanol and acetonitrile were used as solvents.

Jensen-Korte et al. [177] studied the aqueous photodegradation of various types of pesticides: carbamates, phosphates, pyrethroids, triazoles and ureas using a high pressure mercury lamp. In all cases the photodegradation rate increased in the presence of humic substances.

Irradiation by 313 nm light supplied by a high-pressure mercury lamp of 1,3-dihydro-2*H*-benzimidazole-2-thione, 2(3*H*)-benzothiazolethione and 2-chlorobenzothiazole has been studied in the presence of oxygen in 1% acetonitrile, ethanol or benzene solutions. The main photoproducts were disulfides, 2-oxo-derivatives, benzimidazole, benzothiazole and elemental sulfur [178]. The authors discuss a possible mechanism for such processes, starting with a S–H bond homolysis and/or oxidation due to singlet oxygen formation. The intermediates, however, have not been detected.

The UV photolysis of thioamides was studied using low pressure mercury lamps under nitrogen and oxygen atmosphere [179]. The photoproducts found under nitrogen were nitriles and  $\text{H}_2\text{S}$ , while under oxygen, nitriles, amides, carboxylic acids, 3,5-disubstituted-1,2,4-thiadiazoles,  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  were formed. Photodegradation of secondary and tertiary thioamides was negligible both in inert and oxidant atmosphere. The mechanism of photolysis under nitrogen is proposed to take place through an intermediate biradical, centered on the C and S, that would undergo hydrogen transfer followed by elimination of  $\text{H}_2\text{S}$ . The photolysis under oxygen is explained assuming the formation of an intermediate sulphinic acid, that could eliminate  $\text{H}_2\text{SO}_3$  to give a nitrile or hydrolyse to an amide or carboxylic acid and ammonia.

A comparative study between fragmentation processes taking place in mass spectrometry using an electron ionization source and photodegradation processes has been carried out for atrazine (vide supra), simazine (vide supra) and trietazine {6-chloro- $N^2, N^2, N^4$ -triethyl-1,3,5-triazine-2,4-diamine} [180]. Simazine showed the lowest tendency to fragmentation, and atrazine the highest. The same kind of fragmentations were observed for the three compounds: C–N bond cleavage in the lateral chains, C–Cl bond scission and heteroatomic ring cleavage.

Sharma and Chibber [181] studied the sunlight photodegradation of diniconazole {(E)-(RS)-1-(2,4-dichlorophenyl)-4,4-dimethyl-2-(1H-1,2,4-triazol-1-yl)pent-1-en-3-ol} as a thin film on glass surface. The photoproducts generated were separated and identified as the (Z)-isomer of diniconazol, a cyclic alcohol and its corresponding ketone, and an isoquinoline.

Mushtaq et al. [40] studied the photodegradation of emamectin benzoate {4''-deoxy-4''-(epi-methylamino)avermectin B<sub>1a</sub> benzoate} in aqueous solution buffered to pH 7 and natural pond water under sunlight. Avermectins are 16-member lactones, used as insecticides. The sunlight photodegradation in the mentioned media took place in 22 and 7 days, respectively. Upon continuous exposure to light from a Xe lamp, photodegradation of aqueous solutions of the pesticide, buffered to pH 7 and containing 1% acetonitrile or ethanol as cosolvents took place in 64.5 and 8.5 days, respectively. A photoisomer and unknown polar residues were found as photoproducts. The amount of polar residues found increased with the time of irradiation.

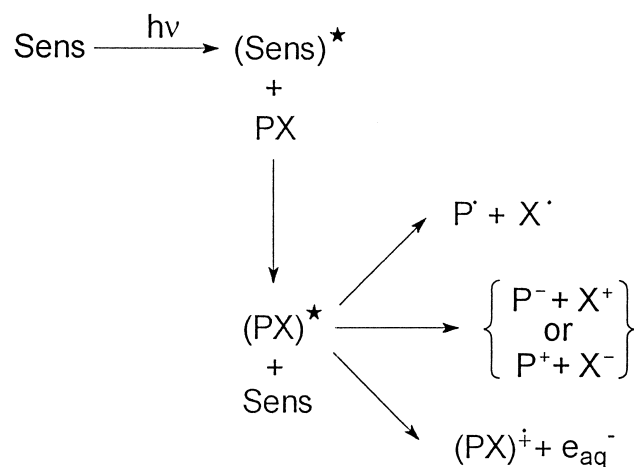
Miller et al. [61] reported a big difference in the rate of photolysis of methylisocyanate which, while stable in water, has a half-life time of less than 1 day under midsummer sunlight.

The influence of soil and sediment composition on the photodegradation of napropamide {(RS)-N,N-diethyl-2-(1-naphthyl)propionamide} has been studied using a photo-reactor emitting with a spectrum  $300 < \lambda < 450$  nm, with a maximum at 365 nm [182]. Soil or sediment reduced the rate of photolysis, although no dependence on its composition was found.

Dureja et al. [183] studied the photodegradation of the insecticide azadirachtin {dimethyl[2aR-[2a $\alpha$ ,3 $\beta$ ,4 $\beta$ (1aR\*,2S\*,3aS\*,6aS\*,7S\*,7aS\*),4a $\beta$ ,5 $\alpha$ ,7aS\*,8 $\beta$ (E),10 $\beta$ ,10a $\alpha$ ,10b $\beta$ ]]-10-(acetyloxy)octahydro-3,5-dihydroxy-4-methyl-8-[2-methyl-1-oxo-2-butenyl]oxy]-4-(3a,6a,7,7a-tetrahydro-6a-hydroxy-7a-methyl-2,7-methanofuro[2,3-b]oxireno[e]oxepin-1a(2H)-yl)-1H,7H-naphthol[1,8-bc:4,4a-c']difuran-5,10a(8H)-dicarboxylate} upon 254 nm irradiation as a thin film on a glass surface. The half-life of azadirachtin was  $\approx 48$  min, yielding an isomerised (Z)-2-methylbut-2-enoate product. Irradiation in the presence of saturated fatty acids and fatty oils led to an increase in the rate of photodegradation. Conversely, irradiation in the presence of unsaturated fatty acids such as oleic, linoleic and elaidic acid reduced the rate of photodegradation.

### 3. Photosensitized degradation

Photosensitized photodegradation is based on the absorption of light by a molecule. In one possible scenario, this can then transfer energy from its excited state to the



Scheme 2. Chemical events taking place upon photosensitized photolysis involving energy transfer.

pesticides, that can undergo different processes, as following direct photodegradation (Scheme 2).

Photosensitization may also involve redox processes, such as the photo-Fenton reaction, where there is an initial electron or atom transfer to produce free radicals, but the oxidised or reduced sensitizer undergoes subsequent reactions to regenerate the initial species [184–186,54,187]. Some examples of this will be given in Section 5.

An important advantage of photosensitized photodegradation is the possibility of using light of wavelengths longer than those corresponding to the absorption characteristics of the pollutants.

#### 3.1. Anilide herbicides

The aqueous photodegradation of butachlor {N-(butoxymethyl)-2-chloro-2',6'-diethylacetanilide} by sunlight in the presence of diethylamine increased significantly relative to the process in its absence [36]. In this case the light is absorbed by the pesticide, and it is probable that, as with other reactions involving excited states of aromatic molecules and aliphatic amines the reaction involves electron transfer [188].

#### 3.2. Carbamate insecticides

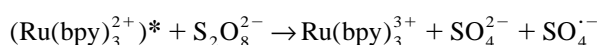
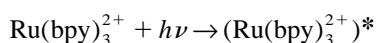
The degradation of mercaptodimethur {4-methylthio-3,5-xyllyl methylcarbamate} and ethiofencarb (vide supra) photosensitized by anthraquinone in an acetonitrile/water mixture, has been studied, using a medium-pressure mercury lamp as radiation source [189]. The degradations were complete after irradiating for 0.5 and 0.8 h, respectively. For mercaptodimethur, the observed photoproducts were 3,5-dimethyl-4-methylsufinylphenol (50%) and 3,5-dimethyl-4-methylthiophenol (49%) and 3,5-dimethyl-4-methylthio-2-N-methylacetamidophenol (1%). For ethiofencarb, the observed photoproducts were 2-hydroxy

benzaldehyde (55.5%), 3-methyl benzo[*e*] [1,3] oxazine-2,4-dione (33.3%) and *o*-hydroxybenzaldehyde (11.3%). The authors hypothesise different mechanisms leading to the observed products, taking place by electron transfer from the pesticide to the excited anthraquinone.

### 3.3. Chloroaromatic pesticides

Julliard et al. [79] investigated the *N,N,N',N'*-tetramethylbenzidine photosensitized reductive dechlorination of chloroneb {2,5-dichloro 1,4-dimethoxybenzene}, 4,4'-DDT {1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane} and MCPA methyl ester {4-chloro-2-methylphenoxy methyl acetate}, in an ethanol/water mixture using sodium sulfite as sacrificial electron-donor. After 7 h of irradiation of chloroneb, 95% dechlorination was observed, with the main photoproducts being 2-chloro-1,4-dimethoxybenzene (80%) and 1,4-dimethoxybenzene (20%). 2 h of irradiation of 4,4'-DDT led to quantitative degradation, the main photoproduct being 4,4'-dichlorodiphenyl dichloroethane, that subsequently dehalogenated. Irradiation of MCPA methyl ester for 2 h led to complete conversion, 2(2-methylphenoxy)methyl ethanoate being formed. The results show that the presence of an electron donor may increase the rate of dehalogenation of haloaromatic pesticides.

