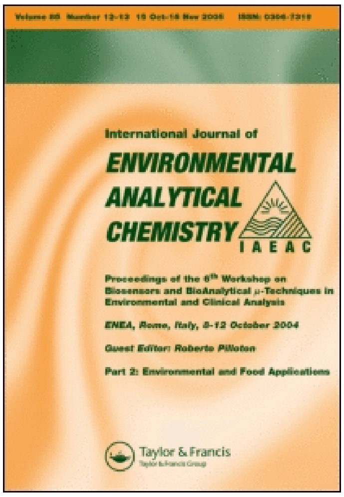

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Gc-Ms Analysis of Photodegradation Products of Dichlophop-Methyl

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GC-MS ANALYSIS OF PHOTODEGRADATION PRODUCTS OF DICHLOPHOP-METHYL

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The photochemical transformation products of 2-[4-(2,4-dichlorphenoxyphenylen]propionic acid methyl ester (**I**), the active ingredient of the herbicide Dichlophop methyl (trade mark Illoxane) after irradiation with Hg (λ_{max}=254 nm) and Xe (λ>290 nm) lamps in solution, in thin film on the glass surface and in soil were studied by GC-MS.

The main photodegradation pathway was found to be reductive and oxidative dechlorination, intramolecular cyclisation and ester bonds cleavage. The photodegradation of Illoxane is considered as a model for chlorophenoxy pesticides degradation and toxic methabolites formation in the environment.

KEY WORDS: Illoxane, dichlophop methyl, photodegradation, photocyclization, GC-MS.

INTRODUCTION

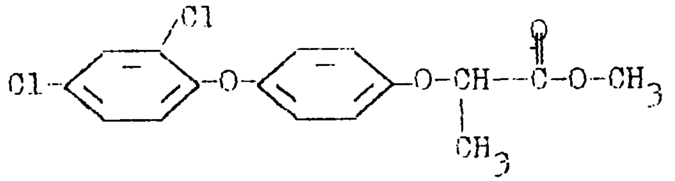
Photolysis is an important transformation pathway for many chlorinated pesticides in the environment and may lead to toxic products formation[1]. Of particular interest is the determination of photochemical transformation products of chlorinated diphenyl ethers because of their structural similarity to some chlorinated dibenzo-p-dioxin and dibenzofuran precursors. Such compounds and their heterocyclic analogs are widely used as pesticides. They are very sensitive to irradiation and their photodegradation was shown to occur principally via reductive or oxidative dechlorination and aryl- or hetaryl- bond cleavage accompanied by chlorophenols formation. Also intramolecular photocyclisation can occur leading to dibenzofurans formation[2].

Some of these chlorinated photodegradation products are very toxic and are considered as environmental priority pollutants[3,4]. The final products distribution depends both on the initial compounds structure and on the conditions of photolysis. With this idea in mind we were interested in evaluating the significance of photocyclisation compared with other photodegradation reactions of some pesticides structurally related to chlorinated diphenyl ethers.

In a previous paper [5] we studied the photodegradation of the active ingredient of the herbicide Goal, 4-nitro-4′-trifluoromethyl-2′-chloro-3-ethoxy diphenyl ether, under a xenon lamp irradiation and found a number of chlorinated and unchlorinated photocyclisation products.

This study was aimed to determine the products of the photochemical transformation of 2-[4-(2,4-dichlorophenoxy)phenylen]propionic acid methyl ester (**I**), the active ingredient of the herbicide Dichlophop-methyl (trade mark Illoxane).

(I)



To estimate the influence of the light source on the photodegradation processes, Illoxane was irradiated in solution with a Hg lamp of medium pressure (λ_{max}=254 nm) and a Xe lamp of ultrahigh pressure (λ>290 nm), the spectrum of the last being similar to that of sunshine of the Northern Hemisphere[6]. Moreover, the composition of the reaction mixture was studied when Illoxane was irradiated on a glass surface with a Xe lamp.

Qualitative and quantitative analysis of the photodegradation products were performed by GC-MS.

