

Effects of Ionizing Radiation on Pesticides in a Food Irradiation Perspective: A Bibliographic Review

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The effects of γ irradiation on pesticides in solution or in food are reviewed. Degradation of pesticides is generally greater in irradiated aqueous solution than in aliphatic solvents or in food. Degradation products of some pesticides have been identified in organic solvents, but very few studies of this type have been performed on irradiated food. Addition products between molecules of solvent and pesticides have been observed. These results are discussed in a food irradiation perspective.

INTRODUCTION

The objective of this bibliographic study is to summarize the available data in the literature about the degradation extent and the nature and toxicity of the degradation products of pesticides upon treatment with ionizing radiations. These data are necessary to assess the toxicological implications of such treatment on these residues in a food irradiation perspective. Because there have been few studies performed specifically on the fate of pesticide residues in irradiated food, this work will be extended to include work performed on pesticides irradiated in solution.

MECHANISMS AND PARAMETERS INVOLVED IN RADIATION-INDUCED DEGRADATION OF ORGANIC MOLECULES

Reactive Species. γ -Radiation-induced chemical modifications of organic compounds in solution are not usually caused by direct action of the incident photons but mostly by a variety of reactive species generated in the solvent by these photons. In fact, at solute concentration smaller than 0.1 M, direct action of the incident photons on the solute is considered unimportant (Spinks and Wood, 1976). Because pesticides are present in small amounts in food, knowledge of the nature, generation, and modes of action of these reactive species is important to understand the parameters involved in the degradation of pesticides upon γ irradiation.

The most important reactive species to consider here are the solvated electrons and the hydroxyl radical. The solvated electron, for example, is especially important in radiation-induced dechlorination of organochlorinated substances. Many pesticides such as DDT, lindane, aldrin, endrin, heptachlor, dieldrin, chlordane, and Mirex are organochlorinated compounds. The solvated electron reacts by dissociative attachment with these substances to generate an organic radical and a chloride anion. The organic radical scavenges a hydrogen atom from the solvent and a dechlorinated molecule is thus obtained. There are a variety of reactive species generated in irradiated solutions, but the solvated electron and the hydroxyl radical are those considered important in the literature discussed here.

Many factors have a direct influence on the nature and on the amounts of the reactive species generated by γ irradiation and thus control the nature and the extent of the chemical transformations.

Physical State. In frozen solution or in the pure crystalline state, the mobility of the various radicals formed

is considerably reduced, thus favoring recombination and considerably decreasing the extent of the chemical transformations compared to liquid solutions.

Dose and Dose Rate. The degradation extent of organic substances increases with increasing irradiation dose. Typically, the relationship between degradation and applied dose is initially linear and, at higher doses, tends to level off asymptotically to completion. Destruction efficiency is higher at lower dose rate. At higher dose rate, the local concentration of the reactive radicals increases and favors radical recombination while radical-substrate reactions decrease. Radiation chemical yields are normally expressed in terms of G values, which represent the number of molecules degraded or formed per 100 eV of absorbed energy. To make the data presented in this review paper more relevant to food irradiation, chemical yields will be generally presented in terms of moles of product degraded per liter of solvent per kilogray of applied dose.

Nature of the Solvent. Some properties of the solvent such as its polarity may influence the degradation extent of organic substances in irradiated solution. For example, polar solvents tend to solvate electrons more efficiently than nonpolar solvents. Thus, organochlorinated pesticides, in which dechlorination is initiated by solvated electrons, will be more degraded in polar than in nonpolar solvents. Irradiation of water solutions also generates the highly reactive hydroxyl radical. Degradation yields in aqueous solutions are generally higher than in organic solvents.

Scavenging of the Reactive Species. The highly reactive nature of these radicals allows them to react with a wide variety of compounds. The extent of radical-pesticide reactions depends on the relative concentration and affinities of these pesticides for the reactive species vs those of other molecules in the solution. For example, oxygen has a very high affinity for solvated electrons, and the degradation yields of chlorinated compounds generally decrease if the solution is not degassed prior to irradiation. Because food is a highly complex matrix containing large amounts of various organic compounds, it is to be expected that, due to the scavenging of the reactive species by the other constituents, the degradation yields of pesticides in food will be lower than in pure and degassed solutions.