The application of tris-2,2'-bipyridylruthenium(II) peroxydisulphate as a photosensitizer for the oxidative photodegradation of 4-chlorophenol has been studied in detail [190]. Tris-2,2'-bipyridylruthenium(II) is water soluble, easy to immobilize in polymers, absorbs strongly in the visible ( $\epsilon(450 \text{ nm}) \approx 1.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) and emits fluorescence at 620 nm. Upon photoexcitation, the excited state of the cation is quenched by  $\text{S}_2\text{O}_8^{2-}$  to generate the strong oxidants  $\text{Ru}(\text{bpy})_3^{3+}$  and  $\text{SO}_4^{\cdot-}$ :



The photodegradation was carried out using a medium pressure mercury lamp with cut-off filters to suppress the short wavelengths. 4-Chlorophenol undergoes rapid photo-oxidation. The main photoproducts found were benzoquinone, 1,4-dihydroxybenzene, 4-chlorocatechol, chloride and sulphate. Prolonged irradiation leads to generation of  $\text{CO}_2$  and HCl. The reaction mechanism probably involves one-electron oxidation yielding a radical cation (4-chlorophenol) $^{\cdot+}$  and or phenoxyl radicals. Further addition-elimination processes are proposed, eventually leading to 4-chlorodihydroxycyclohexadienyl radicals.

The photodegradation of MCPA {4-chloro-2-methylphenoxy acetic acid} was studied in aqueous solutions of naturally occurring photosensitizers, using low intensity 300–450 nm UV light and sunlight [54]. Upon UV irradiation, MCPA was photooxidized at significant

rates, by hydroxyl radicals produced by nitrate and nitrite, and by photo-oxidants generated by humates, probably singlet oxygen or peroxy radicals. Tests performed using combinations of these photosensitizers led to first-order rate constants ranging from 0.03 to 0.048  $\text{h}^{-1}$ . Although  $\text{HO}^{\cdot}$  radicals tend to enhance the photooxidation, their effect is diminished due to scavenging by humates. The authors point out that photo-oxidants generated by humates appear to be of greater environmental significance than  $\text{HO}^{\cdot}$  in the photodegradation of MCPA.

### 3.4. Imidazolinone herbicide

The photodegradation of imazapyr {2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid} by simulated sunlight was studied at pH 7 in the presence of humic acids [191]. The study was carried out at different ratios of imazapyr to humic acid (1:0.1, 1:0.5, 1:1), and the concentration of remaining herbicide followed by HPLC. The photolysis followed first-order kinetics, with the presence of humic substances slowing down the photodegradation rate.

### 3.5. Organophosphorus pesticides

Barceló et al. [166] studied the photodegradation of fenitrothion (vide supra) in distilled water and artificial seawater using a suntest apparatus to simulate sunlight. Direct photolysis was very slow and no breakdown products were observed after 3 h of irradiation. When 20% acetone was added as photosensitizer, different metabolites were observed, which were tentatively assigned to fenitrooxon, carboxy-fenitrothion and 3-methyl,4-nitrophenol.

The photodegradation of vamidothion (vide supra) by simulated sunlight has been studied in water/methanol (2–4%) with 5% acetone added as a photosensitizer [64]. The major photoproduct observed was vamidothion sulfoxide.

Kamiya and Kameyama [192] studied the photochemical effects of humic materials on the degradation of various organophosphorus pesticides: bensulide {*S*-2-benzenesulfonamidoethyl *O,O*-di-isopropyl phosphorodithioate}, chlorpyrifos (vide supra), diazinon (vide supra), EPN {*O*-ethyl *O*-4-nitrophenyl phenylphosphonothioate}, fenitrothion (vide supra), fenthion (vide supra), isofenphos {*O*-ethyl *O*-2-isopropoxycarbonylphenyl isopropylphosphoramidothioate}, isoxathion {*O,O*-diethyl *O*-5-phenylisoxazol-3-yl phosphorothioate}, malathion {diethyl (dimethoxythiophosphorylthio) succinate}, parathion (vide supra) and tolchlofos-methyl {*O*-2,6-dichloro-*p*-tolyl *O,O*-dimethyl phosphorothioate}. The authors suggest the sensitization effects of humic substances depends on the binding affinity of pesticides to the radical source of the humic material. It was also found that metal ions having paramagnetic property inhibit the degradation of organophosphorus pesticides sensitized by humic acids [193].

A photosensitizing process was suggested to explain the enhanced degradation of iprobenfos {*S*-benzyl *O,O*-di-isopropyl phosphorothioate} when poly(3-octylthiophene-2,5-diyl) films were blended with perylene and *N,N,N',N'*-tetramethylbenzidine (a cation scavenger) [194]. The effect could be ascribed to an enhancement in  $O_2^-$  production.

Cyclodextrins have been shown to have an important enhancing effect on the rate of photodegradation of organophosphorus pesticides in water containing humic substances [193]. Such enhancing effects are attributed to the inclusion effects of cyclodextrins to catalyze the interaction of pesticides with radicals generated by the photosensitizing humic acids, that are trapped in the cyclodextrins.

### 3.6. Oxadiazole herbicides

The aqueous photodegradation of oxadiazon (ronstar) {5-tert-butyl-3-(2,4-dichloro-5-isopropoxyphenyl)-1,3,4-oxadiazol-2(3*H*)-one} by sunlight significantly increases in the presence of diethylamine, added as a photosensitizer, relative to the process in the absence of sensitizer [36].

### 3.7. Phenylamide fungicides

Hustert and Moza [195] reported on the aqueous photodegradation of carboxin {5,6-dihydro-2-methyl-1,4-oxathine-3-carboxanilide} and oxycarboxin {2,3-dihydro-6-methyl-5-phenylcarbonyl-1,4-oxathine 4,4-dioxide} in the presence of humic and fulvic substances and inorganic soil components, using both a high-pressure mercury lamp and a xenon lamp for irradiation. The presence of humic and fulvic materials enhanced photodegradation, possibly by forming reactive oxygen species such as singlet oxygen and hydroxyl radicals. The main photoproduct observed for both was oxanilic acid.

### 3.8. Pyrimidine fungicides

García et al. [196] studied the Rose Bengal dye-sensitized singlet oxygen-mediated photodegradation of 2-hydroxypyridine, 3-hydroxypyridine, 4-hydroxypyridine, 4-hydroxyquinoline, 8-hydroxyquinoline, 2-hydroxypyrimidine and 4-hydroxypyrimidine in water and in the mixture MeOH/MeCN, aiming to use them as models for pesticides. The photooxidation quantum yields ranged from 1 to 50%, with the higher values occurring in aqueous media. The authors suggest a charge-transfer mechanism, involving an initial excited encounter complex. More recently, the same authors studied the kinetics of Rose Bengal dye-sensitized photooxidation of the model compound 2-amino-4-hydroxy-6-methylpyrimidine in water and in acetonitrile/water [197]. The photooxidation quantum yields ranged from 0.5 to 41%, with the higher values observed in alkaline medium. Rate constants in the range  $9 \times 10^4$  to  $2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  are reported for the

overall and singlet molecular oxygen quenching processes. Again, a charge-transfer mechanism, involving an initial excited encounter complex is suggested.

### 3.9. Triazine herbicides

Acetone (1%) was used as a photosensitizer in a study of the photodegradation of atrazine (vide supra), atraton (vide supra) and ametryn (vide supra) in water by light with  $\lambda > 290 \text{ nm}$  from a medium pressure mercury lamp [198]. The photostability increased in the order ametryn < atrazine < atraton. The main photoproducts in all cases were the corresponding de-*N*-alkyl and de-*N,N'*-dialkyl triazines, as well as the hydroxytriazines. The observation of two different de-*N*-alkyl products suggests the de-*N*-alkylation to take place in two steps. Higher yields of de-*N*-ethyl triazines were observed than those of de-*N*-isopropyl triazines. Irradiation of ametryn yielded also de(methylthio)ametryn. The reaction was strongly sensitized by acetone. No breakdown products were observed for control dark reactions over 96 h, showing that the degradation was exclusively due to photolysis.

The products of sensitized photooxidation of ametryn (vide supra), atraton (vide supra), atrazine (vide supra), propazine (vide supra) and simazine (vide supra) have been studied in water, and using sunlight irradiation [199]. Methylene blue, Rose Bengal, riboflavin and flavin mononucleotide were used as sensitizers. The primary photodegradation products were dealkylated *s*-triazines and oxidation products, with a yield of  $\approx 60\%$ .

The photosensitized degradation of atrazine (vide supra) was investigated in distilled water and artificial seawater containing humic acids, using simulated sunlight [166]. The main photoproduct was hydroxyatrazine. The rate of degradation was faster in seawater, with evidence for photosensitized degradation of hydroxyatrazine.

The photodegradation of five non-commercial unsaturated triazines with pesticide activity was investigated in water containing a 5% acetone as photosensitizer, using a mercury lamp [154]. The observed photodegradation efficiency was higher than in the absence of acetone.

Bendig et al. [200] studied the photosensitized photocatalytic oxidation of triazine herbicides by natural sunlight. Tris(bipyridyl)ruthenium complexes adsorbed on  $\text{TiO}_2$  were used as sensitizers. The authors discuss the thermodynamic and kinetic requirements for the photosensitized process. The efficiency of the sensitization seems to be related to the adsorption of the sensitizer and triazines on  $\text{TiO}_2$ .

### 3.10. Urea-based pesticides

Crank and Mursyidi [201] studied the Rose Bengal dye-sensitized singlet oxygen-mediated oxidation of thio-

ureas in ethanol, using low pressure mercury lamps emitting mainly at  $\approx 254$  nm. According to their results, and in contrast with a previous work in which the irradiation was carried out in pyridine [202], thiourea do not undergo photolysis or photo-oxidation in the absence of sensitizers. Thiourea was shown to react with singlet oxygen when using Rose Bengal, methylene blue and chlorophyll as sensitizers. The reaction was inhibited by  $\beta$ -carotene. The photoproducts found were cyanamides, ureas, products of heterocyclic condensation and sulfur-containing fragments of the starting materials. Possible reaction mechanisms are suggested.