EXPERIMENTAL

Substrates

Illoxane (I) was purchased from Riedel-de Haen AG (N.35511, 99%). Water-methanol solutions of **I** (10 ng/ml) were irradiated in quartz cells (3.5 x 10 mm) with capillary caps under Hg or Xe lamps. **I** was irradiated also as thin films on the glass surface of Petry dishes (diameter 6.5 mm, 0.45 mg) under a Xe lamp. Control runs were made by holding of the solutions or films in darkness during the same time. The temperature was 26±1°C.

Irradiation experiments

The irradiation by Xe lamp was carried out during 2, 5 and 13 h, which is equivalent to 0.4, 1.0 and 2.5 medium daily sunlight exposition at the Moscow latitude[9]. The irradiation by Hg lamp was extended to 37 h. The irradiation of thin films was performed during 15.6 h, which is equivalent to 3 medium daily sunlight exposition.

After irradiation, 1 ml of the solution was taken for analysis. The solvent was evaporated and the residue was dissolved in methanol. The glass surfaces were rinsed with methanol and the solvent was evaporated.

GC-MS analysis

The photodegradation products were analyzed by GC-MS using a gas chromatograph HP 5890A coupled to an ion trap detector Finnigan MAT ITD 700. The instrument was equipped with a fused silica capillary column 12 m x 0.32 mm coated with HP Ultra-2 (film thickness 0.52 µm). The temperature was raised from 60°C (1 min hold) to 270° at a rate of 10°C/min. The interface and injector temperatures were 240°C and 250°C, respectively. Helium was used as carrier gas at a flow rate of 1 ml/min. Mass spectra were scanned at each second under the electron impact mode (electron energy 70 eV, manifold temperature 240°C).

The identification of the photodegradation products was based on the interpretation of their electron impact mass spectra according to spectra-structure correlations and on the comparison with the mass spectrum of the initial compound **I**.

Quantitation was performed using peak areas of the analyte and the internal standard dibromdiphenyl ether. Response factors were supposed to be the same for all components.

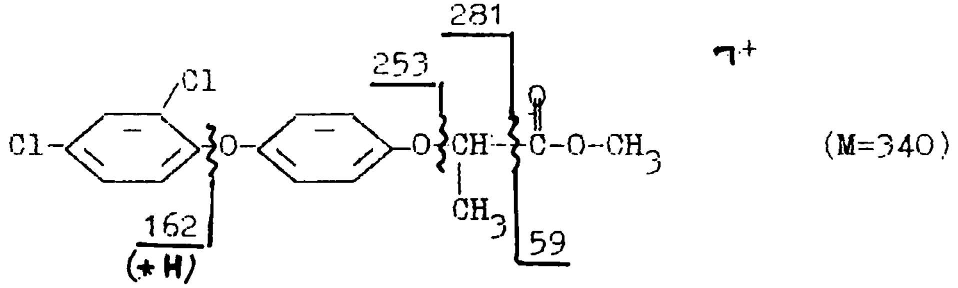
Table 1 Mass spectra of photodegradation products of Dichlophop methyl (Molecular masses are indicated in bold; only the dominant ion (*) of an isotopic cluster is shown)

Compound	*Ion intensity (% of the base peak)*
I	**340**(86)*, 281(38)*, 253(100)*.219(10). 184(22)*. 164(11). 163(11), 162(27), 139(12). 120(51)
V	173(100)*, 145(24)*, 139(4). 110(7). 109(28). 111(11).
VI	173(100)*, 145(31)*, 111(18). 110(15). 109(28).
VII	173(100)*, 147(10), 145(16). 111(8). 109(25).
VIII	173(100)*, 147(12), 145(17). 111(9). 109(21).
IX	**196**(68)*, 148(4), 146(6). 139(14). 138(16). 137(56). 115(17). 110(100)*, 109(32).
X	**238**(100)*, 140(21), 139(45).
XI	**254**(96)*, 219(23)*, 184(100)*. 163(9). 162(7). 128(15). 127(14), 109(51)*.
XII	**254**(98)*, 219(16)*, 184(60)*. 162(11). 109(22).
XIII	**268**(100)*. 253(62)*, 199(12). 198(18). 162(44)*. 123(16).
XIV	**282**(53)*, 267(87)*, 254(50)*. 233(51). 220(42). 219(51). 218(100), 184(75). 181(51). 173(29). 162(46)*. 155(46). 109(32).
XV, XVI	**306**(100)*, 247(26)*, 221(30), 220(33), 219(59), 191(4.0), 163(13), 139(14), 128(32), 127(19).
XVII	**272**(93.9), 213(23), 186(38). 185(100), 157(17). 141(10). 139(9), 115(29), 77(93).
XVIII	**304**(100.0)*, 246(13), 245(32), 219(13), 218(17), 217(19), 189(17)*, 173(16)*, 155(6), 138(13), 137(9), 127(4), 126(30).
XIX	**270**(84), 211(43), 183(100), 165(16), 156(14), 139(41).
XX	**218**(100)*, 190(12), 162(26), 155(33), 136(10), 128(13), 127(42), 126(35).
XXII	**280**(100)*, 251(22)*, 217(14), 184(28), 162(18), 147(12), 119(22), 93(13), 92(29), 91(76).