EFFECTS OF γ IRRADIATION ON PESTICIDES IN SOLUTION

DDT. Sherman et al. (1971) made the first systematic study dealing with γ irradiation degradation of DDT in

Table I. Degradation of Pesticide Solutions Irradiated at 3 kGy in Aqueous Solution^a

commercial product	active agents	(%)	active agent in samples, ppm	active agent destroyed, (mol L ⁻¹)/kGy
Fostox	parathion	20	10	8.5 × 10 ⁻⁶
BPD (powder)	lindane	0.3	0.6	3.4 × 10 ⁻⁷
	dieldrin	0.7	1.4	9.7 × 10 ⁻⁷
	DDT	5	10	4.6 × 10 ⁻⁶
	paraquat	17.8	50	6.5 × 10 ⁻⁵
Basudin	Diazinon	20	10	8.8 × 10 ⁻⁶
Dalf	methyl parathion	0.5	10	1.2 × 10 ⁻⁵
Neocid	lindane	2	10	1.3 × 10 ⁻⁶
Sana Flor	lindane	1	10	3.6 × 10 ⁻⁶
	malathion	1	10	5.1 × 10 ⁻⁶
	zineb	2.5	25	1.3 × 10 ⁻⁵
Paraderil	rotenone	1	10	3.5 × 10 ⁻⁶
Timor	lindane	2	10	4.6 × 10 ⁻⁶
	allethrin	0.06	0.3	3.2 × 10 ⁻⁷
simazine	simazine	technical	10	8.6 × 10 ⁻⁶
dimethoate	dimethoate	technical	10	1.4 × 10 ⁻⁵
Tetradifon	Tetradifon	technical	10	1.3 × 10 ⁻⁶
malathion	malathion	technical	10	9.1 × 10 ⁻⁶
lindane	lindane	technical	10	7.4 × 10 ⁻⁶
methyl parathion	methyl parathion	technical	10	8.6 × 10 ⁻⁶
atrazine	atrazine	technical	10	1.5 × 10 ⁻⁵
heptachlor	heptachlor	99	10	2.8 × 10 ⁻⁶
Tomorin	coumachlor	1	10	9.7 × 10 ⁻⁶
Tordon 101	triisopropanolamine	10.2	10	6.9 × 10 ⁻⁶
	salt of 4-amino-3,5,6-trichloropicolinic acid			
	triisopropanolamine salt of 2,4-D	39.6	38.8	2.7 × 10 ⁻⁵

^a From Cappadona et al. (1975).

solution. This study was conducted in dilute 2-propanol solutions, and the only degradation products observed were 2,2-bis(4-chlorophenyl)-1,1-dichloroethane (DDD), the monodechlorinated product of DDT, and HCl. The formation of these substances is explained by a reductive dechlorination mechanism. The dose range used in Sherman's work varied from 0.23 to 6.5 kGy for a DDT concentration of 7000 ppm. A 2.3×10^{-3} (mol L⁻¹)/kGy degradation of DDT was observed at 6.5 kGy at a dose rate of 0.22 kGy/min, while at 0.0078 kGy/min, a 2.1 kGy dose gave a 7.0×10^{-3} (mol L⁻¹)/kGy destruction. Thus, at a higher dose rate, the degradation of the starting material was less efficient than at a lower dose rate. Other authors also reported irradiation of DDT in organic solvent. Lippold et al. (1969) obtained a 2.1×10^{-7} (mol L⁻¹)/kGy reduction in a 5 ppm solution of DDT in hexane upon irradiation at 50 kGy, and Ceurvels et al. (1974), working with a 1 ppm solution of DDT in hexane, obtained a 8.7×10^{-8} (mol L⁻¹)/kGy degradation at 15 kGy.