A study of the photocatalytic degradation of metobromuron {3-(4-bromophenyl)-1-methoxy-1-methylurea} and isoproturon (vide supra) using UV/TiO<sub>2</sub> showed the rate of degradation was always lower than when using hydroxyl radicals [203]. The solution resulting from photodegradation of metobromuron was bio-recalcitrant due to accumulation of bromide intermediates, which was not the case for the solution resulting from photodegradation of isoproturon.

### 3.11. Miscellaneous

The anthraquinone photosensitized degradation of perthane {1,1-dichloro-2,2-bis(4-ethylphenyl)ethane} has been studied in an acetonitrile/water mixture, using a medium-pressure mercury lamp as radiation source [189]. The degradation was complete after irradiating for 2 h. The observed photoproducts were 1,1-dichloro-2,2-bis(4-acetylphenyl)ethane (74%), 4-acetyl-4'-ethylbenzophenone (21%), 1-chloro-2,2-bis-(4-acetylphenyl)ethane (3.5%), and 4,4'-diethylbenzophenone (1.5%). The authors indicate different possible mechanisms leading to the observed products, which are suggested to take place by electron transfer from the pesticide to the excited anthraquinone.

Mushtaq et al. [40] studied the photodegradation of emamectin benzoate (vide supra) in aqueous solution buffered to pH 7 containing 1% acetone as sensitizer. The sunlight photodegradation in this medium took place in 1 day, much faster than in the absence of sensitizer (see above). Upon continuous exposure to the radiation supplied by a Xe lamp the photodegradation took place in 0.5 days, also much faster than in the absence of sensitizer. A photoisomer, epoxide derivatives and unknown polar residues were found as photoproducts. The amount of polar residues found increased with the time of irradiation.

Different authors have described the ability of humic acids as photosensitizers to promote photooxidation of common pollutants. Canonica et al. [187] proved the enhanced photodegradation of electron-rich phenols in presence of humic acids. Increased photodegradation of monuron and fenuron photosensitized by soil extracted humic substances has been reported by Aguer and co-workers [184,182].

## 4. Photocatalytic degradation

Although different definitions have been suggested for photocatalysis [204–206], and a detailed discussion is beyond the scope of this review, we use photocatalytic degradation to mean cyclic photoprocesses in which the pesticides photodegrade, but spontaneous regeneration of the catalyst occurs to allow the sequence to continue indefinitely until all the substrate is destroyed. For a detailed description of this field, readers are referred to two excellent multi-author volumes [207,208]. It is clear, however, that there will be some overlap between this section and that describing photosensitized processes.

### 4.1. Amide herbicides

Pathirana and Maithreepala [209] examined the photodegradation of 3,4-dichloropropionamide in aqueous TiO<sub>2</sub> suspensions, using 365 nm light. They found acidic medium to be suitable for the degradation, that occurred quantitatively via dechlorination within 5 h, yielding Cl<sup>-</sup>, H<sup>+</sup>, NO<sub>3</sub><sup>-</sup> and CO<sub>2</sub>. The presence of O<sub>2</sub> seems to be relevant. Degradation took place also under sunlight, with 30% yield after 7 h in the absence of TiO<sub>2</sub> and with 70% yield in its presence. A mechanism for the complete photodegradation was tentatively proposed.

### 4.2. Bipyridinium herbicides

The photocatalytic degradation of paraquat (vide supra) in water was studied using TiO<sub>2</sub> and a batch of six long wavelength UV lamps ( $\lambda = 365$  nm) [210]. Under these conditions, at high pH complete photodegradation of paraquat and the reaction intermediates took place in less than 3 h, while direct photolysis led to 60% photodegradation.

### 4.3. Carbamate insecticides

A comparison was made of the photocatalytic degradation of carbetamide (vide supra) in water, using TiO<sub>2</sub> and ZnO and irradiation at  $\lambda > 310$  nm [211]. The main photoproducts detected were hydroxylated compounds and products of cyclization of the side chain. After a long irradiation time carbetamide underwent complete mineralization.

Tanaka et al. [212] studied the photocatalytic degradation of MCC {methyl 3,4-dichlorocarbanilate}, MIPC {2-(1-methylethyl)phenyl methylcarbamate}, MPMC {3,4-dimethylphenyl methylcarbamate}, MTMC {*m*-tolyl methylcarbamate} and XMC {3,5-xylyl methylcarbamate} in water, using TiO<sub>2</sub> and irradiating with a super-high pressure mercury lamp. The rate of degradation is governed by the adsorbability of the pesticides to TiO<sub>2</sub>. The degradation was proposed to take place by successive hydroxylation of the aromatic ring or polyhydroxylation,

leading to opening of the aromatic ring to yield oxygenated aliphatic intermediates. The degradation was fast, with its rate being dependent on the acidity of the medium.

The effect of ionic and non-ionic surfactants on the degradation of carbaryl {1-naphthyl *N*-methylcarbamate} has been studied using simulated solar light and catalysed by aqueous TiO<sub>2</sub> suspensions [213]. An inhibition of the degradation rate was observed, depending on the surfactant and on the acidity of the medium. The kinetics of photodegradation followed a pseudo-first order kinetic law below the critical micellar concentration, and a complex behaviour above it. Carbaryl was mineralized to CO<sub>2</sub>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>.

The photolysis of propoxur {2-(1-methylethoxy)phenyl methylcarbamate} has been studied in water using 266 nm laser flash photolysis in water, with 2,4,6-triphenyl pyrylium encapsulated inside supercages of zeolite Y as photocatalyst under conditions in which propoxur is not directly altered [214]. According to the authors, the process could be initiated by one-electron transfer between the excited 2,4,6-triphenylpyrylium cation and propoxur to form the corresponding 2,4,6-triphenylpyrylium radical and propoxur radical cation.

#### 4.4. Chloronicotinoid insecticides

The TiO<sub>2</sub>-catalyzed photodegradation of imidacloprid (vide supra) has been followed as the formulated product Confidor in tap water. In the presence of TiO<sub>2</sub> a first-order rate equation was followed, and the observed half-life was 144 min, longer than in the absence of TiO<sub>2</sub> (126 min, see Part 2) [113].

#### 4.5. Chlorophenol pesticides

Tseng and Huang [215] studied the removal of phenol; 2-, 3- and 4-chlorophenol; 2,3-, 2,4-, 2,5-, 2,6- and 3,4-dichlorophenol; 2,4,6-trichlorophenol and pentachlorophenol from water by photocatalytic oxidation using TiO<sub>2</sub>/UV. The rate of photocatalyzed degradation follows first-order kinetics, independent of the pH. The rate increases with increase in TiO<sub>2</sub> concentration until a maximum of 3 g l<sup>-1</sup>, and then decreases. The influence of the degree of chlorination was described.

The photodegradation of 2,4-dichlorophenol and pentachlorophenol was studied in O<sub>2</sub>-free aqueous medium, in the presence of the hole scavengers polyethyleneimine, triethylamine, 2-propanol and ethylenediaminetetraacetic acid [216]. The photodegradation of both chlorophenols was inhibited by the above mentioned hole scavengers.

#### 4.6. Dinitroaniline pesticides

UV and sunlight induced photolysis of fluchloralin (vide supra) in aqueous methanol (80%) in the presence of TiO<sub>2</sub> yielded an additional product to those found upon direct

photolysis, which the authors attribute to result from a dimerization pathway [56].

#### 4.7. Halobenzonitrile pesticides

The sunlight photodegradation of aqueous solutions of bromoxynil (vide supra) was studied in the presence of TiO<sub>2</sub> and Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> [217]. When the pure pesticide was used, TiO<sub>2</sub> was more efficient as a photocatalyst. When the pesticide was used as a formulated solution, W<sub>10</sub>O<sub>32</sub><sup>4-</sup> became more efficient. The authors suggest that the difference in reactivity can be accounted for by the different nature of the active species involved in the photodegradation: HO· in the case of TiO<sub>2</sub> and an excited polyoxometalate in the case of W<sub>10</sub>O<sub>32</sub><sup>4-</sup>.

#### 4.8. Organochlorine insecticides

Vidal [218] has tested the feasibility of photocatalytic oxidation of lindane {1,2,3,4,5,6-hexachlorocyclohexane} using TiO<sub>2</sub>, a high pressure xenon arc lamp and a parabolic reflector, and found that it is possible to reduce 99.9% of lindane levels in water in acceptable times.

Hupka et al. [219] investigated the photocatalytic degradation of lindane in water, using a medium pressure mercury lamp and TiO<sub>2</sub>/O<sub>2</sub>. TiO<sub>2</sub> was used in the form of rutile, anatase and supported on glass hollow microspheres. The lowest efficiency of catalysis was observed for rutile and the highest for TiO<sub>2</sub> supported on glass microspheres. 1,2,3-trichloro benzene,  $\gamma$ -2,3,4,5,6-pentachloro-cyclohex-1-ene and a hexachlorocyclohexane (lindane) isomer,  $\alpha$ -HCH, were detected as reaction products after 150 min irradiation. Similarly, they studied the photocatalytic degradation of *p,p'*-DDT {1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane} under the same conditions, and with similar results in relation to the photocatalysts. Up to ten photoproducts were identified in this case.

#### 4.9. Organophosphorus pesticides

The solar TiO<sub>2</sub> photocatalyzed mineralization of malathion (vide supra) has been studied in rinse water of agricultural sprayers and in polluted well water [220]. The observed half-life was about 1 h in the presence of TiO<sub>2</sub> and absence of H<sub>2</sub>O<sub>2</sub>. Using polyethylene-film covered vessels it was observed that efficient photodegradation occurred in sealed systems.

The photocatalytic removal of fenitrothion (vide supra) from TiO<sub>2</sub> suspensions has been studied [221]. Several intermediates of the photocatalytic photodegradation have been identified. These subsequently underwent mineralisation into CO<sub>2</sub>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>.