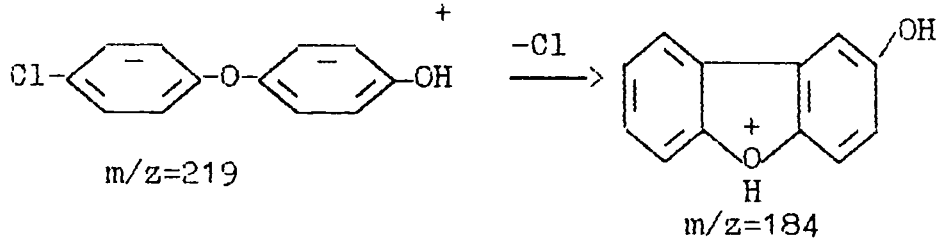
RESULTS AND DISCUSSION

Mass spectrum of Illoxane (**I**)

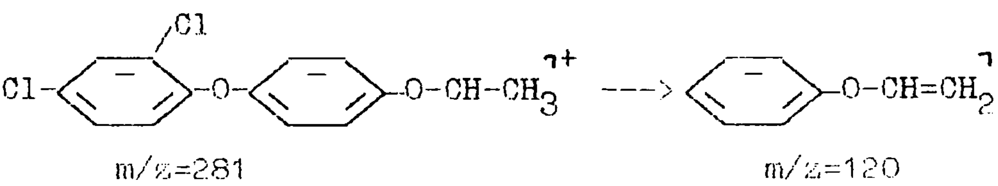
Mass-spectrum of **I** (Table 1) contains a rather large molecular ion M^+. The principal fragmentation pathways are indicated in the following figure (insert) Characteristic isotope ions profile that indicates two chlorine atoms confirms the pathways of these ions formation



The ion m/z 219 contains only one chlorine atom and can not be formed by further degradation of one of the above ions. Probably its formation seems to be from the ion $(M\text{-}Cl)^+$ that is apparently not stable. This ion dissociates further to form ion m/z 184, probably via cyclization:



The pathway of the ion m/z 162 formation is the aromatic ether bond cleavage and H-migration, predominantly from the tertiary carbon atom. The ion m/z 120 is formed as follows, also with H-migration:



Therefore, degradation of **I** under electron impact occurs principally via rupture of the skeleton ester and ether bonds with charge localization on any part of the molecule. The knowledge of these degradation pathways makes identification of the photodegradation products on the base of their mass spectra more easy and reliable.