In aqueous solutions, Cappadona et al. (1975) (Table I) observed a 4.6×10^{-6} (mol L⁻¹)/kGy degradation in a commercial pesticide mixture containing 10 ppm of DDT irradiated at 3 kGy. Shastri and Rao (1980) observed complete degradation upon irradiation at 2 kGy of a 9.4 ppm DDT in 1% sodium lauryl sulfate aqueous solution for a chemical yield of 1.3×10^{-5} (mol L⁻¹)/kGy. At this radiation dose, 50% of the initial DDT was transformed into DDD. Formation of addition products between DDT and solvent molecules was observed by Lépine et al. (1991) when cyclohexane or a methyl ester of a saturated fatty acid was used as solvent at radiation doses varying between 5 and 10 kGy.

PCBs. The degradation of polychlorinated biphenyls (PCBs) induced by γ radiation was first described by Sawai et al. (1972, 1974). Like most organochlorinated substances, the main decomposition mechanism is reductive dechlorination. These experiments have been conducted with Kanechlor 400, a complex PCB mixture, in 2-propanol at concentrations of 0.3, 1.0, and 10% v/v. It was observed that at high substrate concentrations the de-

chlorination yield increased from 1.25×10^{-4} to 2.5×10^{-4} to 6.25×10^{-4} (mol L⁻¹)/kGy, respectively, at 20 kGy. The higher degradation yields at higher concentrations simply reflect a more efficient scavenging of solvated electrons by the substrate. Finally, the intrinsic reactivity of PCBs toward radiation was shown to increase with increasing number of chlorine substituents on the biphenyl ring.

In the environment and in food, PCBs are found as complex mixtures. Because a dechlorinated byproduct of a specific PCB congener is itself another PCB congener, irradiation of a PCB mixture will modify the chromatographic profile of the mixture. This was first reported by Sawai (1974) in basic 2-propanol. Because a small number of specific PCB congeners are much more toxic than others, an isomer-specific gas chromatographic study was performed on a PCB mixture irradiated in various organic solvents for a 4 ppm PCB solution irradiated at 1.25 Mrad (Lépine and Massé, 1990a). These results showed that considerable modifications of the PCB's profile occurred at this radiation dose and that the modifications are generally greater in polar solvents than in nonpolar ones. The degradation pathways of some pure model PCB congeners were investigated in aliphatic and methanolic solvents to explain these results (Lépine and Massé, 1990b).

Vollner and Korte (1974) also studied the degradation of di- and tetrachlorinated PCB congeners. The degradation yields were 2.1×10^{-4} and 1.6×10^{-4} (mol L⁻¹)/kGy, respectively, after a 540-kGy treatment of a 50 000 ppm hexane solution.

The effects of other sources of ionizing radiation such as electron beams were also investigated by Merrill et al. (1978), who studied the degradation of PCBs in various solvents using the 2',3,4-trichlorobiphenyl congener. A 13.5-kGy dose was required to obtain a 5.6×10^{-7} (mol L⁻¹)/kGy degradation of a 4 ppm solution in hexane, while a 9.7×10^{-7} (mol L⁻¹)/kGy degradation was obtained at 8 kGy in hexanol/water solution. In water containing 0.5 and 0.1% sodium stearate, 3.8×10^{-6} and 5.4×10^{-6} (mol L⁻¹)/kGy degradations were achieved for a 0.7 ppm solution at 0.35 and 0.25 kGy, respectively. For the other

congener used in Merrill's study, namely the 4-chlorobiphenyl congener, a 1.2×10^{-4} (mol L⁻¹)/kGy degradation was obtained at 0.025 kGy for a 0.8 ppm aqueous solution. Once again, these results illustrate the larger degradation yields obtained in aqueous solutions. In this study, the authors claim, but without providing experimental evidence, that hydroxylated PCB derivatives were formed.

Schweitzer et al. (1987) also studied the effects of γ irradiation on PCBs in water using the 2,3',4',5-tetrachlorobiphenyl congener. The destruction yield was 2.9×10^{-7} (mol L⁻¹)/kGy at 0.28 kGy for a 50 ppb solution. Finally, Kinoshita and Sunada (1973) studied the irradiation of a 100 ppb PCB mixture in aqueous suspension at 100 kGy, and a 9.6×10^{-8} (mol L⁻¹)/kGy destruction was observed.

