γ-Irradiation-Induced Degradation of DDT and Its Metabolites in Organic Solvents

François L. Lépine,*,† François Brochu,† Sylvain Milot,† Orval A. Mamer,‡ and Yvon Pépin§

Institut Armand-Frappier, 531 Boulevard des Prairies, Laval, Quebec, Canada H7N 4Z3, Biomedical Mass Spectrometry Unit, McGill University, 1130 Pine Avenue West, Montreal, Quebec, Canada, and Chemistry Department, Université du Québec à Montréal, P.O. Box 8888 Succ. A, Montréal, Quebec, Canada

γ-Irradiation of DDT and its metabolites DDD and DDE was performed in 2-propanol, cyclohexane, and cyclohexene. The degradation yields of these compounds were quantitated and the dechlorinated products identified by gas chromatography/mass spectrometry. Compounds corresponding to addition products between the solvent and these organochlorines were isolated and identified by mass spectrometry and NMR. Oxidation products of these organochlorines were also observed.

Keywords: *DDT; γ-irradiation; dechlorination; degradation*

INTRODUCTION

The widespread use of DDT on a planetary scale has led to a worldwide contamination of the food chain with this pesticide and its two major degradation products, 2,2-bis(4-chlorophenyl)-1,1-dichloroethane (DDD) and 2,2-bis(4-chlorophenyl)-1,1-dichloroethylene (DDE). Although DDT has been banned in developed countries for many decades, it is still in use in many developing countries. Because of their resistance to biodegradation, DDT and its metabolites are still found in many food products, especially fish.

This raises the question of the effects of various food treatments, such as food irradiation, on these organochlorinated substances. There has been very little work performed on the effects of γ-irradiation on DDT (Lépine, 1991, and references cited within) and even less on its degradation products, such as DDD and DDE, although they often represent more than 90% of the total DDT-derived compounds found in fish (Schmitt et al., 1985). All of the publications dealing with the effects of γ-irradiation on DDT almost exclusively report the degradation yield of DDT without identifying the degradation products so obtained. Other authors have demonstrated that the degradation products of a chlorinated pesticide obtained after irradiation in aliphatic solvent were similar to those observed in a biological matrix such as vegetable oil and lard (Carp et al., 1972a,b). The objective of this work is to identify the degradation products obtained by γ-irradiation of DDT and these two metabolites in various polar and nonpolar solvents as models for the lipidic matrix in which these hydrophobic substances are concentrated in living organisms.

MATERIALS AND METHODS

Chemicals. DDT, DDD, and DDE and other chemicals were purchased from Aldrich (Milwaukee, WI) and their purity checked by GC/MS. Cyclohexene was distilled prior to use. All other solvents were of "spectrograde" quality and used without further purification.

Gas Chromatography/Mass Spectrometry. A Varian 3500 gas chromatograph equipped with a fused silica DB-5 column (30 m × 0.3 mm i.d., film thickness 0.250 μm) with helium as carrier gas was used. Column temperature was initially set to 75 °C and programmed to 180 °C at 20 °C/min, then to 220 °C at 5 °C/min, then to 280 °C at 6 °C/min, and finally to 310 °C at 10 °C/min. The detector used was a Finnigan Ion Trap 800 working in electron impact (EI) mode. The scanning mass range was from 100 to 500 Da. A Hewlett-Packard 5890 GC/MS using a similar column and temperature program was also used to perform electron capture negative chemical ionization (ECNCI) with methane as reagent gas.

Sample Preparation and Irradiation. Typically, 1.0-mL volumes of 100 ppm solutions of the organochlorinated derivative in 2-propanol, cyclohexane, or cyclohexene were put in a 1.4-mL glass vial and closed with a Teflon-lined screw cap. The same procedure was also repeated with fully deuterated 2-propanol and cyclohexane. Irradiation was performed with a Gammacell 220 (Nordion International, Kanata, ON) using a ^{60}Co source delivering 12.9 Gy/min. Experiments were done in triplicate. Decachlorobiphenyl in cyclohexane was added after irradiation as internal standard at a final concentration of 96 ppm. Quantification of the chromatographic peaks of the various degradation products was performed using their integrated areas relative to the internal standard divided by the areas of the starting material relative to the internal standard. This value was corrected with the response factors of DDD and DDE relative to DDT to allow comparison between the various experiments.

Isolation of Addition Products. To obtain sufficient amounts of addition products to allow NMR analysis, irradiation of DDE in 2-propanol was performed with 500 mL of a 200 ppm solution at 20 kGy. This radiation dose is considerably greater than the 10-kGy maximum recommended by the World Health Organization (1981), but the addition products obtained at such a radiation dose could be detected at 10 kGy, as seen in Tables 3–5. Isolation of the 2-propanol addition products was performed using silica thick-layer chromatography. In cyclohexane, irradiation of DDT and DDD was performed with 250 mL of 1000 ppm solutions for a 10-kGy dose. For DDE, a 2000 ppm concentration and a 15-kGy radiation dose were used. The solvents were evaporated in vacuo and the residues purified by HPLC with a Varian Vista 5500 equipped with a reversed-phase C_{18} Supelcosil SPLC-18 column (10 × 250 mm) (Supelco, Oakville, ON) with UV detection (234 nm). A methanol–water gradient was used. The NMR spectra of all the addition products were taken in deuterated chloroform with a Varian Gemini 300 MHz.