Doon and Chang [222] studied the photocatalytic degradation of diazinon (vide supra), EPN (vide supra), malathion (vide supra), methamidophos {*O,S*-dimethyl

phosphoramidothioate} and phorate {*O,O*-diethyl *S*-[(ethylthio)methyl] phosphorodithioate}, in water, assisted by TiO<sub>2</sub> and using the UV radiation supplied by a medium pressure mercury lamp. The efficiency of degradation followed the order phorate > methamidophos > malathion ≈ diazinon > EPN. Apparently, methamidophos and phorate photodegrade mainly through direct photolysis, while TiO<sub>2</sub> enhances the photodegradation of diazinon, malathion and EPN. The use of UV/H<sub>2</sub>O<sub>2</sub> was more effective than that of UV/TiO<sub>2</sub>, with the combination UV/H<sub>2</sub>O<sub>2</sub>/TiO<sub>2</sub> being the most promising.

Ku and Jung [223] studied the photocatalytic degradation of monocrotophos {dimethyl (*E*)-1-methyl-2-(methylcarbamoyl)vinyl phosphate} in water by UV/TiO<sub>2</sub> (80% anatase, 20% rutile) irradiation at different pH values, TiO<sub>2</sub> dosages, light intensities and dissolved oxygen levels. The presence of oxygen inhibited the recombination of electrons and holes, enhancing the photodegradation of monocrotophos. An excess of oxygen had no effect. The degradation was more effective in acid solution than in alkaline medium. Increasing the light intensity enhanced the decomposition.

The use of 2,4,6-triphenylpyrylium ion encapsulated within Y zeolite as a photocatalyst for the photodegradation of methyl parathion {*O,O*-dimethyl *O*-4-nitrophenyl phosphorothioate} in aqueous solution has recently been studied, using both sunlight and the radiation supplied by high-pressure mercury lamps [109]. It was found that the zeolite encapsulation stabilizes the 2,4,6-triphenylpyrylium ion, leading to degradation efficiencies comparable to those obtained using TiO<sub>2</sub>. The authors rule out the intermediacy of singlet oxygen in the photodegradation process, as well as a direct photoinduced electron transfer process from 2,4,6-triphenylpyrylium ion to methyl parathion. They also suggest that radicals, resulting from interaction of 2,4,6-triphenylpyrylium ion with water and oxygen, are involved in the process.

Recently, Albanis et al. [38] reported on the photocatalytic degradation of methyl parathion (vide supra), ethyl parathion {*O,O*-diethyl *O*-4-nitrophenyl phosphorothioate}, methyl bromophos {*O*-4-bromo-2,5-dichlorophenyl *O,O*-dimethyl phosphorothioate}, ethyl bromophos {*O*-4-bromo-2,5-dichlorophenyl *O,O*-dimethyl phosphorothioate} and dichlofenthion {*O*-(2,4-dichlorophenyl) *O,O*-diethyl phosphorothioate} in aqueous TiO<sub>2</sub> suspensions using simulated sunlight from a xenon lamp, suppressing wavelengths below 290 nm with transmission filters. The observed half-life times varied from 10 to 40 min in the presence of TiO<sub>2</sub>, one or two orders of magnitude lower than in its absence. The major photo-products of photodegradation of ethyl bromophos and dichlofenthion were identified from the corresponding GC–MS (EI) fragmentation patterns, corresponding to oxidation and photohydrolysis pathways. The authors hypothesize a mechanism for the photodegradation of irgarol under the above mentioned conditions.

#### 4.10. Phenol-based pesticides

The photocatalytic decomposition of 2,4-D (vide supra) over TiO<sub>2</sub> and ZnO in water has been shown to take place with complete mineralisation to CO<sub>2</sub> and HCl [224]. Two mechanisms were proposed for the oxidation: oxidation with HO· radicals and direct oxidation by holes created on the semiconductor. The rate of photodegradation increased as the acidity of the medium decreased, and the presence of Cl<sup>-</sup> or HCO<sub>3</sub><sup>-</sup> slowed down the photodegradation rate by scavenging HO· radicals.

Herrmann et al. [225] studied also the photocatalytic degradation of 2,4-D at a pilot scale under solar irradiation. 2,4-D disappearance followed first-order kinetics and eventually yielded complete mineralization products within a residence time of less than 1 h. The main photoproduct of degradation of 2,4-D was 2,4-dichlorophenol.

The photodegradation of 4-nitrophenol in TiO<sub>2</sub> aqueous suspension has been studied as a function of the initial concentration of 4-nitrophenol, light intensity, partial pressure of oxygen, concentration of catalyst, pH, chloride concentration and temperature [226]. A kinetic expression was obtained incorporating the influence of the many factors.

The sunlight photodegradation of aqueous solutions of phenol, 4-chlorophenol and 2,4-dichlorophenol has been studied in the presence of TiO<sub>2</sub> and Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> [217]. When pure pesticides were used, TiO<sub>2</sub> was more efficient as a photocatalyst. When the pesticides were used in formulated solutions W<sub>10</sub>O<sub>32</sub><sup>4-</sup> became more efficient. The authors suggest that the difference in reactivity can be accounted for by the different nature of the active species involved in the photodegradation: with HO· in the case of TiO<sub>2</sub> and an excited polyoxometalate in the case of W<sub>10</sub>O<sub>32</sub><sup>4-</sup>.

The photodegradation of 4-chlorophenol using light of λ > 290 nm was used to model the photocatalytic properties of industrial TiO<sub>2</sub> catalysts and to compare their efficiencies [227]. Physical characteristics such as the particle size or the structure of the active site seem of importance for the photocatalytic activity.

Mazellier and Bolte [228] studied the goethite (α-FeOOH) light-induced transformation of aqueous 2,6-dimethylphenol, using 365, 436 and 546 monochromatic light. The rate of disappearance of the phenol increased with the concentration of oxygen. The involvement of hydroxyl radicals was discarded on the basis of the lack of influence of isopropanol. The authors suggest the phenol may react with positive holes in goethite, the electron being trapped by oxygen.

Topalov et al. [229] studied the photocatalytic mineralization of mecoprop (vide supra) in water, using TiO<sub>2</sub> as photocatalyst and irradiating with a medium-pressure mercury lamp. The rate of degradation was also followed using a Cl<sup>-</sup> selective electrode. Complete mineralization was observed, and a possible scheme suggested on the

basis of NMR spectra taken at different times. The same authors reported also on the photodegradation of MCPA {4-chloro-2-methylphenoxy acetic acid} over  $\text{TiO}_2$ . After 15 h of irradiation the mineralization was complete. As in the case of mecoprop, the proposed pathway of MCPA photodegradation in the presence of  $\text{TiO}_2$  also involves the formation of radicals [230].

#### 4.11. Pyrimidine pesticides

The photocatalytic degradation by sunlight of pyrimethanil {*N*-(4,6-dimethylpyrimidin-2-yl)aniline} was studied in its pure form and as commercial formulation in a preindustrial pilot plant, using  $\text{TiO}_2$  as a photocatalyst [231]. Complete photodegradation took 230 min, without total mineralization. Twenty two photoproducts were detected, several of which were identified. Some of the major photoproducts characterized were aniline, formamide, 1,3-benzenediol and 4,6-dimethyl-2-pyrimidinamine. Two mechanistic routes are suggested for the photodegradation, one involving reaction of hydroxyl radicals with the pyrimidine and benzene rings, with subsequent ring openings and the other involving photoinduced hydrolysis.

#### 4.12. Thiocarbamate herbicides

Albini et al. [232] studied the  $\text{TiO}_2$  photocatalyzed degradation of molinate {*S*-ethyl azepane-1-carbothioate}, eptam {*S*-ethyl dipropylcarbamothioate}, tiocarbazil {*S*-benzyl di-*sec*-butylthiocarbamate} and thiobencarb (vide supra) in water by 340–380 nm light. They consider the process to be efficient, although the maximum quantum yield is  $\approx 12\%$ . The process is rationalized as being initiated by hydrogen abstraction by  $\text{HO}^\cdot$  from the *N*-alkyl chains, rather than from the *S*-alkyl ones, except in the cases where this is a benzyl group.

#### 4.13. Triazine herbicides

Pelizzetti et al. [233] studied the  $\text{TiO}_2$  photocatalyzed degradation of atrazine (vide supra), simazine (vide supra), trietazine (vide supra), prometon (vide supra) and prometryn (vide supra) by simulated sunlight in aqueous solution, using a Xe lamp. All the herbicides were rapidly degraded. Full mineralization was not observed. Different intermediates have been identified, cyanuric acid being the common final photoproduct of all herbicides. A mechanism is proposed for the generation of the observed photoproducts.

The solar  $\text{TiO}_2$  photocatalyzed mineralization of atrazine (vide supra) has been studied in agricultural water and in polluted well water [220]. The observed half-life time was less than 1 h in the presence of  $\text{TiO}_2$  and absence of  $\text{H}_2\text{O}_2$ . The use of polyethylene-film covered vessels showed that efficient photodegradation takes place in sealed systems.

Bellobono et al. [234] used photocatalytic composite membranes immobilizing 30 wt%  $\text{TiO}_2$  to study photomineralization of atrazine (vide supra) solutions saturated with ozone. Co-immobilization of  $\mu$ -peroxo-bis[*N,N'*-ethylene-bis(salicylideneiminato)dimethylformamide cobalt (III)] and of a mixture of tri-(*t*-butyl)- and tri-(*i*-propyl)vanadate (V) led to rate enhancements of, respectively, 1.5- and 10-fold.

The photodegradation of prometryn (vide supra) and prometon (vide supra) has been followed in aqueous solution using membranes immobilizing  $\text{TiO}_2$ , and using  $\text{H}_2\text{O}_2$  as an oxygen supplier [235]. The observed kinetics followed a first-order equation. The quantum yields for photodegradation were rather high, 40% for prometryn and 66% for prometon. Cyanuric acid was found as photostable photoproduct.