Formation of addition products between chlorinated aromatics and solvent molecules upon irradiation has also been described. Polychlorinated benzene derivatives, which are structurally related to PCBs, were shown to form addition products with the solvent when γ irradiated in basic 2-propanol (Shimokawa and Sawai, 1977). Irradiation of PCBs in dimethyl disulfide was described by Buser (1985) as a method to generate methylthio-PCBs, which are known metabolites of PCBs. Lépine et al. (1990) observed the formation of PCB solvent adducts when pure PCB congeners and a PCB mixture were irradiated in cyclohexane or cyclohexene.

Lindane. Ceurvels et al. (1974) observed a 1.5×10^{-8} (mol L⁻¹)/kGy degradation for a 0.2 ppm hexane solution of lindane irradiated at 25 kGy. The degradation products were not identified. Vollner and Korte (1974) obtained a 2.2×10^{-4} (mol L⁻¹)/kGy reduction in the same solvent at 540 kGy for a 50 000 ppm concentration. Once again, the higher degradation yield obtained in the latter study is caused by the large concentration of lindane used in the experiment. More than 77% of the degradation products identified were hexachlorinated cyclohexene, cyclohexadiene, and benzene. Another 19% were mostly mono-, di-, and tridechlorinated lindane degradation products containing one, two, or three double bonds.

A similar study was performed by Hamada et al. (1981) with a 1500 ppm 2-propanol solution irradiated at 10 kGy at a dose rate of 5 kGy/h. The degradation yield was 2.4×10^{-4} (mol L⁻¹)/kGy. Four degradation products were identified, two being tetrachlorocyclohexene isomers and the two others being monodechlorinated analogues of the starting material. The chromatographic pattern of these degradation products was similar to the one obtained when lindane was irradiated with UV light.

Irradiation of aqueous lindane solutions has also been reported by Shastri and Rao (1980), and a degradation yield of 1.8×10^{-4} (mol L⁻¹)/kGy was obtained for a 14 ppm solution at 0.15 kGy. These authors also performed the irradiation of aqueous lindane solutions containing 1% sodium lauryl sulfate. Under these conditions, a 6.0×10^{-5} (mol L⁻¹)/kGy degradation yield was obtained at 4 kGy for a 174 ppm concentration. When irradiation was performed in water saturated with nitrous oxide, a solvated electron scavenger that produces hydroxy radicals, the degradation yield of lindane did not decrease. This indicates that, in water, there are reactive species other than the solvated electron which can be involved in the decomposition of lindane.

Finally Cappadona et al. (1975) reported the irradiation of aqueous solutions of commercial pesticide mixtures containing various amounts of lindane. These results are presented along with other data obtained for other pesticides in Table I. It is interesting to note that, depending on the composition of the commercial mixtures,

the degradation yield of lindane varied significantly, even if its relative concentration was held constant (10 ppm, with one exception for BPD). The highest degradation yield, 7.4×10^{-6} (mol L⁻¹)/kGy, is obtained with pure technical lindane. This is likely due to competition for the various reactive species by the other constituents of the mixtures. This phenomenon is likely to play an important role when a complex matrix such as food is involved.

Aldrin. Ceurvels et al. (1974) reported a 4.9×10^{-8} (mol L⁻¹)/kGy destruction of Aldrin in a 1 ppm hexane solution irradiated at 5 kGy. Vollner and Korte (1974) obtained a 1.67×10^{-4} (mol L⁻¹)/kGy decrease in concentrated (50 000 ppm) hexane solutions irradiated at 540 kGy. From the degradation products identified, 21% were monodechlorinated aldrin, 22% were photoaldrin (an isomer of aldrin), and 57% were addition products containing one hexyl group. Carp et al. (1972a) also studied the fate of aldrin irradiated in hexane solutions. A degradation product, identified as a monodechlorinated isomer of aldrin, was observed. This compound represented 37% of the initial aldrin concentration (1000 ppm) at 60 kGy for a degradation yield of 2.5×10^{-5} (mol L⁻¹)/kGy (55% destruction of the starting material). Irradiation of aldrin in aqueous solution was described by Shastri and Rao (1980), who obtained a 1.0×10^{-6} (mol L⁻¹)/kGy degradation at 0.28 kGy for a 0.2 ppm solution.