RESULTS

The degradation yields of DDT and its metabolites after a 10-kGy irradiation in various solvents are presented in Table 1. In any solvent DDT is more

† Institut Armand-Frappier.
‡ McGill University.
§ Université du Québec à Montréal.

0021-8561/94/1442-2012$04.50/0

Table 1. Percent Degradation of DDT, DDD, and DDE after 10-kGy Irradiation in Various Solvents[a]

	DDT	DDD	DDE
2-propanol	99.2 (1.4)[b]	24.5 (1.2)	47.5 (0.5)
cyclohexane	71.8 (3.5)	60.4 (1.7)	53.9 (1.4)
cyclohexene	47.8 (2.1)	42.0 (4.7)	25.0 (4.3)

[a] Relative to the starting material. [b] Numbers in parentheses are the standard deviations.

Table 2. Dechlorination Product Yields for DDT and DDD after 10-kGy Irradiation in 2-Propanol[a]

	DDT	DDD[b]
DDD	63.1 (0.9)[c]	
1a	10.8 (0.4)	11.1 (0.7)
1b	5.9 (0.2)	9.0 (0.3)
1c	1.4 (0.1)	1.9 (0.9)

[a] In percent relative to the starting material. [b] Corrected with the response factor of DDD relative to DDT. [c] Numbers in parentheses are the standard deviations.

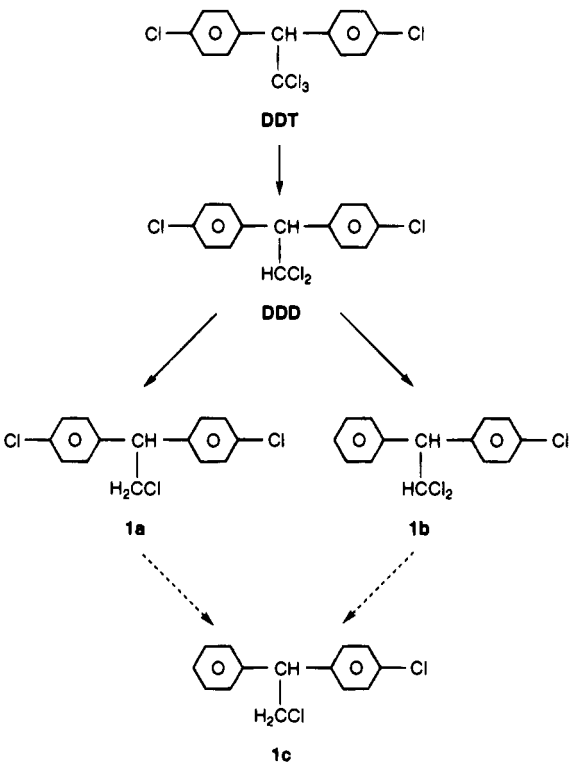

Figure 1. Dechlorination pathways of DDT and DDD in 2-propanol.

extensively degraded than its metabolites. The degradation yields of DDT and its metabolites are also lower in cyclohexene than in cyclohexane.

2-Propanol. Upon irradiation of DDT and DDD in 2-propanol, a series of peaks were obtained with gas chromatographic retention times shorter than those of the starting materials. These compounds are dechlorinated products of the starting materials, and their relative abundances are presented in Table 2. The only monodechlorinated product of DDT is DDD, as reported by Sherman and co-workers who studied the γ-irradiation-induced degradation of DDT in basic 2-propanol (Sherman et al., 1971). In the present study, two other didechlorinated products, **1a** and **1b**, were also detected (Figure 1). Compound **1a** presents a mass spectrum identical to that of 1,1-bis(4-chlorophenyl)-2-chloroethane, a well-known DDT metabolite (NIST/EPA/NIH, 1992). The most likely precursor of **1a** is DDD, through loss of a β chlorine, as **1a** is also produced upon

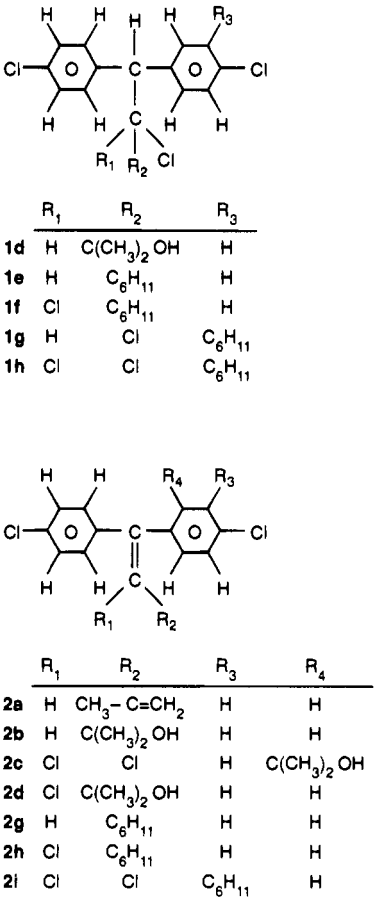

Figure 2. Structure of the addition products of DDT, DDD, and DDE formed in 2-propanol and cyclohexane.

