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On-fiber photodegradation after solid-phase microextraction of *p,p′*-DDT and two of its major photoproducts, *p,p′*-DDE and *p,p′*-DDD

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Abstract

The potential of performing photochemical studies in solid phase microextraction (SPME) fibers, ''photo-SPME'', to study the photodegradation of *p,p′*-DDT and two of its major degradation products, *p,p′*-DDE and *p,p′*-DDD, is shown. Analyses were carried out by gas chromatography mass spectroscopy detection. DDT was extracted from aqueous solutions using five different commercial coatings. The fibers were then exposed to UV light emitted by a low-pressure mercury lamp. After 30 min of irradiation, the degradation of DDT only occurred in polydimethylsiloxane fibers. The on-fiber degradation kinetics of *p,p′*-DDT was studied from 2 to 60 min. A large number of photoproducts were generated and their kinetic behavior was studied. In order to clarify the possible photoreaction pathways for DDT, individual water solutions containing *p,p′*-DDD or *p,p′*-DDE were prepared and photo-SPME was performed for each compound at different irradiation times. On the basis of the photoproducts identified, some photodegradation pathways are proposed. Finally, aqueous photodegradation studies followed by SPME were performed and compared to the photo-SPME. This work will show the enormous potential of photo-SPME to perform photodegradation studies.

Keywords: Photodegradation; Solid-phase microextraction; DDT; DDE; DDD; Pesticides

1. Introduction

Light is involved in a large number of reactions in the atmosphere, in natural waters, on soil and in living organisms. Photochemical reactions are the main way of eliminating organic substances in the atmosphere and they play a significant role in the degradation of slightly biodegradable compounds in surface waters. Special attention is focused on the fate of organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and pesticides, which are widely distributed in the environment [1].

Although the use of DDT has been banned in developed countries, it is still manufactured and used in other countries: its widespread use in the past has led to worldwide contamination of the food chain with this pesticide and its major degradation products [2].

Because DDT solubility in water is very low, early work on DDT photochemistry was carried out in organic solvents such as alkanes and alcohols [3–6],

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but these solvents, especially the alkanes, are poor mimics of water, the environmental solvent; however, some work in water has been done [7]. Hong et al. [7] studied the photodegradation of DDT in water and they proposed different photodegradation pathways based mainly in reactions of reductive dechlorination, oxidation, isomerization and chlorination.

Solid phase microextraction (SPME) is a suitable technique which has been successfully applied to the extraction of persistent organic pollutants (POPs) [8–13]. This technique has the advantage of simplicity and allows very low limits of detection (LODs). SPME is of increasing interest in the field of pesticide residue analysis. Recently, headspace SPME (HS-SPME) has also been used to determine pesticide compounds in water [14,15] and other kinds of samples [16–18].

In various publications, SPME has been applied in photodegradation studies of different pollutants such as PCBs [19] and pesticides [20] in water samples. But in these studies SPME only acts as a technique to extract the samples after photodegradation. SPME is used only as the extraction technique and not as the photoreaction support. This means that extraction selectivity could play an important role in the obtained information because only readily extractable photoproducts will be seen. In contrast, if photolysis takes place directly on the SPME fiber, photoproducts will be generated in the coating, and all, with the exception of the very volatile, will be determined simultaneously with the primary compounds.

Very recently, the possibility of performing photochemical studies in SPME fibers has been demonstrated [21,22]. This new analytical tool, ''photo-SPME'', has been successfully applied to study the photodegradation kinetics of PCBs. Photoproducts were generated in the SPME coating and could thus be studied without the need of any additional sample preparation steps. Photo-SPME and aqueous photodegradation of PCBs were also extensively studied and compared.

In this paper, the potential of this new technique, photo-SPME, to study the photodegradation of some representatives of another group of POPs, the pesticides, is shown. *p,p′*-DDT and some of its major photoproducts were extracted from aqueous solutions by different coatings, and the fibers were then exposed to UV light emitted by a low-pressure mercury lamp. Finally, the fibers were inserted into the injector port and GC–MS analyses were carried out. Under the photo-experimental conditions of this study, DDT was only degraded using PDMS fibers. After confirming the photolysis of DDT in PDMS (thermal and dark test were also run), kinetic studies were carried out. A large number of products were detected and their kinetics were also studied. In addition, some reasonable photodegradation pathways of DDT were also proposed on the basis of product identification. Most of these pathways were coincident with those proposed by Hong et al. [7]. Some aqueous photodegradation studies were also carried out to confirm the parallelism between photo-SPME and aqueous photolysis.