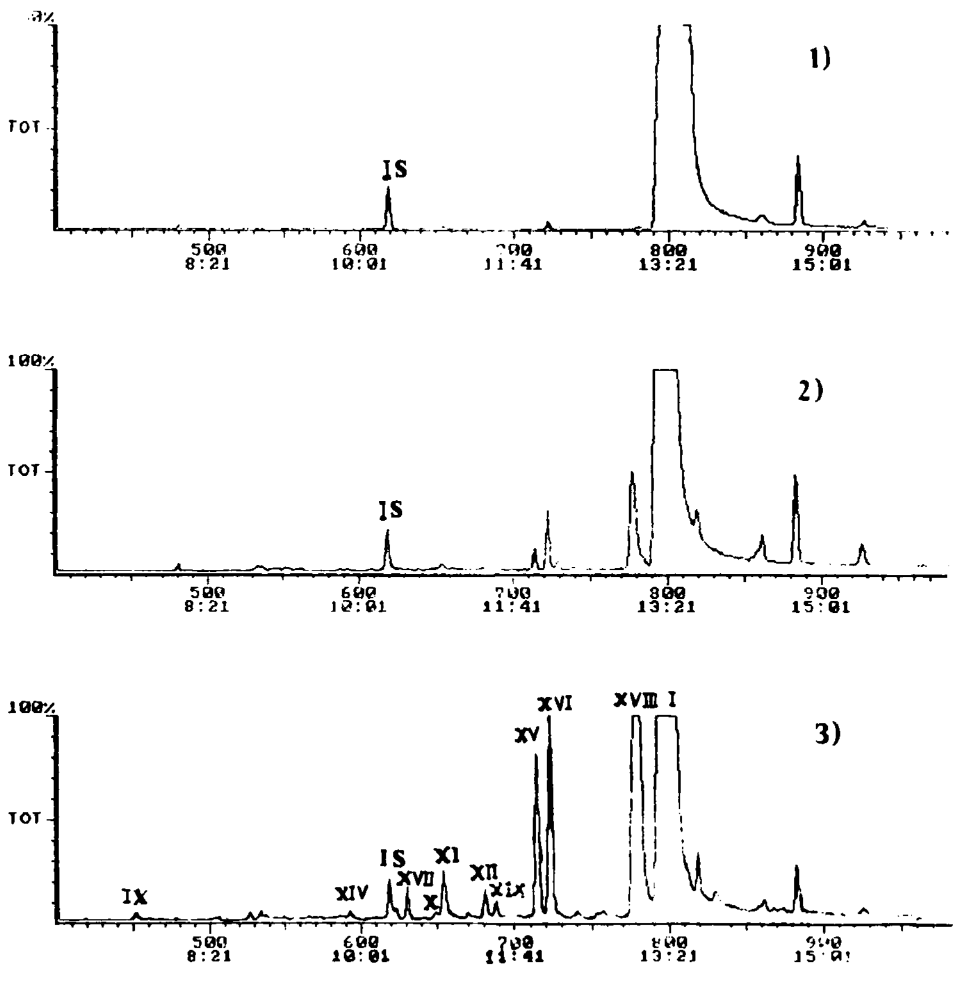


Figure 1 Mass chromatograms of photodegradation products of I. 1—dark control run; 2—Xe lamp, 2 h.; 3—Xe lamp, 5 h. Compound numbers are the same as in the Table 1. IS—internal standard.

Photodegradation products

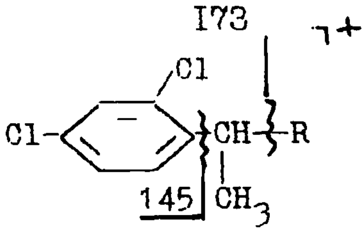
The TIC mass chromatogram of photodegradation products of **I** is shown in Figure 1. The following compounds were found by interpretation of their mass spectra:

—2,4-dichlorobenzene (**II**), identified by the characteristic molecular ion isotope cluster m/z 146:148:150 (1:0.7:0.2) and characteristic fragment ions m/z 111 $(M\text{-}Cl)^+$ and m/z 75 $(M\text{-}Cl\text{-}HCl)^+$);

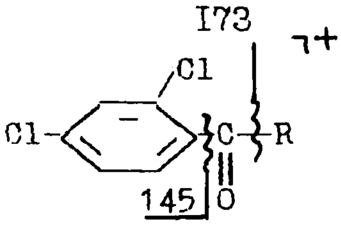
—p-chlorophenol (**III**) (molecular ion isotopes m/z 128:130 (1:0.3), fragment ion m/z 75 $(M\text{-}Cl)^+$);

—2,4-dichlorophenol (**IV**) (molecular ion isotopes m/z 162:164:166 (1:0.7:0.2) and characteristic fragment ions m/z 127:129;