irradiation of DDD. The EI mass spectrum of **1b** shows a base peak at 201 Da and no fragment ion at 235 Da. The mass spectrum of a compound such as DDT, DDD, and **1a**, which contain a 1,1-bis(4-chlorophenyl)methyne moiety, always presents a base peak at 235 Da. The 201-Da base peak of **1b** corresponds to the (4-chlorophenyl)phenylmethyne ion. The mass spectrum of **1b** has been published from the work of Plimmer and coworkers, who studied the photochemical degradation of DDT (NIST/EPA/NIH, 1992). The most likely precursor of **1b** is DDD, through loss of an aromatic chlorine, as **1b** is also produced in irradiated DDD solutions. Finally, a tridechlorinated compound, **1c**, was also observed. Its mass spectrum shows a molecular ion at 250 Da and a base peak at 201 Da. Compound **1c** is thus an analog of DDD having lost one β and one aromatic chlorine. Compounds **1a** and **1b** are both potential precursors of **1c**. These three compounds were all observed upon irradiation of DDD.

Surprisingly, dechlorination products, which normally appear at retention times shorter than that of the starting material, were not observed upon irradiation of DDE. New peaks were detected at retention times longer than that of the starting material, and analysis of their mass spectra shows that they are addition products between DDE and 2-propanol. These compounds, **2a**, **2b**, **2c**, **2d**, and **1d**, amount to 12.6, 1.3, 1.0, 5.4, and 1.6%, respectively, of the initial DDE. The structures of these compounds are presented in Figure 2. Compound **1d** was also observed in small amounts upon irradiation of DDT and DDD (0.5 and 1.3% of the starting materials, respectively). These compounds were isolated by thick-layer chromatography and analyzed by NMR and ECNCI mass spectrometry.

The EI mass spectrum of **2a** presents a molecular ion at 288 Da. The NMR shows three multiplets at 7.32, 7.24, and 7.12 ppm, corresponding to eight aromatic protons, a singlet at 6.62 ppm, corresponding to the β proton on the sp^2 carbon, and another singlet at 5.02 ppm for the two other protons of the methylene function. The methyl function appears as a singlet at 1.5 ppm. Compound **2a** is then an analog of DDE that has undergone addition on the β carbon of an isopropyl function followed by loss of two chlorine atoms and a water molecule.

The EI spectrum of **2b** shows an ion cluster characteristic of a fragment containing two chlorines at 291 Da. This fragment arises from the loss of a methyl radical from the molecular ion. The NMR spectrum shows four doublets ($J = 8.5$ Hz) at 7.37, 7.23, 7.17, and 7.09 ppm, corresponding to the para-chloro-substituted aromatic rings, and a singlet at 6.21 ppm, corresponding to the hydrogen on the β sp^2 carbon. The isopropyl methyls appear as a singlet at 1.56 ppm.

The heaviest ions of the EI spectrum of **2c** are in a cluster characteristic of a fragment containing three chlorines at 323 Da. This fragment arises from the loss of HCl and a methyl radical from the molecular ion. The higher field portion of the NMR spectrum shows two doublets coupled to each other ($J = 8.6$ Hz) at 7.44 and 7.18 ppm, which correspond to one para-chloro-substituted ring. At lower field, a doublet ($J = 2.0$ Hz, 6.90 ppm), a doublet of doublets ($J = 2.0$ and 8.3 Hz, 6.77 ppm), and a doublet ($J = 8.3$ Hz, 6.49 ppm) were observed. This can be rationalized as being the other para-chloro-substituted ring bearing an isopropyl function meta to the chlorine atom. In such a structure, the hydrogen atom adjacent to the isopropyl and the chlorine substituents should present a small J_4 coupling constant (2.0 Hz) with the other hydrogen ortho to the chlorine, the latter being also coupled to the hydrogen adjacent to it ($J = 8.3$ Hz). The methyls of the isopropyl function appear as a singlet at 1.56 ppm.

The EI mass spectrum of **2d** shows a molecular ion cluster at 340 Da characteristic of a molecule containing three chlorines. The NMR spectrum shows only two symmetrical multiplets at 7.29 and 7.14 ppm for the aromatic protons and a singlet at 1.49 ppm for the two methyls of the isopropyl function. This implies that the isopropyl function is located on the β carbon. Irradiation in 2-propanol of pure **2d** generates **2b**, suggesting that **2d** is a precursor of **2b**.

The EI mass spectrum of **1d** shows an ion cluster containing three chlorines at 289 Da and a base peak at 235 Da. The 289-Da fragment probably arises from loss of HCl and OH or from loss of Cl and H_2O from the molecular ion of 342 Da. The NMR spectrum shows a symmetrical multiplet at 7.30 ppm, corresponding to the aromatic protons, and two doublets ($J = 7.7$ Hz) at 4.68 and 4.43 ppm, corresponding to the β and α protons, respectively. The two methyls appear as two singlets at 1.25 and 1.20 ppm.