The aim of this paper is not to present an exhaustive study of the photoreactive behavior of DDT but to show the tremendous potential of photo-SPME to perform these kinds of studies.

2. Experimental

2.1. Reagents and materials

The compounds used in this study, *p,p′*-DDT, *p,p′*-DDD and *p,p′*-DDE, were supplied by Supelco (Supelco, Bellefonte, PA, USA). Isooctane individual stock solutions of 2000 μg/g were prepared. Water solutions (20 ng/ml) were prepared by dilution of a pesticide intermediate acetone solution of 20 μg/ml. All the remaining solvents (analytical grade) used were purchased from Merck (Mollet del Vallés, Barcelona, Spain).

2.2. GC–MS analysis

Analyses were carried out on a Varian 3800 gas chromatograph (Varian Chromatography Systems, Walnut Creek, CA, USA), equipped with a 1079 split/splitless injector and an ion trap mass spectrometer Varian Saturn 2000 (Varian Chromatography Systems). Experimental parameters were as follows: column: BP-1, 25 m×0.32 mm I.D., 0.17-μm film; temperature program: 60 °C, hold 2 min, rate 15 °C/min to 115 °C, hold 5 min, rate 3 °C/min to 175 °C, rate 30 °C/min to 250 °C, hold for 2 min,

rate 5 °C/min to a final temperature of 280 °C, hold for 10 min. Helium was employed as carrier gas, with a flow of 1.4 ml/min. Injector was programmed to return to the split mode after 2 min from the beginning of a run. Split flow was set at 50 ml/min. Injector temperature was held constant at 270 °C. Trap, manifold and transfer line temperatures were 50, 120 and 280 °C, respectively. The mass spectrometer was used in the positive electron impact mode at 70 eV. A mass range of 45–325 u was scanned. The automatic gain control was selected, and the electron multiplier was set at a nominal value of 1600 V.

2.3. Solid-phase microextraction and photodegradation procedures

Commercially available 100-μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB), 85 μm polyacrylate (PA), 74 μm Carboxen–polydimethylsiloxane (CAR–PDMS) and 65 μm Carbowax–divinylbenzene (CW–DVB) fibers housed in manual SPME holders were used (Supelco).

A 5-ml aliquot of a water sample containing the target compounds was placed in a 22-ml headspace vial. The vial was sealed with a headspace aluminum cap with a PTFE-faced septum. Then the vial was immersed in a water bath at 100 °C and allowed to equilibrate for 5 min before extraction. The fiber was then exposed to the headspace over the water (HS-SPME) for 30 min and thermally desorbed in the GC injection port for 5 min.

A laboratory photoreactor model was used for photolysis experiments: two low-pressure mercury lamps (8–10 W) were so arranged that the subject to be irradiated was easily positioned. For on-fiber photodegradation experiments, after HS-SPME extraction, the SPME fiber with the analytes already adsorbed, was subjected to 254-nm irradiation for the required time (2–60 min) in an efficient hood which complied with security conditions. For aqueous photodegradation experiments, two 3-ml portions of an aqueous solution containing the 10-PCB mixture were both placed in synthetic quartz precision cells and submitted to UV radiation as described above. After the required irradiation time (2–60 min), 5 ml of the photolized solution were placed in a 22-ml headspace vial and subjected to the same SPME procedure.

For every set of experiments a control extraction (same SPME procedure but without irradiation) was carried out.

2.4. Dark and thermal tests

Dark tests were carried out by placing the fiber inside a glass vial and covering the whole device with aluminum foil; the irradiation was kept as in the remainder of the experiments. For thermal tests, a laboratory heater kept at 50 °C was used, a sufficiently high temperature taking into account that inside the photoreactor the temperature never reaches more than ambient ± 1 °C, due to efficient cooling devices.