Dieldrin. Ceurvels et al. (1974) observed a 6.6×10^{-8} (mol L⁻¹)/kGy destruction of dieldrin in a 1 ppm hexane solution at 10 kGy. Vollner and Korte (1974) obtained a 1.8×10^{-4} (mol L⁻¹)/kGy degradation in concentrated (50 000 ppm) acetone solution at 540 kGy. The degradation products identified were monodechlorinated (92%), didechlorinated (7%), and tridechlorinated (1%) dieldrin derivatives. Cappadona et al. (1975) reported the irradiation of dieldrin in water (Table I), and a 9.7×10^{-7} (mol L⁻¹)/kGy degradation was obtained at 3 kGy for an aqueous solution of a commercial pesticide mixture containing 1.4 ppm of dieldrin.

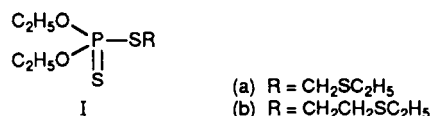
Chlordane. Vollner and Korte (1974) observed a 1.5×10^{-4} (mol L⁻¹)/kGy reduction in the amounts of chlordane in a concentrated (50 000 ppm) hexane solution after 540-kGy radiation treatment. From the total of the characterized degradation products 55, 23, 21, and 2% were, respectively, mono-, di-, tri-, and tetradechlorinated chlordane analogues. In water, Shastri and Rao (1980) obtained 5.0×10^{-7} to 4.4×10^{-6} (mol L⁻¹)/kGy degradation at 4 kGy for 1 and 10 ppm concentrations, respectively.

Other Halogenated Pesticides. Ceurvels et al. (1974) observed a 5.1×10^{-8} (mol L⁻¹)/kGy reduction of heptachlor from a 1 ppm hexane solution irradiated at 20 kGy. For the same insecticide in aqueous solutions, Shastri and Rao (1980) obtained a 2.3×10^{-6} (mol L⁻¹)/kGy degradation at 4 kGy for a 3.7 ppm solution. Cappadona et al. (1975) obtained similar degradation yields, as described in Table I. In the latter study, a 10 ppm heptachlor solution gave a 2.8×10^{-6} (mol L⁻¹)/kGy degradation at 3 kGy. Heptachlor epoxide was found to be slightly more resistant than heptachlor, since a 1.1×10^{-6} (mol L⁻¹)/kGy degradation was observed at 4 kGy for a 3.9 ppm aqueous solution (Shastri and Rao, 1980).

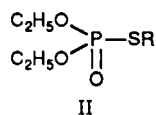
Other Types of Pesticides. There is very little information available on the extent and the nature of the degradation products of the other classes of pesticides. Cappadona et al. (Table I) provide the only systematic data set on many other types of pesticides.

Grant et al. (1969) studied the degradation and deg-

radiation products of two organophosphorus pesticides, phorate (Ia) and disulfoton (Ib).



Irradiation was performed with 2000 ppm solutions in various solvents, and the largest destruction yield of these two pesticides was observed in hexane rather than water. For example, disulfoton gave a 1.1×10^{-4} (mol L⁻¹)/kGy degradation at 40 kGy in hexane, while, in water, no apparent degradation took place at the same radiation dose. Phorate gave a 6.9×10^{-5} (mol L⁻¹)/kGy degradation at 40 kGy in hexane, while, in water, only a 1.7×10^{-5} (mol L⁻¹)/kGy degradation was obtained at the same dose. For both compounds, some degradation products were identified, but not quantified, in irradiated acetone solutions. These products were the corresponding sulfoxide [R = (CH₂)_nS(O)C₂H₅] and sulfone [R = (CH₂)_nS(O)₂C₂H₅] along with the corresponding oxo analogues II.