—a number of compounds (**V-VII**) of which molecular ions were not detected in the mass spectra. Abundant clusters of fragment ions m/z 173 and m/z 145, containing two chlorine atoms are observed, the latter being specific for substituted chlorobenzenes as follows:

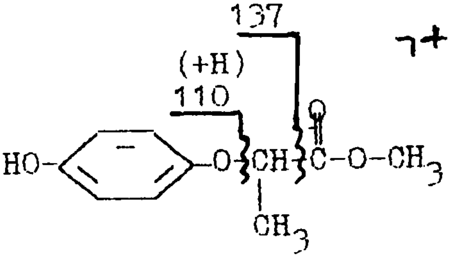


or



The formation of products **V–VIII** which not straight fragments of the initial molecule can be explained by "cell effect" recombination of free radicals originated from various parts of the molecule.

The single photodegradation product formed from the unchlorinated aromatic ring is **IX**:



IX (M=196)

The diphenyl ether fragment was found to be very stable and it was identified in number of photodegradation products:

—2,4-dichlorodiphenyl ether (**X**) (M=238);

—2,4-dichloro-hydroxydiphenyl ethers (**XI** and **XII**) (M=254), mass-spectra of these isomers have different distribution of the ions $(M\text{-}Cl)^+$, m/z 219, and $(M\text{-}2Cl)^+$, m/z 184;

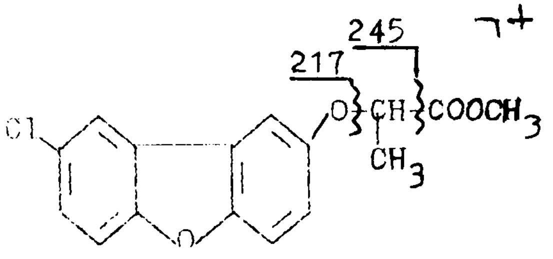
—2,4-dichloro-4′-methoxy-diphenyl ether (**XIII**) (M=268);

—2,4-dichloro-4′-ethoxy-diphenyl ether (**XIV**) (M=282);

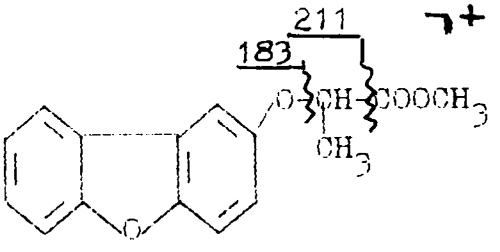
—dechlorinated **I**, formed by the loss of one chlorine atom; there are two isomers, 2-chloro- and 4-chloro-substituted compounds (**XV** and **XVI**) (M=306), their positions in the chromatogram were established by analogy with related compounds[7];

—dechlorinated **I**, formed by the loss of two chlorine atoms—compound **XVII** (M=272);

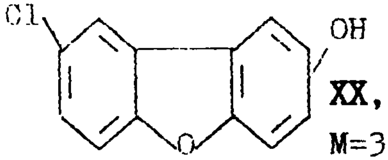
A number of substituted dibenzofurans (**XVIII–XXI**) produced by intramolecular cyclization of **I**, were detected:



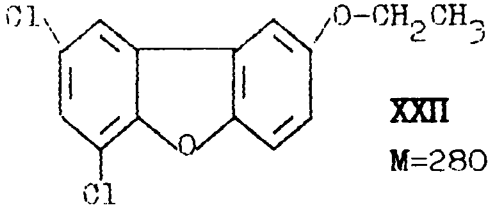
XVIII (M=304)



XIX (M=270)



XX, XXI
M=318



XXII
M=280

The relative yields of the photodegradation products formed at various irradiation times are presented in Table 2. The distributions of the products formed by Hg and Xe lamps irradiation have only a little difference when conversions are similar. But in the former case the relative content of compounds **IX, X, XI** and **XXII** was slightly above.