The UV photodegradation of acidified aqueous solutions (pH=2.4) of atrazine (vide supra) was studied in the presence of  $\text{TiO}_2$  and  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  [236]. GC-MS, HPLC, radioactivity counting and TLC on  $^{14}\text{C}$ -labelled solutions were used. Both catalysts are efficient, leading to substantial increases in the rate of photodegradation. The mechanisms of photodegradation in the presence of each photocatalyst are different. The authors suggest that in the presence of  $\text{TiO}_2$ ,  $\text{HO}^\cdot$  radicals are the oxidant species, while in the case of  $\text{Na}_4\text{W}_{10}\text{O}_{32}$ ,  $\text{H}^\cdot$  abstraction on the alkyl side chains of atrazine and dehalogenation by electron transfer on the dealkylated metabolites takes place. Neither of these photocatalysts is able to mineralise the aromatic ring of atrazine.

Héquet et al. [237] showed that porphyrin and phthalocyanine complexes, used as photocatalysts for the degradation of atrazine (vide supra) are able to cleave the triazine ring more efficiently than  $\text{TiO}_2$ . The best degradation half-life time found was  $\approx 200$  min, using iron phthalocyanine as photocatalyst.

Recently, Albanis et al. [38] studied the photocatalytic degradation of atrazine (vide supra), propazine (vide supra), cyanazine (vide supra), prometryn (vide supra) and irgarol (vide supra) in aqueous  $\text{TiO}_2$  suspensions under simulated sunlight, supplied by a xenon lamp from which wavelengths below 290 nm had been suppressed using transmission filters. The observed half-life times varied from 10 to 40 min in the presence of  $\text{TiO}_2$ , one order of magnitude lower than in its absence. Eleven major photoproducts were detected from GC-MS (EI) fragmentation patterns for irgarol, corresponding to oxidation, dealkylation and dechlorination pathways. The authors hypothesize a mechanism for the photodegradation of irgarol under the above mentioned conditions.

Macounová et al. [238] studied the photodegradation of metamitron {4-amino-6-phenyl-3-methyl-1,2,4-triazin-5(4*H*)-one} on a plate photoreactor with immobilized  $\text{TiO}_2$  or as Q- $\text{TiO}_2$  particles. The main photoproducts found were deaminometamitron {6-phenyl-3-methyl-1,2,4-triazin-5(4*H*)-one}, deaminohydroymetamitron {6-(2'-hydroxy-



phenyl)-3-methyl-1,2,4-triazin-5(4*H*)-one} and hydroxy-metamitron {4-amino-6-(2'-hydroxyphenyl)-3-methyl-1,2,4-triazin-5(4*H*)-one}. The proposed mechanism accounts for the formation of the mentioned products in terms of the coexistence of two pathways: heterogeneous catalysis and homogeneous direct photolysis. According to the authors, photocatalysis is the major route when the plate photoreactor is used, while the homogeneous direct photolysis has the same weight as photocatalysis in colloidal solutions of the Q-TiO<sub>2</sub> particles.

#### 4.14. Miscellaneous

Turchi and Ollis [239] proposed different mechanisms to explain the reactivity with HO<sup>•</sup> radicals in photocatalytic systems. The cases of reaction on the surface, in the fluid and through a Rideal mechanism yielded rate equations analogous to Langmuir–Hinshelwood expressions. The proposed model allows estimation of the photocatalytic degradation rate from data on the physical properties of the photocatalyst, knowledge of the electron-hole recombination and trapping rates and the values of the second order rate constants for HO<sup>•</sup> radicals.

The photocatalyzed degradation of the pesticides propyzamide {3,5-dichloro-*N*-(1,1-dimethyl-2-propynyl)-benzamide}, iprobenfos (vide supra), simazine (vide supra) and fenobucarb {2-(1-methylpropyl)phenyl methylcarbamate} irradiating poly(2,5-dihexoxy-*p*-phenylene) and poly(3-oxylthiophene-2,5-diyl) films was studied with a 400-W high-pressure mercury lamp [240]. Photoexcitation of the polymer films leaves holes in the valence band and electrons in the conduction band. These electrons are trapped by O<sub>2</sub> to form O<sub>2</sub><sup>•-</sup>, from which HO<sup>•</sup> radicals can be formed, that can react with the pesticides. Degradation can be initiated also from the holes in the valence band.

The photocatalytic degradation of methoxychlor {1,1,1-trichloro-2,2-bis(4-methoxyphenyl)ethane} in water was investigated by Hupka et al. [219], using a medium pressure mercury lamp and TiO<sub>2</sub>/O<sub>2</sub>. The results were similar to those obtained for lindane and *p,p'*-DDT (vide supra).

A comparison of the photodegradation of phenol by direct photolysis and by TiO<sub>2</sub>-assisted photocatalysis was studied by Chun et al. [241] using various experimental conditions: λ > 200 nm in the presence of O<sub>2</sub> or N<sub>2</sub> or using O<sub>2</sub>/TiO<sub>2</sub>. Direct photolysis yielded a brownish-yellow polymer, both under O<sub>2</sub> and in inert atmosphere. Complete mineralization takes place under UV irradiation in O<sub>2</sub> atmosphere or in O<sub>2</sub>/TiO<sub>2</sub>. The polymer was found to be more difficult to degrade than the products of hydroxylation from TiO<sub>2</sub>-assisted photocatalysis.

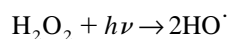
Malato et al. [242] described the use of a pre-industrial solar TiO<sub>2</sub> photocatalytic treatment for the photodegradation of high pesticide content waters from rinsing of pesticide containers. The authors used oxamyl as a model. Oxamyl was completely photodegraded, but the miner-

alization process was slow when using TiO<sub>2</sub> alone. The use of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> as electron scavenger enhanced the photo-mineralization process.

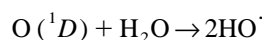
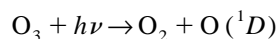
### 5. Degradation by reaction with the hydroxyl radical (HO<sup>•</sup>)

Some of the most frequently used AOPs involve molecules that upon photolysis generate the hydroxyl radical (HO<sup>•</sup>). This can be achieved by different ways, such as:

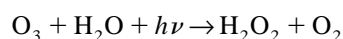
- (i) Addition of hydrogen peroxide that undergoes homolysis upon photolysis:



- (ii) Photolysis of ozone, either with generation of atoms of singlet oxygen that then react with water to generate HO<sup>•</sup>:

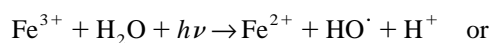
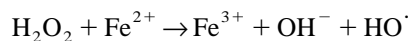


or which react directly with water to produce hydrogen peroxide [17]:

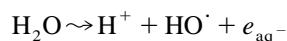


followed by its homolysis to generate hydroxyl radicals.

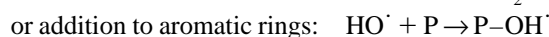
- (iii) Aqueous photolysis of Fe<sup>3+</sup>, generated by oxidation of Fe<sup>2+</sup> by H<sub>2</sub>O<sub>2</sub>:



- (iv) Radiolysis of water:



The HO<sup>•</sup> radical can then react either by:



#### 5.1. Acetamide herbicides

Brekken and Brezonik [243] studied the reaction between acetochlor {2-chloro-*N*-ethoxymethyl-6'-ethylaceto-*o*-toluidide} and HO<sup>•</sup>, assuming that the primary source of HO<sup>•</sup> is nitrate photolysis. The measured rate constant was  $k(\text{HO}^\bullet + \text{acetochlor}) = 7.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , a value that is close to the one previously reported for alachlor, based on structure–activity relationships [244].

The reported data do not eliminate the possibility that direct photolysis takes place, but indicate that it would be much slower than HO $\cdot$ -mediated degradation.

### 5.2. Anilide herbicides

The photo-Fenton degradation of metolachlor (vide supra) in water has been studied using 330–400 nm light [245]. Apparently, irradiation at these wavelengths did not enhance the rate of degradation.

### 5.3. Carbamate insecticides

Benítez et al. [43] studied the aqueous photolysis of carbofuran (vide supra) by the polychromatic light supplied by a high-pressure mercury lamp (emitting from 185 nm to far into the visible) in the presence of H $_2$ O $_2$ . Hydroxyl radicals accelerate the degradation relative to the case in which no H $_2$ O $_2$  is added. A simple rate equation is proposed, taking into account both the contribution of direct photolysis and that of the reaction with HO $\cdot$ .

### 5.4. Chlorophenol pesticides

Hirvonen et al. [246] studied the degradation of 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol in aqueous solution by the HO $\cdot$  radicals generated by 254 nm photolysis of H $_2$ O $_2$ . Hydroxylated chlorophenols and dimeric intermediates were found as transient intermediates in the degradation. Eventually, a complicated mixture of products was obtained, and the authors suggest the necessity of toxicity testing to assess the detoxification effects of the treatment. Furthermore, they consider the dechlorination degree to be insufficient.

The degradation of pentachlorophenol by photo-Fenton systems has been analysed by Fukushima and Tatsumi [247], possible degradation pathways by such photo-Fenton systems being proposed.

### 5.5. Organophosphorus pesticides

Cernák and Cernáková [248] studied the application of a H $_2$ O $_2$ /UV (254 nm) combination for removing parathion-methyl (vide supra) and phenitroton {*O,O*-dimethyl *O*-4-nitro-*m*-tolyl phosphorothioate}. The maximum degradation took place within the first 5 min, longer exposures did not significantly increase the efficiency.