Cyclohexane and Cyclohexene. The yields of the various dechlorination products obtained in cyclohexane are presented in Table 3. Contrary to what was observed in 2-propanol, two monodechlorinated products of DDT, DDD, and an important amount of DDE were produced (Figure 3). The didechlorinated product **1a** was obtained along with another compound having a retention time and mass spectrum identical to those of authentic 2,2-bis(4-chlorophenyl)-1-chloroethylene (DDMU). The precursors of DDMU can be either DDD or DDE produced by the first dechlorination of DDT, as DDMU is observed upon irradiation of DDD and DDE in cyclohexane (Table 3). The most abundant degradation product observed in Table 3 has a retention time and mass spectrum identical to those of 4,4′-dichlorobenzophenone (DCBP). Reduction with sodium borohydride in methanol of authentic 4,4-dichlorobenzophenone generates bis(4-chlorophenyl)methanol, which presents a retention time and mass spectrum identical to those of compound **3**.

Table 3. Dechlorination Product Yields for DDT, DDD, and DDE after 10-kGy Irradiation in Cyclohexane[a]

	DDT	DDD	DDE
DDD	10.0 (0.7)[b]		ND[c]
DDE	5.9 (0.6)	0.9 (0.05)	
1a	0.2 (0.02)	1.0 (0.04)	ND
1b	ND	2.4 (0.3)	ND
DDMU	1.0 (0.1)	9.3 (0.3)	30.4 (0.9)
2e	ND	1.6 (0.1)	ND
2f	ND	ND	3.6 (0.03)
3	3.5 (0.5)	ND	ND
DCBP	9.1 (2.0)	14.8 (0.3)	9.5 (0.09)
4	ND	ND	0.6 (0.02)

[a] In percent relative to the starting material corrected with the response factor of the starting material relative to DDT. [b] Numbers in parentheses are the standard deviations. [c] Not detected.

Irradiation of DDD in the two hydrocarbons generated small amounts of DDE along with the monodechlorinated products **1a**, **1b**, and DDMU. The latter is the most abundant and is likely produced by a mechanism similar to that involved in the formation of DDE from DDT. Compounds **1a** and **1b** were produced in a relative proportion different from that observed in 2-propanol. The only tridechlorinated product observed upon irradiation of DDT, apart from DCBP and **3**, is **2e**. The mass spectrum of this compound presents a molecular ion at 248 Da in an ion cluster characteristic of a compound containing two chlorines. Its mass spectrum differs slightly from the already published spectrum of 1,1-bis(4-chlorophenyl)ethylene (NIST/EPA/NIH, 1992). Another didechlorinated product of DDE, compound **2f**, presents an excellent match with the above-mentioned published spectra and also presents a retention time different from that of **2e**. On this basis, the structure of **2e** was determined to be an analog of DDE having lost a β and an aromatic chlorine (Figure 3). Because **2f** is the only didechlorinated product of DDE, the latter cannot be the precursor of **2e** in the DDD experiment. This also implies that DDMU undergoes dechlorination exclusively at the β position. The most likely precursor of **2e** is then **1b**, which already lacks one aromatic chlorine. The mechanism responsible for the formation of DDE from DDT and of DDMU from DDD is probably also involved in the formation of **2e** from **1b**. As in the DDT experiment, an important amount of DCBP is also observed upon irradiation of DDD.

Irradiation of DDE in cyclohexane generates DDMU through loss of a β chlorine. The latter is the precursor of the didechlorinated compound **2f** through loss of the other β chlorine. As for DDT and DDD, a large amount of DCBP is also produced. Finally, the degradation product **4**, which presents a molecular ion at 246 Da, was detected. Its mass spectrum is identical to the one of 9-(dichloromethyl)fluorene as published from the work of Plimmer and co-workers, who studied the UV irradiation of DDE (NIST/EPA/NIH, 1992). To confirm the structure of **4**, a solution of DDE was UV irradiated (254 nm) in 2-propanol and a compound presenting a