Bucholtz and Lavy (1977) reported that irradiation of dilute (1 ppm) aqueous atrazine solutions at 50 kGy caused extensive degradation of this herbicide and that its degradation products consist mainly of other members of the triazine pesticide family. Interestingly, the study of Cappadona et al. demonstrates that at a much smaller radiation dose (3 kGy) a 90% degradation of atrazine is already achieved for a 10 ppm solution [1.5×10^{-5} (mol L⁻¹)/kGy]. Working with electron beams, Merrill et al. (1978) studied the degradation of monuron in water. For a 0.3-kGy irradiation dose a 6.6×10^{-5} (mol L⁻¹)/kGy destruction was observed for a 4 ppm solution, while, at 0.1 kGy, a 1.5×10^{-4} (mol L⁻¹)/kGy destruction was achieved.

Finally, it is interesting to compare the degradation yields of parathion, malathion, and Tetradifon as obtained by Lippold et al. (1969) in a 5 ppm hexane solution and by Cappadona et al. in a 10 ppm aqueous solution (Table I). In the former study, the degradation yields were 9.3×10^{-8} , 2.1×10^{-7} , and 7.9×10^{-8} (mol L⁻¹)/kGy, respectively, at 50 kGy and, for the latter, 8.5×10^{-6} , 9.1×10^{-6} , and 1.3×10^{-6} (mol L⁻¹)/kGy, respectively, at 3 kGy. Once again, the degradation yields in aqueous solutions are greater than in aliphatic solvents. Pure malathion aqueous solutions displayed a 9.1×10^{-6} (mol L⁻¹)/kGy degradation at 3 kGy, but in a commercial mixture such as Sana Flor, a 5.0×10^{-6} (mol L⁻¹)/kGy degradation was obtained for the same concentration (10 ppm) and at the same radiation dose (Table I). This further illustrates the phenomenon of competition for the reactive species, which decreases the degradation of a given substrate in a mixture compared to a pure solution.

EFFECT OF γ IRRADIATION ON ADSORBED PESTICIDES

Schweitzer et al. (1987) studied the radiation-induced decomposition of PCBs adsorbed on activated carbon. No degradation occurred, while, in the absence of the adsorbent, destruction was significant. Getzin and Rosefield (1968) reported the irradiation of Diazinon, malathion, and Zinophos at 20 ppm in sand and soil. Decomposition

yields were 9.9×10^{-7} , 1.6×10^{-6} , and 3.4×10^{-6} (mol L⁻¹)/kGy, respectively, at 10 kGy for irradiated sand and 1.1×10^{-6} (mol L⁻¹)/kGy for Diazinon and 1.9×10^{-6} (mol L⁻¹)/kGy for Zinophos in soil irradiated at the same dose. Once again, compared to Cappadona's degradation yields (Table I) of 8.9×10^{-6} and 9.1×10^{-6} (mol L⁻¹)/kGy for 10 ppm aqueous solutions of Diazinon and malathion, respectively, at 3 kGy, the effect of the adsorbent is evident. Finally, Cogburn and Mahany (1969) reported the irradiation of malathion sprayed and dried on paper strips and on wheat. In both cases, no measurable degradation was observed even up to 40 kGy.

EFFECTS OF γ IRRADIATION ON PESTICIDES IN FOOD

Carp et al. (1972b) studied the effects of γ irradiation on aldrin dissolved in corn oil and lard (1000 ppm, 60 kGy). Three degradation products were observed by gas chromatography but were not identified. These results were essentially similar to those obtained with aldrin in hexane solutions (Carp et al., 1972a) but for the degradation yields, which was 9.1×10^{-6} (mol kg⁻¹)/kGy compared to 3.8×10^{-5} (mol kg⁻¹)/kGy in hexane.

Lane et al. (1976) reported the effects of γ irradiation of duck eggs containing 233 ppm of Mirex at a radiation dose of 45 kGy, and the observed degradation yield was 6.0×10^{-6} (mol kg⁻¹)/kGy, which corresponds to a 64% decrease in concentration. The degradation products were identified as mono- and didechlorinated Mirex compounds. Of the five degradation products observed, only one was specific to γ irradiation, the other four being also produced upon UV irradiation of the eggs. Cin and Kroger (1982) also reported the γ irradiation of fish contaminated at the 8 ppm level. The degradation yield was 1×10^{-7} (mol kg⁻¹)/kGy at 50 kGy for a 38% decrease in Mirex concentrations.