More recently, Doon and Chang [249] investigated the photodegradation of parathion (vide supra) in water, and in the presence of TiO $_2$ , Fe compounds and H $_2$ O $_2$ , using a 100-W medium pressure mercury lamp. The addition of TiO $_2$  or Fe in combination with H $_2$ O $_2$  was effective to degrade the pesticide. The authors measured the apparent first-order rate constants for disappearance of parathion. These increased with increasing load of TiO $_2$ , but when

the dose was higher than 2 g TiO $_2$  l $^{-1}$  decreased again. The system Fe $^{3+}$ /H $_2$ O $_2$  was shown to be involved in the degradation when Fe/H $_2$ O $_2$  were combined. Oxidant oxyanions were shown to act as electron scavengers, enhancing the degradation in the sequence ClO $_2^-$  > IO $_3^-$  > BrO $_3^-$  > ClO $_3^-$ . Oxygen had little effect on the photodegradation process. Diethylphosphoric acid, *p*-nitrophenol, diethylmonothiophosphoric acid, *O,O*-ethyl *p*-nitrophenyl monothiophosphoric acid and oxalate were identified as intermediates, which were subsequently oxidized.

Miller et al. [57] developed a method based on the technique of solid-phase microextraction to determine the rate of reaction of chlorpyrifos (vide supra) with HO $\cdot$  in the gas phase at high temperatures. The half-life observed for chlorpyrifos was 1.4 h. Changing the temperature from 60 to 80 °C did not affect the rate of photodegradation.

### 5.6. Phenol-based pesticides

The aqueous photodegradation of 2,4-D {2,4-dichlorophenoxyacetic acid} by UV radiation in the presence of H $_2$ O $_2$  was faster than in its absence, with more than 98% of the starting material having disappeared within the first 10 min of treatment [131]. The authors suggest the main processes taking place involve substitution of Cl by OH at the *o*- and *p*- positions of the aromatic ring, and elimination of H $\cdot$  from the  $\alpha$ -methylene of phenoxyacetic acid.

HO $\cdot$  reactivity with bromoxynil (vide supra), adsorbed on highly dispersed thin layer of silicon dioxide powder, used as unreactive carrier, was studied [84]. The degradation was fast, and was mainly attributed to direct photolysis.

Mazellier and Bolte [250] studied the degradation of 3-chlorophenol by reaction with HO $\cdot$ , generated via an intramolecular photoredox process in iron(III) excited hydroxy-complexes, specially Fe(OH) $^{2+}$ . Monochromatic 365 nm radiation was used as excitation source. The quantum yields observed for 3-chlorophenol disappearance were in all cases rather low,  $\approx$ 5%. The main reaction products observed were 2-chlorohydroquinone, 2-chlorobenzoquinone, 3-chlorocatechol and 4-chlorocatechol.

### 5.7. Phosphorothioate insecticides

Miller et al. [57] developed a method based on the technique of solid-phase microextraction to determine the rate of reaction of diazinon (vide supra) with HO $\cdot$  in the gas phase at high temperatures. The half-life observed for diazinon was 0.5 h. Changing the temperature from 60 to 80 °C did not affect the rate of photodegradation.

### 5.8. Triazine herbicides

Haag and Yao [244] measured the rate constants for reaction of HO $\cdot$  radicals with different drinking water contaminants, including atrazine (vide supra) and simazine

(vide supra). A variety of HO $\cdot$  generation methods were used, among which is the photo-Fenton method, that was used with both compounds. The rate constants found were, respectively,  $2.6 \pm 0.4 \times 10^9$  and  $2.8 \pm 0.2 \times 10^9$  M $^{-1}$  s $^{-1}$ .

Cernák and Cernáková [248] studied the application of a H $_2$ O $_2$ /UV combination for removing atrazine (vide supra), prometryn (vide supra), terbuthylazine (vide supra), terbuthryne (vide supra). They observed a maximum of degradation in the first 5 min, longer exposures being inefficient.

A comparison of the photochemical oxidation of atrazine by combined UV/H $_2$ O $_2$  and other advanced oxidation methods was carried out [251]. A monochromatic light source emitting at 254 nm was used for irradiation. Hydroxyatrazine, *N* and *N,N'*-dealkylated, deaminated and hydroxyderivatives of atrazine were the major photo-products found.

UV/H $_2$ O $_2$  photolysis of two products of photodegradation of atrazine (vide supra), namely deethylatrazine and deisopropylatrazine was studied [151]. Significant reductions in the rate of photodegradation were observed in surface waters, which the authors attribute to the presence of natural radical scavengers. No attempts were made to identify by-products of these photolysis reactions.

Hapeman et al. [252] examined the reaction of HO $\cdot$  radical reaction with atrazine (vide supra). HO $\cdot$  was generated by irradiation of nitrate solutions with 290 nm light from a xenon lamp. The products found were 20% 6-amino-2-chloro-4-isopropylamino-*s*-triazine, 10% 6-amino-2-chloro-4-ethylamino-*s*-triazine, 6% 4-acetamide-2-chloro-6-isopropylamino-*s*-triazine, 3% 4-acetamide-2-chloro-6-ethylamino-*s*-triazine, 16% chlorodiamino-*s*-triazine and 3% hydroxy atrazine, at 87% atrazine conversion. The reaction was found to be much faster than direct photolysis that, at 23% photolysis led to 14% hydroxy atrazine and  $\approx$ 9% of chloroalkoxydized and chloro-dealkylated products.

A study of the reaction patterns of photooxidation of metribuzin (vide supra) in water by the UV radiation supplied by a mercury lamp showed a pronounced effect of oxygen on the degradation rate, with a small influence from the presence of H $_2$ O $_2$  [253]. The authors suggest that the process starts via a reaction of excited metribuzin with H $_2$ O $_2$  or O $_2$ .

The photo-Fenton degradation of atrazine (vide supra) in water, using 330–400 nm light has been studied [245]. According to the authors, irradiation at these wavelengths did not enhance the degradation of the herbicides. The main pathways of degradation of atrazine were *N*-dealkylation and dechlorination.

Bellobono et al. [254] used competition kinetics to obtain the rate constants for reaction of ametryn (vide supra), atrazine (vide supra), propazine (vide supra) and prometryn (vide supra) with HO $\cdot$  radicals at pH 7.0 on photocatalytic membranes, in the presence and absence of trialkyl vanadates as photocatalytic promoters of immobilized

TiO $_2$ . The rate constants so-obtained are  $k(\text{triazine} + \text{HO}\cdot) = 1.5 \times 10^{10}$ ,  $0.95 \times 10^{10}$ ,  $1.1 \times 10^{10}$  and  $1.3 \times 10^{10}$  M $^{-1}$  s $^{-1}$ , respectively, for ametryn, atrazine, propazine and prometryn. The authors point out that the presence of a methylthio group in the 6-position (ametryn, prometryn) instead of a chlorine (atrazine, propazine) seems to induce a higher reactivity.

HO $\cdot$  reactivity has been studied with simazine (vide supra) and terbuthylazine (vide supra) adsorbed on highly dispersed thin layer of silicon dioxide powder, used as unreactive carrier [84]. The HO $\cdot$  radicals were produced by photolysis of hydrogen peroxide in the gas phase with sunlamps. In this way, the first-order degradation rates observed for simazine and terbuthylazine were similar ( $k_{\text{HO}\cdot} \approx 1.1 \times 10^{-1}$  M $^{-1}$  s $^{-1}$ ).

Von Gunten et al. [255] recently revisited the degradation of atrazine (vide supra) by reaction with HO $\cdot$  during advanced oxidation processes, identifying the main degradation products: 6-amino-2-chloro-4-isopropylamino-*s*-triazine, 6-amino-2-chloro-4-ethylamino-*s*-triazine, 4-acetamido-2-chloro-6-isopropylamino-*s*-triazine, 4-acetamido-6-amino-2-chloro-*s*-triazine, chlorodiamino-*s*-triazine, 2-chloro-4-ethylimino-6-isopropylamino-*s*-triazine, 6-amino-2-chloro-4-ethylimino-*s*-triazine. The rate constant for reaction between atrazine and HO $\cdot$  was determined as  $3 \times 10^9$  M $^{-1}$  s $^{-1}$ , approximately three times higher than those measured for the different degradation products. HO $\cdot$  attack on the ethyl group was favoured relative to HO $\cdot$  attack on the isopropyl group.

### 5.9. Uracil herbicides

Muszkat et al. [253] studied the reaction patterns of photooxidation of bromacil {5-bromo-3-*sec*-butyl-6-methyluracil} in water by UV light from a mercury lamp, and showed a small effect of oxygen on the degradation rate, but a strong influence from the presence of H $_2$ O $_2$ . The authors suggest the reaction is initiated by HO $\cdot$  radicals generated by H $_2$ O $_2$  photolysis.

### 5.10. Urea-based pesticides

From a study of the application of a H $_2$ O $_2$ /UV (254 nm) combination for removing chlorbromuron {3-(4-bromo-3-chlorophenyl)-1-methoxy-1-methylurea}, linuron (vide supra) it was concluded that the maximum extent of degradation took place within 5 min, with longer exposures being inefficient [248].

The degradation of diuron {3-(3,4-dichlorophenyl)-1,1-dimethylurea} photoinduced by Fe $^{3+}$ , using different Fe $^{3+}$  species and exciting at 365 nm and under sunlight has been studied [256,257]. Apparently, the mechanism of photo-induced degradation involves only attack by HO $\cdot$  radicals, yielding 3-(3,4-dichloro-phenyl)-1-formyl-1-methylurea as

the major degradation product, in a relatively slow process ( $t_{1/2} \approx 1\text{--}2$  h to a few days depending on  $[\text{Fe}^{3+}]$ ).

### 5.11. Miscellaneous

Draper and Crosby [258] studied the sunlight and near-UV induced photodegradation of different classes of pesticides, such as thiocarbamates, chlorophenoxy acids, organophosphorus pesticides, *N*-methylcarbamate, cyclodienes and others in the presence of dilute  $\text{H}_2\text{O}_2$ .  $\text{HO}^\cdot$  radicals were found to be the major reactants, and appropriate reaction mechanisms have been proposed in some cases.

A method has been developed for determining rates of generation and consumption of  $\text{HO}^\cdot$  radicals in natural waters, based on measurement competition kinetics with a trace compound, using both a high pressure mercury lamp and sunlight irradiation [259]. Possible interference's arise from the presence of nitrate in natural waters.