Table 2 Photodegradation products of **I** (initial concentration **I** is equal to 1000)

	Molecular mass	*RRT*	*samples*					
			1	*2*	*3*	*4*	*5*	*6*
III	128	0.460	—	—	0.07	0.11	—	0.07
IV	162	0.435	—	—	0.10	0.30	—	0.37
V	(173)	0.572	—	—	0.01	0.03	—	0.02
VI	(173)	0.725	—	—	0.03	0.06	—	0.06
VII	(173)	0.848	—	—	0.02	0.06	—	0.04
VIII	(173)	0.883	—	—	0.03	0.11	—	0.14
IX	196	0.731	—	—	0.07	0.17	—	0.39
XX	218	1.050	—	—	0.01	0.03	—	0.09
XXI	218	1.086	—	—	0.01	0.02	—	0.02
XI	254	1.058	—	—	0.23	0.47	—	0.88
XII	254	1.100	—	—	0.21	0.40	—	0.18
XIII	268	1.003	—	—	0.06	0.04	—	—
XIV	282	0.957	—	—	0.03	0.04	—	0.01
X	238	1.008	—	0.01	0.02	0.07	—	0.36
XVII	272	1.019	—	0.01	0.18	0.20	—	—
XIX	270	1.110	—	—	0.05	0.20	—	—
XXII	280	1.003	—	—	—	0.03	—	0.49
XV	306	1.155	0.02	0.46	1.79	3.12	0.70	2.29
XVI	306	1.170	0.14	1.16	3.15	4.46	3.30	4.85
XVIII	304	1.261	—	3.00	5.00	17.10	14.00	8.13
I	340	1.314	1000	833	420	233	432	405

1—dark control run; 2—Xe lamp, 2 h.; 3—Xe lamp, 5 h.; 4—Xe lamp, 13 h.; 5—thin film, Xe lamp, 15.6 h; 6—Hg lamp, 37 h.
RRT—retention time (relative to dibromdiphenyl ether).

When compound **I** was irradiated on the glass surface the photodegradation products mixture consisted of compounds **XV, XVI** and **XVIII** only. When **I** was irradiated in soil, a 12% conversion was achieved but no photodegradation products were detected.

Photodegradation pathways

A possible formation pathway of isomers **XX** and **XXI** is HCl elimination from the isomeric 2,4-dichlorophenoxyphenols **XI** and **XII**. The formation of compounds **XVIII** and **XIX** is probably due to HCl elimination from **I** and **XV**, respectively. On the contrary, cyclic compound **XXII** is formed by dehydrogenation without Cl elimination.

Therefore, the main pathways of photochemical conversion of **I** by Xe lamp, in solution, are reductive and oxidative dechlorination, intramolecular cyclisation and ether bonds cleavage.

Comparison of the relative probabilities of the photodegradation pathways is shown in Table 3. Obviously, dechlorination is the main process of the photodegradation of **I**. The predominant is chlorine atom loss from 2-position, like the other known photodegradation processes of polychlorbiphenyls[8], 2- and 4-phenoxysubstituted polychlorinated pyridines[9] and chlorinated derivatives of phenoxyacetic acids[10]. The loss of the chlorine atom from the 2-position may occur as reductive dechlorination. Elimination of HCl followed by photocyclization leads to the monochlorodibenzofuran **XVIII** formation. This compound can be formed also by oxidative photocyclization of the isomer **XVI**, with one chlorine atom in p-position but the probability of this process is apparently small because only one photooxidative cyclisation product was detected—the compound **XXII**. The dibenzofuran **XIX** containing no chlorine can be formed both by elimination of HCl from the o-Cl-substituted isomer **XVI** and by reductive photocyclization of the compound **XVIII**. Among all cyclization processes those accompanied by HCl elimination are dominating.

It should be specially emphasized that the dichlorodibenzofuran **XXII** was detected in the photodegradation products mixture. Its formation can be considered as an evidence of the oxydative cyclization process occurring. Previously, a similar conversion process was found to be in the photodegradation of 4-nitro-4′-trifluoromethyl-2′-chloro-3-ethoxy diphenyl ether[5].