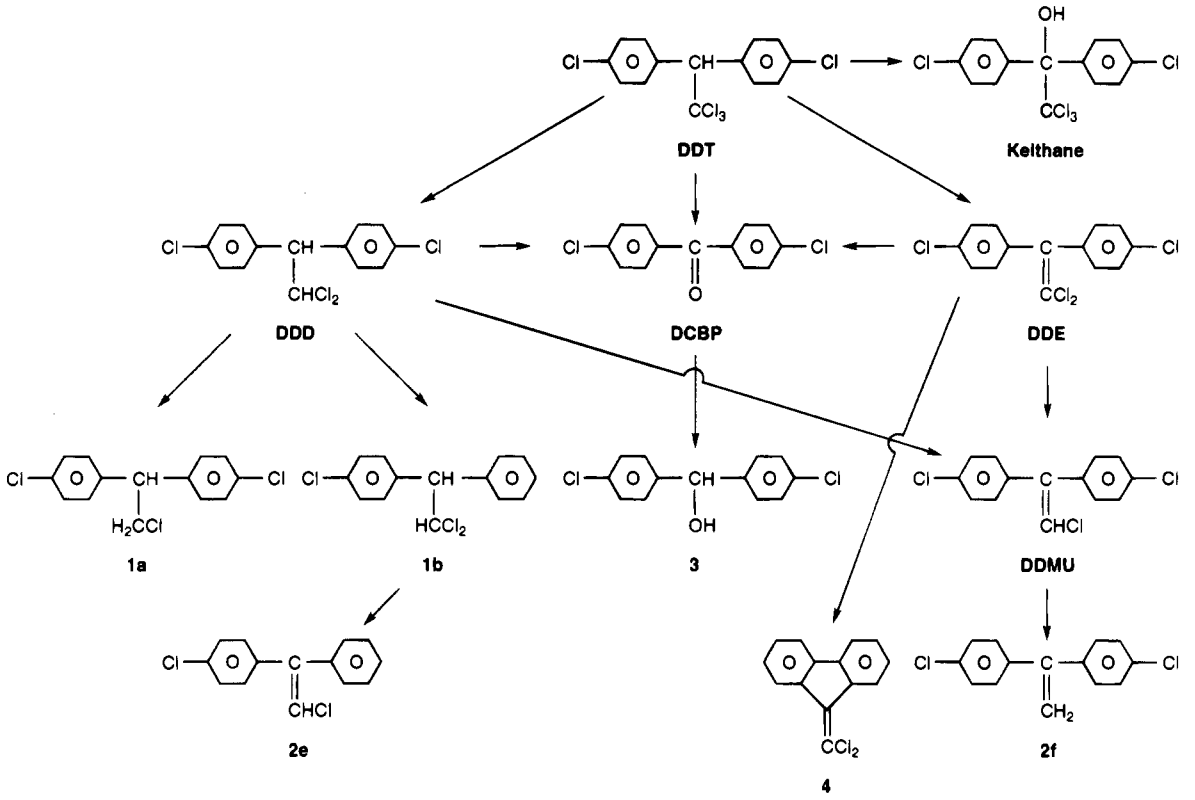

Figure 3. Degradation pathways of DDT, DDD, and DDE in cyclohexane.

Table 4. Dechlorination Product Yields for DDT, DDD, and DDE after 10-kGy Irradiation in Cyclohexene[a-c]

	DDT	DDD	DDE
DDD	17.4 (0.3)[b]		ND[c]
DDE	2.5 (0.1)	0.3 (0.06)	
1a	1.2 (0.1)	12.1 (4.7)	ND
1b	ND	2.4 (0.4)	ND
DDMU	0.5 (0.1)	8.8 (2.2)	37.1 (2.3)
2e	ND	1.9 (0.4)	ND
2f	ND	ND	3.6 (0.3)
3	0.4 (0.02)	ND	ND
DCBP	0.9 (0.1)	6.6 (1.3)	0.8 (0.04)
4	ND	ND	ND

[a-c] For footnotes, see Table 3.

retention time and mass spectrum identical to those of **4** was indeed observed.

In cyclohexene (Table 4), the same degradation products as in cyclohexane were observed but in different proportions. A major difference is the large reduction in the amounts of DCBP in all experiments. A considerable increase in the formation of **1a** from DDD can also be observed in the DDD experiment and also, proportionally, in DDT.

Addition Products in Cyclohexane and Cyclohexene. Upon irradiation in cyclohexane, a variety of peaks occurring at retention times longer than that of the starting material were observed in GC/MS. The relative abundances of these compounds are presented in Table 5. One of these compounds presents a GC retention time and mass spectrum identical to those of 2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol (kelthane), an α-hydroxylated analog of DDT (Figure 3). The EI mass spectra of many of these compounds do not show any ions with masses higher than their base peak at 235 Da, which indicates a bis(4-chlorophenyl)methyl moiety. To propose structures for these compounds, HPLC purification and NMR analysis were performed. From the irradiated DDT and DDD solutions, four

Table 5. Yields of Addition Products Formed upon Irradiation of DDT, DDD, and DDE in Cyclohexane[a-c]

	DDT	DDD	DDE
kelthane	0.7 (0.1)[b]	ND[c]	ND
1e	0.4 (0.1)	0.4 (0.03)	ND
1f	0.5 (0.02)	1.1 (0.3)	ND
1g	0.5 (0.27)	1.2 (0.3)	ND
2g	0.5 (0.3)	0.2 (0.02)	0.4 (0.2)
2h	0.5 (0.3)	ND	1.3 (0.1)
2i	0.2 (0.01)	ND	0.2 (0.07)

[a-c] For footnote, see Table 3.

addition products, **1e**, **1f**, **1g**, and **1h**, were isolated.

The EI mass spectrum of **1e** only shows the 235-Da fragment. The ECNCI mass spectrum shows a molecular ion cluster at 364 Da characteristic of a trichloro compound. The NMR of **1e** shows a multiplet at 7.1 ppm, which corresponds to the eight aromatic protons, and a doublet of doublets (J = 1.8 and 10.8 Hz) at 4.50 ppm and a doublet (J = 10.8 Hz) at 4.24 ppm coupled to each other. They correspond to the β and α hydrogens, respectively, the former being also coupled to the methyne of the cyclohexyl ring (Figure 2). The other cyclohexyl protons appear as a multiplet at 1.5 ppm. Thus, **1e** is a DDD analog in which one of the β chlorines is replaced by a cyclohexyl function. A possible precursor of **1e** is **1f**.