The rate of aqueous photodegradation of atrazine (vide supra), ametryn (vide supra), prometon and prometryn (vide supra) using the radiation supplied by a medium-pressure mercury lamp was greatly enhanced by the addition of  $\text{Fe}^{3+}$  [260]. The rate enhancement is attributed to the reaction with  $\text{HO}^\cdot$ . Quenchers of  $\text{HO}^\cdot$  reduced the rate of photodegradation. The photoproducts found were the ones expected for a Fenton reaction. The reaction rate decreased also in the absence of  $\text{O}_2$  and in natural water.

Mabury and Crosby [261] studied the reactivity of  $\text{HO}^\cdot$  toward ten different pesticides: atrazine (vide supra), carbaryl (vide supra), carbofuran (vide supra), 2,4-D (vide supra), hexazinone, MCPA (vide supra), picloram {4-amino-3,5,6-trichloropicolinic acid}, propanil (vide supra) and quinclorac {3,7-dichloro-8-quinolinecarboxylic acid}. The reaction rates were estimated by competition kinetics, using *p*-nitroso-*N,N*-dimethylaniline as a standard competitor.  $\text{HO}^\cdot$  radicals were generated by photolysis of  $\text{H}_2\text{O}_2$  using a 40-W fluorescent UV lamp, with a maximum in its UV emission at 310 nm. The most reactive compound was carbaryl ( $3.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ), and the least reactive hexazinone ( $0.62 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). However, the estimated values are rather lower than those determined by Haag and Yao [244] by photo-Fenton reaction. The authors estimated for the reaction of  $\text{HO}^\cdot$  with benzoic acid a rate constant of  $3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , to be compared with the authentic value of  $5.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , obtained by Buxton et al. [262] by pulse radiolysis.

Armbrust and Reilly [263] measured the rate constants for reaction of methomyl {(*Z*)-*S*-methyl *N*-(methylcarbamoyloxy)thioacetimidate}, oxamyl {*N,N*-dimethyl-2-methylcarbamoyloxy-imino-2-(methylthio)acetamide}, bensulfuron-methyl {methyl 2-[(4,6-dimethoxypyrimidin-2-yl)carbamoylsulfamoylmethyl]benzoate}, azimsulfuron {1-(4,6-dimethoxypyrimidin-2-yl)-3-[1-methyl-4-(2-methyl-2*H*-tetrazol-5-yl)-pyrazole-5-yl]sulfonyl}urea} and sul-

fometuron-methyl {methyl 2-[4,6-dimethylpyrimidin-2-yl-carbamoylsulfamoyl]benzoate} with photochemically generated hydroxyl radical. The obtained values suggest indirect photolysis is most relevant in the photodegradation of the studied compounds.

Bauer et al. [264] proved the photo-Fenton method to be very powerful for treating mixtures of ten pesticides: acrinathrin {cyano(3-phenoxyphenyl)methyl 2,2-dimethyl-3-[3-oxo-3-[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]-1-propenyl]cyclopropanecarboxylate}, abamectin {(10*E*,14*E*,16*E*,22*Z*)-(1*R*,4*S*,5'*S*,6*S*,6'*R*,8*R*,12*S*,13*S*,20*R*,21*R*,24*S*)-6'[(*S*)-*sec*-butyl]-21,24-dihydroxy-5',11,13,22-tetramethyl-2-oxo-3,7,19-trioxatetracyclo-[15.6.1.1<sup>4,8</sup>.0<sup>20,24</sup>]-pentacosa-10,14,16,22-tetraene-6-spiro-2'-(5',6'-dihydro-2'*H* pyran)-12-yl-2,6-dideoxy-4-*O*-(2,6-dideoxy-3-*O*-methyl- $\alpha$ -*L*-arabino-hexopyranosyl)-3-*O*-methyl- $\alpha$ -*L*-arabino-hexopyranoside}, endosulfan {(1,4,5,6,7,7-hexachloro-8,9,10-trinorborn-5-en-2,3-ylenebismethylene)sulfite}, formetanate {3-dimethylaminomethyleneimino-phenyl methylcarbamate}, imidacloprid (vide supra), lufenuron {(*RS*)-1-[2,5-dichloro-4-(1,1,2,3,3,3-hexafluoropropoxy)-phenyl]-3-(2,6-difluorobenzoyl)urea}, methamidofos {*O,S*-dimethyl phosphoramidothioate}, oxamyl {*N,N*-dimethyl-2-methylcarbamoyloxyimino-2-(methylthio)acetamide}, propamocarb {propyl 3-(dimethylamino)propylcarbamate} and pyrimethanil {*N*-(4,6-dimethylpyrimidin-2-yl)aniline}. The mixtures were used as a model for a plant conceived for destroying pesticides in the wastewater of a pesticide bottle recycling plant. All the pesticides underwent degradation, some of them rather slowly. The degradation was incomplete, a residual amount remaining in solution. Addition of oxalate accelerated the degradation, but did not improve the level of degradation. The results seem to be better than those previously obtained by photocatalysis in the presence of  $\text{TiO}_2$ .

## 6. Other papers of interest

A seminal detailed study of the photo-Fries reaction, including a comprehensive mechanistic scheme is due to Sandner et al. [265] These authors present evidence that the photo-Fries rearrangement takes place via a 1,3-sigmatropic shift originating from an upper singlet state. The process is of most interest in relation to the photodegradation of pesticides such as carbamates and ureas.

Bent and Hayon [266] studied by 265-nm laser flash photolysis the formation and the reactivity of the triplet state of *s*-triazine in acetonitrile, cyclohexane and isopropanol. The triplet-triplet absorption spectrum showed maxima at 245 and 303 nm, and shoulders at 345 and 450 nm. The rate of decay in acetonitrile was  $\approx 1.1 \times 10^6 \text{ s}^{-1}$ . The triplet state was efficiently quenched by H-atom donors, and probably by  $e^-$ -donors.

Wells et al. [267] described the photochemistry of the

pyrimidinic fungicides dimethirimol {5-butyl-2-dimethylamino-6-methylpyrimidin-4-ol} and ethirimol {5-butyl-2-ethylamino-6-methylpyrimidin-4-ol}, as well as the structurally related compound 2-dimethylamino-5,6-dimethylpyrimidin-4-ol. The fluorescence, phosphorescence and other photophysical properties have also been described.

Bersohn et al. [268] studied the photodissociation of *s*-triazine at 248 and 193 nm, finding three HCN molecules as photoproducts. Different considerations are made about the dynamics of the system and of the kinetic energy distributions of the molecules at both wavelengths.

Getoff et al. [269] studied the pulse radiolysis of paraquat (vide supra) in air-free aqueous solution at various pHs. The very fast reaction of paraquat with the solvated electron took place with  $k(\text{paraquat} + e_{\text{aq}}^-) = 7.5 \times 10^{10} \text{ mol M}^{-1} \text{ s}^{-1}$ , yielding a long-lived radical cation showing to absorption maxima at 392.5 and 600 nm, respectively. Other processes undergone by paraquat have also been characterized.

Wardman [270] measured by pulse-radiolysis the one-electron reduction potential for various bipyridinium compounds. Among them, the one-electron reduction potential for paraquat is  $E^\circ(\text{methyl viologen}^{2+}/\text{methyl viologen}^{\cdot+}) = -0.45 \text{ V vs. NHE}$ .

Katagi [271] has performed quantum chemical estimations of the environmental fate of pesticides, expected to be useful in making considerations about the photooxidation and photosensitized degradation of pesticides. The photoinduced decarboxylation and isomerization of pyrethroids were successfully explained using a photolysis index based on the change of electron population at each bond upon excitation.

Halmann et al. [272] studied the photodegradation of xenobiotic contaminants in water samples from a heavily polluted well by sunlight, using three different combinations of photocatalysts:  $\text{TiO}_2/\text{H}_2\text{O}_2$ ,  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$  and  $\text{TiO}_2/\text{Fe}^{3+}/\text{H}_2\text{O}_2$ . Among these, were acetamides, benzonitriles, ureas and triazines. The third combination led to appreciable degradation within 3–4 h. More complete photodegradation required long exposures.

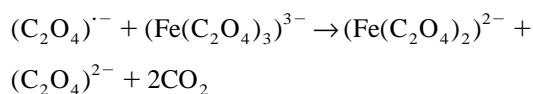
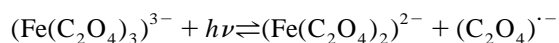
Fischer and Nwankwoala [273] studied the photolysis of 1,2,3-triazine in hexane and methanol and in vapour phase. They found decreasing photodissociation quantum yields as the wavelength increases, and independence of the quantum yields with the nature of the solvent and the presence of air in solution. Acetylene and an unidentified compound were the major photoproducts, indicating that photofragmentation is not the main photodegradation pathway. This is not the case in vapour phase, where acetylene and HCN were the main products, suggesting a concerted mechanism.

Scaiano et al. [274] studied the laser flash photolysis of carbamates derived from 9-fluorenone oxime. The authors propose a mechanism involving N–O and C–N bond scission upon excitation and subsequent generation of a

triplet radical pair in a solvent cage, that can then decay by three different pathways: (i) intersystem crossing to the singlet radical pair that then forms the (2,5-dimethoxyphenyl)hydrazone of 9-fluorenone, (ii) separation of the triplet radical pair, and (iii) disproportionation yielding 9-fluorenone ketimine and triplet (2,5-dimethoxyphenyl)nitrene.

Schmidt et al. [275] carried out an NMR and molecular mechanics study of alachlor (vide supra) conformation, and of its implications on the mechanism of photodegradation. The authors conclude that environmental factors affecting the conformation of alachlor at the molecular level may alter both the rate and pathway of alachlor degradation.