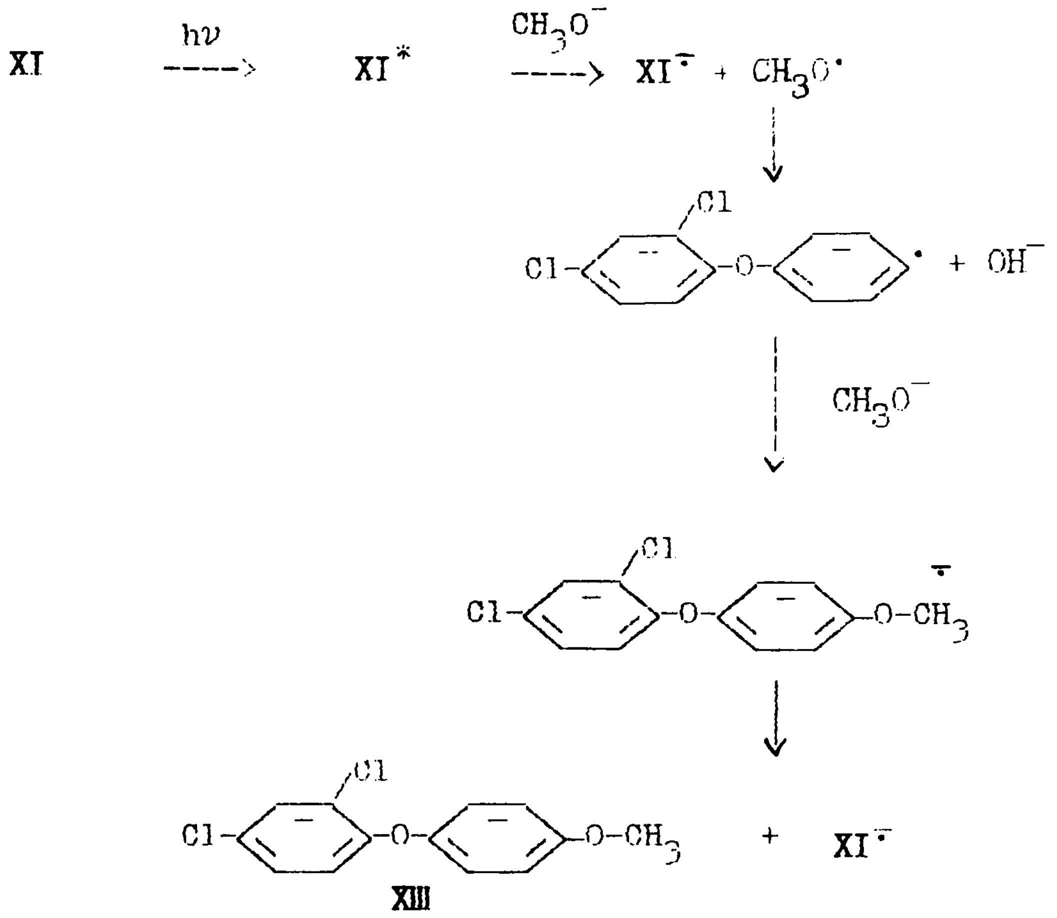
Table 3 Major photodegradation pathways of **I**

Photoreactions	*samples*					
	1	*2*	*3*	*4*	*5*	*6*
Reductive dechlorination	0.16	1.62	5.12	7.78	4.50	7.14
Reductive cyclisation	—	3.00	5.05	17.30	14.00	8.13
Oxidative cyclisation	—	—	—	0.03	—	0.49
Cleavage C-O(aryl)	—	—	0.33	0.87	—	1.87
Cleavage C-C, C-O (aliph.)	—	0.01	0.55	1.02	—	1.43
XVI/XVIII-ratio	7	2.5	1.8	1.4	4.7	2.1

1—dark control run; 2—Xe lamp, 2 h.; 3—Xe lamp, 5 h.; 4—Xe lamp, 13 h.; 5—thin film, Xe lamp, 15.6 h; 6—Hg lamp, 37 h.

Another pathway of primary photodegradation of **I** is a cleavage of the aryloxidic bond and other bonds in the aliphatic part of the molecule followed by formation of (2,4-dichlorophenoxy)phenol isomers (**X** and **XII**), 2,4-dichloro-4′-ethoxydiphenyl ether (**XIV**) and 2.4-dichlorodiphenyl ether (**X**). A cleavage of the diphenyloxide bond leads to 2,4-dichlorophenol (**IV**), p-chlorophenol (**III**) and 2-(4-phenoxy)lactic acid methyl ether (**IX**) formation.