3. Results and discussion

3.1. SPME preliminary experiments

In preliminary studies the five commercial SPME fibers described in the Experimental section, were used. The purpose of these studies was to establish the viability of performing on-fiber photodegradation studies of DDT. A spiked water solution with 10 ng/ml of DDT was prepared and 5-ml aliquots were extracted by the different fibers using the experimental conditions indicated in the Experimental section. The fibers were then desorbed in the GC injector and GC–MS analyses were performed. In a second set of experiments, 5-ml aliquots of the same solution were extracted by the different fibers and each fiber was then exposed to UV radiation for 30 min. The results for both sets of experiments, showing the responses without and with irradiation for the various fibers, are summarized in Table 1. Comparing the results of all the fibers without irradiation (after conventional SPME), it is evident that PDMS has the highest extraction efficiency. Furthermore, a comparison of the change in response after UV irradiation (photo-SPME) is only statistically significant for PDMS fiber. For this coating the peak area obtained in the irradiation experiments was ~2% of that obtained without irradiation. These results indicate that photodegradation of DDT only

Table 1
Responses obtained (area counts) for HS-SPME experiments without irradiation and with irradiation of the SPME coatings

	PDMS	CAR–PDMS	PDMS–DVB	PA	CW–DVB
No irradiation	1 234 325±31 997	81 297±2030	877 557±117 644	113 352±22 223	869 254±53 583
UV irradiation	14 453±2296	74 201±18 452	828 616±76 916	125 953±7314	772 000±39 650

takes place using one of the tested coatings (PDMS), under the irradiation conditions used in these experiments (low pressure mercury lamp, 18 W and 30 min). Similar behavior had been observed in experiments performed in our laboratory to study the photolysis of PCBs in PDMS and PDMS–DVB fibers (unpublished results).

The absence of photoreactions in four of the tested coatings could be due to several reasons, such as the strong absorption of radiation by the sorbent material, or changes in the molecular configuration of the compound when it is retained in these sorbents. We are currently carrying out further studies to explain the lack of photolysis in these materials.

Several important conclusions can be drawn from these preliminary experiments. Firstly, PDMS is the most efficient material for SPME of DDT under the selected experimental conditions; secondly, PDMS is the only fiber suitable for studying the photolytical behavior of DDT; and, thirdly, the other materials, especially PDMS–DVB and CW–DVB, might be good media to extract this analyte (the extraction efficiency is good) while protecting it from light photodegradation in field sampling. In all subsequent studies performed for this research, only PDMS fibers were used.

It is common practice when working in photolysis experiments to check if decreases in analytical responses are due exclusively to the action of photons or, if in addition, some volatilization or thermal degradation losses have occurred as well. In the current study, dark and thermal tests were also carried out as described in the Experimental section, demonstrating that no losses of analytes through volatilization and/or thermal degradation occurred. Therefore, we can conclude that the clear differences in DDT peak areas obtained in the PDMS experiments with irradiation were due to UV photodegradation.

3.2. Photo-SPME of p,p′-DDT and two of its major photoproducts, p,p′-DDE and p,p′-DDD

The photoreaction kinetics of DDT were monitored by studying the influence of irradiation time on the extent of photodegradation. The analyte was first extracted and then the fiber was exposed to UV light for the designated time: from 0 up to 60 min. Finally GC–MS analysis was carried out. Area changes after UV exposure were evaluated and the second column of Table 2 summarizes the results obtained expressed as percentage of undegraded compound. As can be seen, the photodegradation of *p,p′*-DDT is quite a fast process and after 20 min only some 2% of the compound remains in the fiber.

In these experiments 15 photoproducts were gen-

Table 2
Percentage of undegraded compound after UV irradiation

Irradiation time (min)	*p,p′*-DDT	*p,p′*-DDE	*p,p′*-DDD
0	100	100	100
2	51.4	4.8	83.0
5	39.0	3.5	83.7
10	15.6	2.6	72.7
15	3.4	2.2	48.8
20	2.0	2.7	44.8
30	2.9	2.6	29.8
60	1.2	2.0	10.7

erated and they were identified on the basis of their mass spectra and information found in the literature [3,7]. These compounds are indicated with a "+" sign in the fifth column of Table 3. Their retention times as well as their quantification ions are also included in this table. Of course, these photoproducts were photodegraded as well and Table 4 shows the responses obtained for these compounds at different irradiation times. Responses have been normalized and a value of 100 has been assigned to the maximum response yielded for each compound. Most of these photoproducts showed a maximum peak area for DDT irradiation time of 2–10 min. After 60 min most of the compounds could still be detected. Figs. 1a and 2 show the quantification ion chromatograms obtained for 0, 5 and 30 min of photo-SPME for DDT and some of its photoproducts, respectively. In Fig. 1a, the decrease in DDT response with increase in UV irradiation time can be observed. At 30 min, DDT has almost been completely degraded. For the photoproducts no response is observed for 0 min of irradiation, while for 5 and 30 min the peak corresponding to each photoproduct can be observed.