The EI mass spectrum of **1f** only shows the 235-Da fragment. The ECNCI spectrum shows a molecular ion at 398 Da within an ion cluster characteristic of a tetrachloro compound. This corresponds to a DDD molecule to which is added a cyclohexyl function. The NMR shows two symmetrical multiplets at 7.4 and 7.2 ppm for the aromatic protons. The α hydrogen appears as a singlet at 4.70 ppm, and the cyclohexyl protons appear as a series of multiplets at 2.0−1.0 ppm. Compound **1f** is then an analog of DDD in which the β hydrogen has been substituted by a cyclohexyl function (Figure 2). Compound **1f** can be produced by direct

substitution of a β chlorine of DDT by a cyclohexyl radical, but it is also certainly produced from the DDD generated by the first dechlorination of DDT, as **1f** is also observed upon irradiation of DDD.

The EI mass spectrum of **1g** shows a 317-Da base peak and no 235-Da fragment ion, which is indicative of a cyclohexyl addition on one aromatic ring. The ECNCI spectrum shows a molecular ion at 400 Da within an ion cluster characteristic of a tetrachloro compound. The NMR spectrum presents two doublets (J = 8.1 Hz) at 4.55 and 6.29 ppm for the α and β hydrogens, respectively. The aromatic portion of the spectrum presents a multiplet at 7.3 ppm, corresponding to six protons, and a doublet of doublets at 7.05 ppm with a large coupling constant of 8.7 Hz, characteristic of a J_3 coupling, and a smaller coupling constant of 2.26 Hz, characteristic of a J_4 coupling. The chemical shift of this proton indicates that it is located at the 5-position of the aromatic ring and is coupled to the adjacent 6-hydrogen. The small coupling constant is due to J_4 coupling with the hydrogen in position 3. This indicates that the cyclohexyl function has to be in the 2-position, adjacent to the chlorine-substituted carbon. The methyne proton of the cyclohexyl ring appears as a multiplet at 2.9 ppm due to the deshielding effect of the aromatic ring, and the other protons of the cyclohexyl ring appear as a multiplet at 1.9−1.4 ppm.

HPLC analysis of the concentrated DDT solution in cyclohexane revealed a compound not detected in the GC/MS analysis of the 100 ppm solution. The EI mass spectrum of this compound, labeled **1h**, presents a base peak at 317 Da and a molecular ion cluster at 434 Da in ECNCI characteristic of a pentachloro compound. Although **1h** was obtained in amounts too small to be analyzed by NMR, its mass spectra are consistent with the structure of DDT having cyclohexyl substitution on one aromatic ring. Compound **1h** could be a precursor of **1g**.

From the irradiated DDE solution, three addition products, **2g**, **2h**, and **2i**, were isolated. The EI spectrum of **2g** shows a molecular ion cluster at 330 Da characteristic of a dichloro compound. The NMR shows the eight aromatic protons as a multiplet at 7.2 ppm. The proton on the β carbon appears as a doublet (J = 10.2 Hz) at 5.85 ppm, coupled to the methyne proton of the adjacent cyclohexyl ring. The methyne proton of the cyclohexyl ring appears as a multiplet at 2.1 ppm, and the other protons appear as a multiplet at 1.7−1.2 ppm. Thus, **2g** corresponds to DDE having its two β chlorines replaced by a hydrogen and a cyclohexyl function.

The EI mass spectrum of **2h** shows a molecular ion cluster at 364 Da characteristic of a trichloro compound. The NMR shows the aromatic protons as a multiplet at 7.3−7.1 ppm, the methyne of the cyclohexyl at 2.55 ppm as a multiplet, and the other cyclohexyl protons as a multiplet at 1.8−1.1 ppm. The absence of any proton in the 5−7 ppm region indicates that **2g** corresponds to DDE having one of its β chlorines substituted by a cyclohexyl function.

The EI mass spectrum of **2i** presents a molecular ion cluster at 398 Da characteristic of a tetrachloro compound. The NMR spectrum shows a multiplet at 7.3−7.2 ppm, corresponding to six aromatic protons, and a doublet of doublets at 6.94 ppm with a large J_3 (8.1 Hz) and a small J_4 (2.4 Hz) coupling constant similar to those observed for **1g**. This indicates that **2i** is an analog of DDE substituted by a cyclohexyl function at position 2 of one of its aromatic rings, as observed for **1g**. The methyne of the cyclohexyl ring appears as a multiplet at 2.95 ppm, and the other cyclohexyl protons appear as a multiplet at 1.8−1.2 ppm.

When cyclohexene was used as solvent, some of the same addition products as those observed in cyclohexane were detected in small amounts. In irradiated DDT, compound **1e** represented 0.5% and **1f** 0.2% of the starting material, while in irradiated DDD these two compounds amount to 0.2 and 0.1%, respectively. In irradiated DDE, compounds **2h** and **2g** amount to 0.5 and 0.6%, respectively, of the starting material. No cyclohexenyl addition products were detected.