2,4-Dichloro-4′-methoxydiphenyl ether (**XIII**) is obviously formed by nucleophylic substitution of **XI** by the solvent molecule[6,11].



Compound **XIII** was not detected in the photodegradation products mixture formed by Hg lamp irradiation. Probably, when photon energy raises radical reactions are dominated and nucleophilic substitution processes are less likely to occur for their small rates[11].

A formation of number of other photodegradation products can be explained from the point of view of anion-radical mechanism, including stages of electron transfer from a molecule-donor **D** (nucleophilic reagent or solvent) to an excited substrate molecule **SX***, followed by anion-radical dissociation[1,2,11]:

$$\mathbf{SX^{*} + D \rightarrow SX^{\cdot} + D^{\cdot}}$$
$$\mathbf{SX^{\overline{\cdot}} \rightarrow S^{\cdot} + X^{-}}$$
$$\mathbf{S^{\cdot} + AY \rightarrow SY + A^{\cdot}}$$
$$\mathbf{X^{-} + SX^{*} \rightarrow SX^{\overline{\cdot}} + X^{\cdot}}$$

The possibility of radical reactions also should not be excluded. The detection of radical recombination products **V–VIII** in the reaction mixture can be considered as an indication of radical processes where the aliphatic part of the molecule is fragmented or of radical formation due to anion-radical intermediates dissociation.

Powerful arguments for free radical processes occurring when the aliphatic part of molecule **I** is fragmented and free radical formation when anion-radical intermediates dissociate are the finding in the reaction mixture of products of free radicals recombination.

Yields of photoreductive dechlorination products are increased when the conversion is raised. Irradiation on the glass surface do not seriously affects this process but the increase of photon energy leads to an enhancement of it. Photon energy increasing enhances also the formation of the products due to C-C and C-O bonds cleavage. These observations are in good accordance with the proposed mechanism of these products formation. The probability of the bond cleavage between the aromatic carbon and the aliphatic substituent is larger for the Hg than for the Xe lamp irradiation. The yield of the product of this process, 2,4-dichlorodiphenyl ether (**X**), is twice for the Hg lamp irradiation compared with the Xe lamp for the similar conversion.

When photon energy in increased a probability of oxidative photocyclisation is increased also. This process is obviously less energetically favorable, than photocyclisation with chlorine elimination, because the C-H bond cleavage energy is considerably larger than that of the C-Cl bond (94 and 85 kkal/mol, respectively).

When a solution is irradiated with the Xe lamp, a ratio of the p-/o-isomers (**XV** and **XVI**) formed by dechlorination of **I** is decreased from 2.5 at conversion 20% to 1.4 at conversion 80%. On the glass surface this ratio is larger (4.7) than in solution (1.8) at the same conversion. Therefore, solvent molecules not only induce nucleophilic substitution but also interact with the irradiated substance (solvatation etc.) and can change a distribution of photodegradation pathways particularly enhancing the photocyclisation with HCl elimination. The relative probability of this pathway enhances sharply when conversion 50% is reached.

For irradiation of thin films the only detectable photodegradation products were **XV**, **XVI** and **XVIII**, i.e. products of the reductive photodegradation and photocyclisation, probably due to fixation **I** on the surface and absence of solvent.

Irradiation of **I** on soil leads to a great decreasing of the conversion comparing to irradiation on the glass surface or in solution and to a sharp decrease of the usual pathways of photodegradation apparently due to light absorption by soil.

CONCLUSION

The loss of chlorine atoms due to the photolysis of chlorinated compounds is a relevant environmental process because the products of dechlorination usually are less toxic[11]. However, photolysis of **I** can be considered unfavorably from this point of view. Indeed, chlorobenzenes, chlorophenols and chlorodibenzofurans that are formed are considered priority pollutants. Analogs of **XVIII** containing more chlorine substituents are the most harmful chemical substances. So a detailed study of the environmental fate and toxicological evaluation are need for all such kind of substances largely used in agriculture for plant protecting.

Photodegradation of **I**, the active ingredient of the herbicide Illoxane, can be considered as a model for possible pathways of pesticides degradation and toxic methabolites formation in the environment.

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