In order to clarify the possible photoreaction pathways for DDT, individual water solutions containing *p,p′*-DDD or *p,p′*-DDE were prepared and photo-SPME was performed for each compound at different irradiation times. The ion chromatograms of these compounds for 0, 5 and 30 min of photolysis are shown in Fig. 1b and c. The degradation kinetics for these analytes are also shown in Table 2 (third and fourth columns), where the amount of compound (%) that remains in the fiber after different irradiation times is indicated. As can be seen the degradation for DDE is very fast and almost none of the compound remains after 2 min of photolysis. On the other hand, DDD is much more resistant to photodegradation and after 30 min ~30% of the compound is still undegraded. After 60 min 11% of the compound remains in the fiber.

As occurred with the DDT photolysis study, some degradation products have been detected and they are listed in Table 3 (sixth and seventh columns).

Table 4
Normalized responses obtained for some *p,p′*-DDT photoproducts after UV irradiation

Irradiation time (min)	P2	P4	P6	P7	P8
0	0	0	0	0	17.0
2	0	74.6	100	0	64.0
5	55.8	100	36.7	65.9	100
10	80.6	97.8	45.2	100	91.9
15	100	82.0	48.2	96.4	70.5
20	72.3	72.1	45.2	82.1	48.8
30	58.7	52.6	46.2	69.9	44.4
60	26.5	31.1	30.6	34.3	8.9

Table 3
Photoproducts generated in the on-fiber photodegradation of *p,p′*-DDT, *p,p′*-DDE and *p,p′*-DDD

t_R (min)	Key	Photoproduct	Quantification ion	Photoproducts of		
				p,p′-DDT	*p,p′*-DDE	*p,p′*-DDD
22.09	P1	bis-(4-Chlorophenyl)methane	201	+		
24.22	P2	1,1-Diphenyl-2,2-dichloroethene	178	+		
25.29	P3	2,2-bis(4-Chlorophenyl)ethylene	178		+	
26.01	P4	4,4′-Dichlorobenzophenone	139	+	+	
26.46	P5	9*H*-Fluorene-9-dichloromethylene)	246		+	
27.88	P6	3,6-Dichloro-9-methylenefluorene	246	+	+	+
28.20	P7	4,4′-Dichlorobenzhydrol	139	+		
28.35		DDMU (1)	212	+		+
29.74		DDMU (2)	212	+	+	+
29.92		DDE (1)	318		+	
30.39		DDE (2)	318	+	+	
30.57	P8	2-(4-Chlorophenyl)-2-phenyl-1,1-dichloroethane	201	+		+
31.42		*p,p′*-DDE	318	+		
32.14		*p,p′*-DDD	235	+		
32.86	P9	(Dichloroethenylidene)bis-phenol	280	+	+	