DISCUSSION

The γ-irradiation-induced degradation of organochlorinated compounds generally occurs through reductive dechlorination. This reaction arises from the addition to these electrophilic compounds of solvated electrons generated by the interactions of these highly energetic photons and solvent molecules. The radical anion formed undergoes loss of a chloride anion to become a radical which abstracts a hydrogen atom from the solvent to produce a dechlorinated analog of the starting material. The higher degradation yield of DDT versus those of its metabolites in any solvent, as presented in Table 1, probably reflects the greater electrophilicity of the former molecule due to its higher chlorine content. The same phenomenon was also observed upon γ-irradiation of PCB in organic solvents, the more chlorinated congeners being generally more reactive toward reductive dechlorination than the lesser chlorinated ones (Sawai et al., 1972). In the present study, the degradation yields of DDT and its metabolites were smaller in cyclohexene than in cyclohexane. The same phenomenon was also observed with PCB (Lépine et al., 1990).

It is interesting to note that, in 2-propanol, the first dechlorination reaction occurs exclusively at the β carbon of DDT to produce only DDD, while the second dechlorination occurs at both aromatic and β carbons. The same phenomenon can also be observed in cyclohexane and cyclohexene. This can be rationalized on the basis of the stability of the intermediate radical. With DDT, the radical produced by cleavage of the carbon−chlorine bond on the β carbon is well stabilized by two adjacent chlorine atoms. With DDD, the radical generated at this position would be stabilized by only one adjacent chlorine. This would make cleavage of the aromatic carbon−chlorine an energetically equivalent alternative. Thus, a reduction in the number of chlorines at the β position causes a reduction of the relative reactivity of the β versus the aromatic chlorines. The same phenomenon can be observed for **1a** and **1b**, as their sole dechlorination product, **1c**, contains only one residual β and one aromatic chlorine. When irradiation of DDT and DDD was performed in fully deuterated 2-propanol, the dechlorinated products did not show any modification of the 235-Da ion cluster, indicating that there is no migration of the α hydrogen at the β position. Such migration would have led to deuterium enrichment at the α position by deuterium abstraction from the deuterated solvent by the α radical.

In the irradiation of DDT and DDD, one of the major differences between 2-propanol and cyclohexane/cyclohexene is the formation of compounds bearing a double bond at the α carbon, such as DDE, DDMU, and **2e**, in the two latter solvents. These compounds arise from loss of HCl from their precursor. For example, DDT is

the direct precursor of DDE through loss of HCl, as DDD is the direct precursor of DDMU. Although the DDE produced in the irradiation of DDD can also be a precursor of DDMU, as seen in the irradiation of DDE itself, DDE is produced in amounts too small to account for the observed quantities of DDMU in the DDD experiment (Table 3). Finally, in the DDD experiment, **1b** is the sole precursor of **2e** through loss of HCl, as DDMU generates only **2f** as seen in the irradiation of DDE (Table 3). Loss of HCl could occur through two different mechanisms. The first involves hydrogen atom abstraction at the α-position, leaving a radical at the α carbon. This radical then undergoes loss of a chlorine radical at the β-position and formation of the double bond. The other mechanism involves reductive dechlorination at the β-position, with the radical left at this position. The molecule then loses the α hydrogen atom with formation of the double bond. To discriminate between these two possibilities, DDT was irradiated in cyclohexane containing 0.02 M nitroethane, a solvated electron scavenger. A considerable decrease in the amount of DDE was observed. Because the former mechanism should not be affected by a solvated electron scavenger and the second should, the latter mechanism is more likely. When irradiations of DDT and DDD were performed in fully deuterated cyclohexane, the 235-Da ion cluster of the dechlorinated compounds did not show any deuterium enrichment.

Formation of the benzophenone DCBP, however, probably occurs through oxygen addition on a radical located on the α carbon, ultimately followed by loss of the substituted β carbon as a trichloromethyl radical by analogy to the mechanism proposed by Plimmer and co-workers, who also observed the formation of DCBP upon UV irradiation of DDT in presence of oxygen (Plimmer et al., 1970). The α-hydroxylated compound kelthane is probably a byproduct of these reactions. The yields of DCBP and **3** are considerably reduced in cyclohexene, probably because of the reactivity of the alkene function toward oxygen under γ-irradiation. The solvent would then compete with the organochlorinated compounds for the oxygen, thus inhibiting the formation of DCBP and its reduction product **3**. Restriction of this major degradation pathway in cyclohexene and the observed inhibition of the dechlorination reactions in general in cyclohexene compared to cyclohexane, as seen in Table 1, can account for the accumulation of the more highly chlorinated degradation products as observed in Table 4.

The extent of solvent adduct formation for DDE in 2-propanol is quite surprising, as no compounds arising from simple dechlorination could be observed. 2-Propanol addition occurred at the β-position with displacement of a chlorine to produce **2d**. Since no DDMU was produced by irradiation of DDE, **2d** has to be the sole precursor of **2b** through dechlorination at the β-position as seen upon irradiation of purified **2d** in 2-propanol. As **2a** was not observed in this experiment, **2d** and **2b** are not precursors of **2a** through dechlorination and dehydration.