The use of ferrioxalate  $(\text{Fe}(\text{C}_2\text{O}_4)_3)^{3-}$  as mediator of sunlight photodegradation of organic pollutants in water has been studied [276]. Irradiation of ferrioxalate proceeds as:



In the presence of  $\text{H}_2\text{O}_2$ ,  $\text{HO}^\cdot$  radicals are generated as in the photo-Fenton method (see above). The efficiency of this process for photodegradation of organic pollutants in tap water has been shown to be at least 25 times higher than using sunlight/ $\text{TiO}_2/\text{H}_2\text{O}_2$ .

The fate of peroxy radicals in aqueous medium has been recently reviewed by von Sonntag et al. [277]. Peroxy radicals are formed during drinking-water and wastewater processing by reaction of carbon-centered radicals with dissolved  $\text{O}_2$ , in a reaction that is irreversible in most cases. The carbon-centered radicals from which the reaction starts are generated by reaction of  $\text{HO}^\cdot$  with dissolved organic compounds.

Heit and Braun [278] described different effects observed upon VUV-irradiation (172 nm) of aqueous solutions containing organic compounds. The observed processes are dominated by the very short lifetimes of the intermediates generated by homolysis of water.

Braun and Oliveros [279] recently reviewed the state-of-the-art of methods for water treatment, discussing how to evaluate them. The authors suggest appropriate solutions may be found in the combination of photochemical and thermal (catalyzed) processes.

Wagner et al. [280] described the use of excimer lasers for wastewater treatment; 193 nm and 248 nm excimer lasers were used, with the first showing higher efficiency than the second.

A detailed study that is related to the photodegradation of carbamates and ureas has been carried out by Tsentlovich et al. [281], who investigated the photo-Fries rearrangement of 1- and 2-naphthyl acetates using steady-state photolysis and laser flash photolysis, and proposed a

general mechanism for the photolysis of both compounds. Upon irradiation, naphthyl acetates are excited into the first excited singlet state, that is responsible for most of the generated photoproducts. This singlet state can either dissociate to yield a radical pair or undergo intersystem crossing to the  $T_2$  triplet state, which can then yield the same radical pair as the singlet state or relax to the unreactive  $T_1$  triplet state within few nanoseconds.

The UV–Vis absorption and emission spectra of the fungicide fenarimol in solution have been studied [282]. Comparison of the spectra with those of chlorotoluenes and pyrimidine, as well as the effect of solvent polarity on the absorption spectrum allowed the authors to conclude that the lowest excited singlet state is localized on the pyrimidine ring, having  $n, \pi^*$  character. Higher excited  $\pi, \pi^*$  states are localized on the chlorotoluene and pyrimidine rings. A weak fluorescence from the  $n, \pi^*$  state is observed, with its quantum yield being strongly dependent on the solvent. Phosphorescence was observed at low temperatures, and was attributed to a triplet state with  $\pi, \pi^*$  character.

The use of the photo-Fenton method for degradation of nitrogen-containing compounds was studied [283]. Aromatic compounds degraded to a extent higher than the aliphatic ones. In most cases nitrogen was released as ammonia upon photodegradation.

Solar et al. [284] have studied the degradation aqueous chlorophenol solutions by the  $\gamma$ -radiation obtained from a  $^{60}\text{Co}$ - $\gamma$ -source. The results showed that 50- $\mu\text{M}$  solutions were completely degraded using 600 and 1000 Gy, respectively.

Leintner et al. [285] studied the degradation of aqueous atrazine (vide supra) from solutions containing humic substances, using  $\gamma$ -radiation obtained from a  $^{60}\text{Co}$ - $\gamma$ -source. The studies were carried out with continuous bubbling of  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{N}_2\text{O}$  and  $\text{N}_2\text{O}/\text{O}_2$  (80:20). Atrazine was degraded both by reaction with  $\text{HO}^\cdot$  and with  $e_{\text{aq}}^-$ . For the radiation dose applied ( $\approx 800$  Gy),  $\text{HO}^\cdot$  and  $\text{O}_2^{\cdot-}$  were the most reactive species.

Armbrust [286] used a computerized model to compare the relative importance of the photochemical processes influencing pesticide degradation in rice paddies. Among these, indirect photodegradation processes: degradation by hydroxyl and carbonate radicals, and by singlet oxygen, have been shown to be far more important than direct photolysis.

Esplugas et al. [287] studied the influence of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  in the photodegradation using UV radiation of nitrobenzene in aqueous solution. Both the concentration of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  showed great effect on the rate of photodegradation, with the first being more efficient. The major photoproducts found were nitrophenol isomers.

Atrazine (vide supra) was shown to be completely destroyed in aqueous solution upon  $\gamma$ -irradiation using doses of 0.1–50 kGy from a  $^{60}\text{Co}$  source [288]. Ethyl-

amine, isopropylamine, 2-isopropylamino-*s*-triazine, 2-ethylamino-*s*-triazine and 2-hydroxy-4-ethylamino-6-isopropylamino-*s*-triazine were the observed products. Cleavage of the C–Cl bond was the main process, with halogen substitution by a hydroxyl group.

Dionysiou and co-workers [289,290] recently developed, characterized and evaluated a rotating disk photocatalytic reactor for the photodegradation of organic pollutants. They tested the device using 4-chlorobenzoic acid and chlorophenols as a model compounds and a batch of low pressure mercury tubes. The reactor exhibited advantages such as immobilization of the catalyst, reactions in a thin liquid film and a mixing regime close to that of an ideal continuously stirred tank reactor. Although the photonic efficiency of the reactor was low in some cases, the authors expect to be able to optimize it.

Feng and Nansheng [291] reviewed the photochemistry of hydrolytic iron(III) species and the photoinduced degradation of organic compounds in connection with these inorganic species. They show how the pH,  $\text{Fe}^{3+}$  concentration, wavelength and energy of irradiation source, and the nature of the organic compounds influence the photodegradation processes. All the low-molecular weight derivatives of  $\text{Fe}^{3+}$  can generate  $\text{HO}^\cdot$ , with  $\text{Fe}(\text{OH})^{2+}$  being the most relevant. Hydrolytic  $\text{Fe}^{3+}$  polymers are presumed to also be photoactive. The mechanisms of action of other environmentally relevant species are discussed.

The UV absorption and fluorescence maxima of 2,4,6-triaryl-1,3,5-triazines show a marked bathochromic shift as the acidity of the medium increases. Evidence for a simple protonation equilibrium came from the existence of clearly defined isosbestic points. As the acidity of the medium increases, the fluorescence of the unprotonated triazines is replaced by the much weaker fluorescence of the protonated species, which shifts to longer wavelengths. As with many other aza-nitrogen containing heterocycles, the  $\text{p}K_a$  increases from 6.8 to 9 units upon excitation from  $-1.7$  to  $3.7$  in the ground state to  $7$ – $11$  in the lowest singlet excited state [292,293]. The excited state of the protonated form was calculated to be  $37$ – $51$   $\text{kJ mol}^{-1}$  lower than that of the unprotonated species.

Lester et al. [294] reviewed the abiotic degradation of pyrethroids, triazines and ureas, concluding they are susceptible of photodegradation, and that the potential for their photosensitized degradation is uncertain.

Recently, Cid et al. [295] carried out different bioassays with two freshwater microalgal species, *Chlamydomonas moewusii* and *Chlorella vulgaris*, in an attempt to assess the efficiency of photodegradation of paraquat (vide supra) and isoproturon (vide supra) in water. The evolution of growth and of concentration of photosynthetic pigments of the above microalgae upon a 96-h treatment with the pure herbicides, as well as with solutions of the same that had been photolysed with 248 nm light were measured. The

results show that the attempted photodegradation can effectively reduce the biotoxicity of herbicides.

## 7. Concluding remarks

Photodegradation studies on pesticides have focussed on two distinct, but not unrelated, objectives. Firstly, it is important that for their efficacy they do not photodegrade during the time they are exercising their biocidal activity. On the other hand, for environmental considerations it is important that they can eventually be converted to innocuous, and preferable mineral, photoproducts. Direct sunlight induced photodegradation of most pesticides is a minor event, which leads to the problem of their long-term persistence in the environment. Instead, these are more effectively degraded by using UV light, despite the higher economic cost of the process. Alternatively, photosensitized and photocatalytic processes are also becoming popular for treating pesticide residues, although they do have certain drawbacks, such as the high biotoxicity of some of the sensitized compounds or metal catalysts used. Indirect degradation methods based on the reaction of the pesticides with hydroxyl radicals are also effective and have low cost, but the reaction products produced are in some cases as problematic or more so than the starting materials. In this review, we have discussed examples of these processes with the most important groups of pesticides, herbicides, insecticides and fungicides.

A huge amount of effort has been put into the identification of the photoproducts of degradation of different types of pesticides, using a wide range of methods. As a consequence, most of the main products of photodegradation of pesticides can, in principle, be nowadays quantified in a relatively straightforward manner. Although, in practice, some problems may exist because of low solubilities of pesticides or products.

In contrast to the above situation, there is a dramatic lack of detailed mechanistic studies of the different pathways leading to such photoproducts. Many of the mechanisms that have been put forward so far are purely speculative, and no detailed elucidation has been performed. There are various factors which contribute to this, such as low solubility of the compounds, low quantum yields of degradation, frequent presence of more than one chromophoric group in the pesticide molecules, in addition to the shortage of application of rapid reaction techniques to characterize intermediates. However, the difficulties due to the very short lifetimes expected for most potential intermediates can be nowadays easily overcome by the use of ultrafast kinetic techniques such as laser flash photolysis or pulse radiolysis in the nano- or picosecond regime. In addition, many of the proposed intermediates are radical in nature, and amenable to study by electron paramagnetic resonance spectroscopy, particularly using spin traps. The

effect of factors such as the acidity of the medium, salt concentrations, presence of buffers, etc. are, in general, not properly understood. It will be difficult to model the environmental fate of agrochemicals unless detailed mechanistic studies become available, and these should be taken as a major task and encouraged for the near future.

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