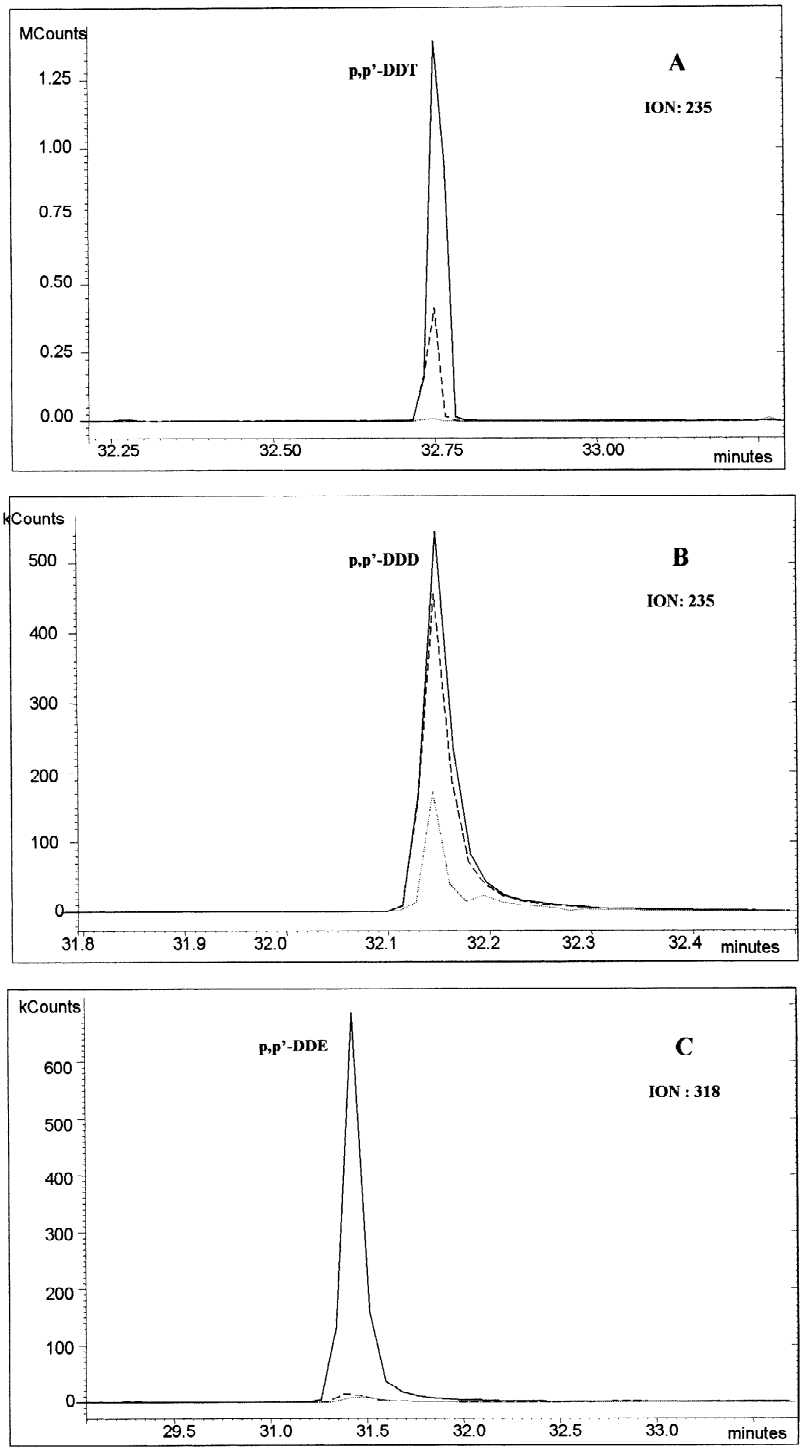

Fig. 1. Quantification ion chromatograms, obtained for 0 (—), 5 (- - -) and 30 (· · ·) min of UV irradiation, for (A) *p,p′*-DDT, (B) *p,p′*-DDD and (C) *p,p′*-DDE.