2-Propanol addition also occurs on the aromatic rings of DDE in a meta-position relative to the chlorine atom as seen in **2c**. Direct addition of 2-propanol at the β-position of the alkene function of DDE could also be observed in **1d**, which is also produced by irradiation of DDT and DDD in 2-propanol. Formation of **1d** from DDT could occur through direct displacement of a β chlorine by an isopropyl radical. In irradiated DDD, **1d** has to be produced through abstraction of the β hydrogen and addition of an isopropyl function onto the resulting radical. The DDD formed in the irradiation of DDT can also be the precursor of **1d** in the DDT experiment.

In cyclohexane, a larger number of addition products were observed than in 2-propanol, especially with DDT and DDD. For compounds **1e** and **1f**, the addition of the cyclohexyl function occurs at the β carbon. In irradiated DDT, compound **1f** can be produced by replacement of a β chlorine by a cyclohexyl radical, and it can also be produced from the DDD generated, as **1f** is also produced in considerable amounts in irradiated DDD. Formation of **1f** in irradiated DDD must occur through abstraction of the β hydrogen prior to cyclohexyl addition. The mechanisms of formation of **1f** in cyclohexane and of **1d** in 2-propanol are probably similar. In irradiated DDT and DDD, compound **1e** can be generated by the same mechanisms or by dechlorination of **1f**.

For **1g**, **1h**, and **2i**, cyclohexyl addition occurs on the aromatic ring. The NMR spectra of **1g** and **2i** show that the addition occurs meta to the aromatic chlorine, while in 2-propanol the isopropyl function was found ortho to the aromatic chlorine as in **2c**.

Other addition products, such as **2g**, **2h**, and **2i**, contain a double bond. In the DDT experiment, these compounds are probably not generated, at least not exclusively, from a DDE intermediate because the relative proportions of **2g**, **2h**, and **2i** in the DDT experiment differ from those observed in the irradiation of DDE itself. In irradiated DDT, **2h** and **2g** can also be produced by loss of HCl from **1f** and **1e**, respectively, by a mechanism similar to the formation of DDE and DDMU from DDT and DDD.

In cyclohexene, only a few addition products were observed and only in small amounts. It is interesting to note that these compounds are cyclohexyl addition products and that no cyclohexenyl addition products could be observed. These addition products must have been formed through electrophilic attack of an organochlorine radical onto the double bond of cyclohexene, with the resulting radical picking up a hydrogen atom from the solvent. The only addition products observed upon irradiation of PCB in cyclohexene were also cyclohexyl derivatives (Lépine et al., 1990).

CONCLUSION

Irradiation of DDT and DDD in 2-propanol proceeds through successive dechlorinations to generate lesser chlorinated derivatives of DDT. Irradiation of DDE in the same solvent generates exclusively isopropyl addition products. In cyclohexane and cyclohexene, the same dechlorination pathways were observed and compounds arising from loss of HCl from their precursors were also found. Cyclohexyl addition products were obtained in cyclohexane and cyclohexene. Finally, large amounts of 4,4′-dichlorobenzophenone are generated upon irradiation of DDT, DDD, and DDE in cyclohexane in the presence of oxygen.

LITERATURE CITED

Carp, A. E.; Liska, B. J.; Ziemer, P. L. Decomposition of Aldrin by Gamma Irradiation I. In Organic Solvent. *Bull. Environ. Contam. Toxicol.* **1972a**, *7* (6), 321–330.

Carp, A. E.; Liska, B. J.; Ziemer, P. L. Decomposition of Aldrin

by Gamma Irradiation II. In Lipid Solutions. *Bull. Environ. Contam. Toxicol.* **1972b**, *7* (6), 331–337.

Lépine, F. L. Effects of Ionizing Radiation in a Food Irradiation Perspective: A Bibliographic Review. *J. Agric. Food Chem.* **1991**, *39*, 2112–2118.

Lépine, F. L.; Milot, S.; Gagné, N. γ Irradiation Induced Formation of PCB-Solvent Adducts in Aliphatic Solvents. *J. Agric. Food Chem.* **1990**, *38*, 1873–1876.

NIST/EPA/NIH. *Mass Spectral Database,* Ver. 4.0: U.S. Department of Commerce: Gaithersburg, MD, 1992.

Plimmer, J. R.; Klingebiel, U. I.; Hummer, B. E. Photooxidation of DDT and DDE. *Science* **1970**, *167*, 67–69.

Sawai, T.; Shinozaki, Y. Radiolytic dechlorination of polychlorinated biphenyls (PCB) in organic solution. *Chem. Lett.* **1972**, 865–868.

Schmitt, C. J.; Zajicek, J. L.; Ribick, M. A. National Pesticide Monitoring Program: Residues of Organochlorine Chemicals in Freshwater Fish, 1980–81. *Arch. Environ. Contam. Toxicol.* **1985**, *14*, 225–260.

Sherman, W. V.; Evans, R.; Nesyto, E.; Radlowski, C. Dechlorination of DDT in Solution by Ionizing Radiation. *Nature* **1971**, *232*, 118–119.

World Health Organization. "Wholesomeness of Irradiated Food"; Report by a Joint FAO/IAEA/WHO Expert Committee; WHO Technical Report Series 659; WHO: Geneva, 1981.

Received for review February 28, 1994. Accepted June 13, 1994.[⊗]

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1994.