Cichy et al. (1979) studied the effects of γ irradiation in lake trout containing 1.8 ppm of PCB. The irradiation dose was 10 kGy, and a 38% reduction in PCB levels was obtained. A reduction in the proportion of the lower chlorinated PCB congener was observed. The authors tentatively explained this phenomenon by postulating the selective formation from these congeners of water-soluble PCB derivatives. However, such compounds were not identified.

Solar et al. (1971) observed the effect of irradiation on aldrin, heptachlor epoxide, and endrin in potatoes. Degradation yields at 8.7 kGy were 1.3×10^{-7} , 1.9×10^{-7} , and 1.2×10^{-6} (mol kg⁻¹)/kGy, respectively, for concentrations of 1.4, 1.5, and 100 ppm. Because of the large difference in concentration, it is difficult to compare the degradation yields of endrin with those of the two other pesticides. Endrin was also injected in the potatoes from a concentrated petroleum ether solution, while the two other pesticides were already present in the untreated potatoes.

Hallab (1968) also studied the fate of endrin, dieldrin, DDT, and toxaphene in oyster homogenates irradiated at 2 and 10 kGy. Variance analysis demonstrates that there was a highly significant ($P < 0.01$) decrease in the pesticide levels at both radiation doses. Finally, Bachman and Gieszczyńska (1982) reported the fate of pesticides in luncheon meat irradiated at 25–48 kGy and found no difference in pesticide levels in the irradiated samples and the controls. DDT residue levels in onions irradiated at 40–80 Gy were not affected. Irradiation at 50 kGy of bone-meat meal resulted in 99% degradation of the initial 0.38 ppm concentration of lindane residues.

TOXICOLOGICAL PROPERTIES OF IRRADIATED PESTICIDES

There are very few available data about the toxicological aspects of irradiation with respect to pesticides. Kimbrough and Gaines (1971) reported having irradiated DDT in triglycerides and feeding the mixture to rats. The 1:2 DDT/tristearin emulsion in water was irradiated at 280 kGy. 2,2-Bis(4-chlorophenyl)-1,1-dichloroethylene (DDE) was the main pesticide degradation product, but DDT-tristearin addition products were detected using thin-layer chromatography. When the irradiated mixture was fed to rats, the LD₅₀ was found to be the same for the irradiated and the nonirradiated mixtures.

Kinoshita and Sunada (1973) studied the toxicity to shrimps of aqueous suspensions of a 100 ppb PCB mixture before and after a 100-kGy irradiation. At this radiation dose, the PCB concentration decreased by 92% and the toxicity of the suspension was considerably reduced. Grant et al. (1969) studied the inhibition of beef liver carboxylesterases by irradiated solutions of two insecticides, disulfoton and phorate. A considerable increase in enzymatic inhibition was observed depending on the radiation dose and type of solvent. For example, disulfoton after irradiation at 10 kGy in hexane was 3.3 times more potent than before irradiation, and phorate at the same radiation dose in the same solvent was 8 times more active. This increase in enzymatic inhibition was attributed to the observed production of the oxo analogues IIa and IIb, which are more potent inhibitors than the two initial insecticides.

The phytotoxicity of irradiated herbicide solutions was reported by Bucholtz and Lavy (1977). Dicamba and trifluralin solutions became less toxic for seedlings after a 50-kGy irradiation, while the atrazine solutions were slightly more toxic after treatment. Atrazine degradation was almost complete at 50 kGy; thus, the enhanced phytotoxicity observed is likely due to its degradation products, probably members of the triazine family.

DISCUSSION

Degradation Yields. An important factor controlling the radiation-induced degradation of an organic substance is its physical state. In the solid, crystalline state, degradation yields are very low. Thus, if irradiation is performed on frozen food, pesticide degradation is likely to be smaller than that in a nonfrozen matrix.