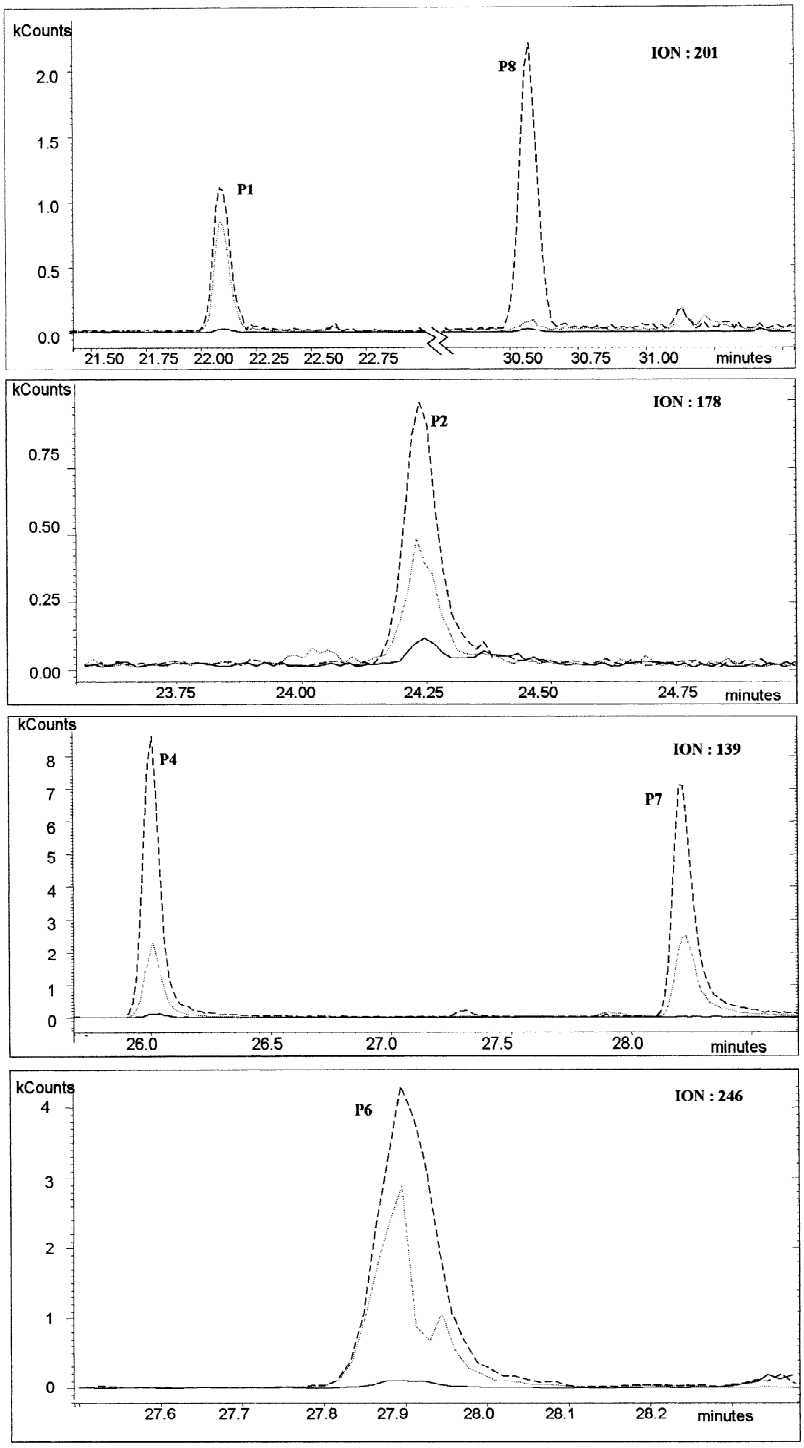

Fig. 2. Quantification ion chromatograms, obtained for 0 (—), 5 (- - -) and 30 (· · ·) min of UV irradiation, for some photoproducts of *p,p′*-DDT.

3.3. Photodegradation pathways

Considering the photodegradation products obtained in the photo-SPME studies of DDT, DDE and DDD and with the aid of information found in the literature [3,7], the degradation pathways of DDT are proposed in Fig. 3.

The photoproduct generation mechanisms were the following: successive dechlorination to generate less chlorinated derivatives, loss of HCl from the precursors, oxidation, isomerization, and formation of a C–C bond between the two aromatic rings.

Three of the photoproducts, P2, P7 and P1 were found only in the photo-SPME of DDT.

DDMU has been found as photoproduct of *p,p′*-DDT, *p,p′*-DDE and *p,p′*-DDD. This compound must be the precursor of P3, through replacement of a β chlorine by a hydrogen radical, and P6, through loss of HCl and formation of a bond between the two aromatic rings.

The formation of P8, found as photoproduct of DDT and DDD, must occur through reductive dechlorination of either of them.

P4 has been found as a photoproduct of DDT and DDE and could be formed through oxidation of DDE and DDMU.

P9 appears as a photoproduct of DDT and DDE, and P5 as photoproduct of DDE. The precursor of both compounds could be DDE producing P9 through substitution of aromatic chlorines by OH radicals and P5 through loss of Cl and HCl and formation of a bond between the two aromatic rings.

Some isomeric photoproducts of DDE and DDMU were also found and, therefore, isomerization must be another photodegradation mechanism.

Most of the proposed mechanisms fit quite well with those proposed by Hong et al. [7] for the photodegradation of DDT in water.

3.4. Comparison of photo-SPME and aqueous photodegradation of *p,p′*-DDT

Sets of experiments were performed in order to compared photo-SPME and aqueous photodegradation of *p,p′*-DDT. In these experiments, 6-ml aliquots of water containing 20 ppb of the selected

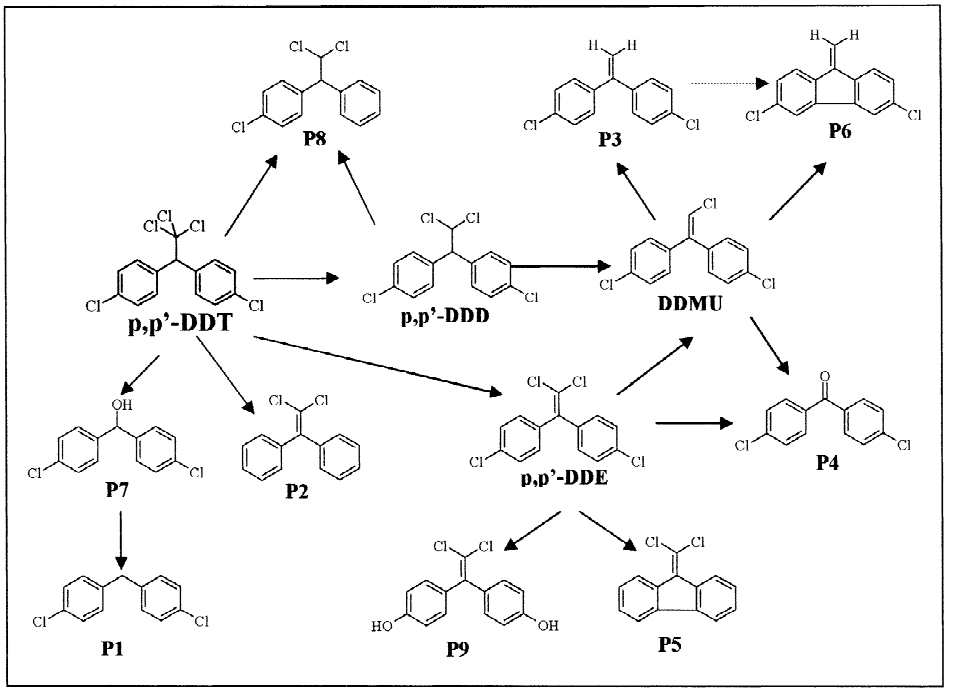

Fig. 3. Proposed photodegradation pathways of DDT, DDD and DDE.

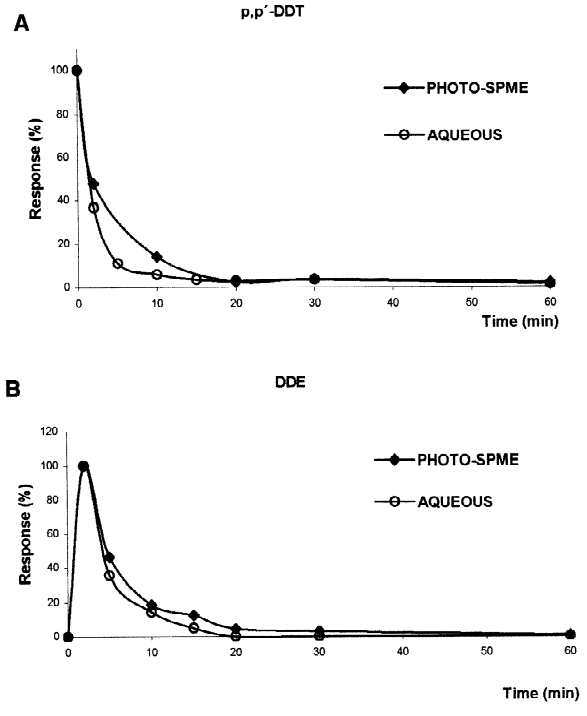

Fig. 4. Photo-SPME versus aqueous photolysis of DDT. Kinetic curves for (A) *p,p′*-DDT and (B) DDE (photoproduct).

analyte were exposed to UV irradiation for different periods of time (from 0 to 60 min) and then HS-SPME GC–MS analysis was performed. The kinetic curves obtained were compared with those obtained for photo-SPME (Fig. 4a). The results show that DDT on-fiber photodegradation is slightly slower than aqueous photodegradation. In Fig. 4b the on-fiber and aqueous kinetic curves for DDE are shown. Again, aqueous photodegradation was slightly slower but the two kinetic curves were completely analogous. As has been already demonstrated for PCBs [21,22], on-fiber photolysis also mimics the aqueous photolytic behavior of these particular compounds quite well.

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