The same is true for pesticide residues adsorbed and irradiated on a dry surface as demonstrated by Cogburn and Mahany (1969). In this study, no measurable destruction took place when irradiation was performed on wheat sprayed with malathion, even at 40 kGy, while a 71% degradation was obtained in hexane solution at 50 kGy as described in Lippold et al. (1969). Even when irradiation of adsorbed pesticide is performed in a solvent, as described by Schweitzer et al. (1987) for PCBs on activated carbon, degradation is inhibited. Such inhibition occurs because these residues become less available to react with the various reactive species generated in the solvent by the radiations. The study of Getzin and Rosefield (1978) on pesticides irradiated in sand or soil also demonstrates a decrease in the degradation of adsorbed pesticides compared to the degradation yields obtained in aqueous solutions by other authors. In Getzin and Rosefield's work, however, factors other than the presence of an adsorbing medium, such as the presence of other organic molecules in soil, might play a role in the lower degradation yields observed. Then if pesticide residues are only present on a dry external surface of a food product, such as the

kernel of wheat, the radiation-induced degradation is likely to be considerably smaller than the one observed in solution models.

Many studies demonstrate that dose rate is another important factor involved in radiation-induced degradation of pesticides. At high dose rate, the concentration of the reactive radicals increases and favors radical-radical recombination and the organic residues are less affected. This could explain some discrepancies in the degradation yields reported by different authors for the same pesticide in the same solvent at the same irradiation dose. Unfortunately, many authors failed to mention the radiation dose rate used in their studies.

Another important parameter to consider is the pesticide concentration in solution. At higher substrate concentrations the degradation yields in terms of (mol L⁻¹)/kGy are higher than at lower substrate concentration due to a more efficient scavenging of the reactive species by the substrate. In terms of percentage of the starting material destroyed, however, degradation yields generally appear to decrease with increasing concentrations. Because in food products pesticide residues, when present, occur only in the low parts per million level, degradation yields of dilute pesticide solutions will be more relevant to food irradiation than those obtained with concentrated solutions. It is also worth noting that at very high concentrations direct action of the ionizing radiation on the solute may come into effect, while in dilute solutions the chemical modifications of the solute are caused by the various reactive species generated in the solvent. Such an effect can potentially modify the nature of the degradation products. In concentrated solutions, polymeric materials are also produced, while in dilute solutions such polymeric materials are not observed.

Because of the small amounts of data dealing with the fate of pesticide residues in irradiated food, one must use the results of radiation experiments performed in solution as a model. With very few exceptions, irradiation of aqueous pesticide solutions gave higher degradation yields than in organic solution. This is caused by the higher concentrations of solvated electrons in irradiated polar vs nonpolar solvents. The solvated electrons are responsible for the reductive dechlorination mechanism which is so important for organochlorinated pesticides. In water, the very reactive hydroxy radical is also formed upon irradiation and, in Shastri and Rao's (1980) study at least, was shown to contribute to the degradation of pesticide. Because food is composed mainly of water, aqueous solutions might be considered a valid model for pesticides in food. However, many pesticides are extremely hydrophobic and will be concentrated in the lipidic portion of food. Most organochlorinated pesticides belong to this class of lipophilic compounds, and hence, aliphatic solvents such as hexane might also be a good model of a lipidic matrix. Although the radiation chemistry of lipids is different from that of saturated aliphatic solvents, the results of Carp et al. (1972a,b) show great similarities in terms of the chromatographic profile of the degradation products of aldrin irradiated at a 1000 ppm concentration in hexane or in corn oil or lard. The only difference is the lower degradation yields obtained in these two latter solvents compared to hexane. It can be concluded, at least on a qualitative basis, that hexane is a suitable model solvent of triglycerides for the irradiation of chlorinated pesticides.

The dilute solution model for pesticide residues in irradiated food suffers from one major drawback. Food contains a large number of organic substances which will

compete with pesticides for the various reactive species generated in the matrix by the radiations. Thus, the degradation yields obtained for pesticides in pure solutions should be higher than those obtained in complex matrices such as food. The work of Cappadona et al. (1975) (Table I) illustrates this phenomenon. In their study, pure pesticides and complex commercial preparations containing the same pesticides were irradiated in solution. Technical lindane displayed a 7.4×10^{-6} (mol L⁻¹)/kGy degradation, while, in commercial mixture, for the same initial concentration of 10 ppm, degradation varied from 1.3×10^{-6} to 4.6×10^{-6} (mol L⁻¹)/kGy. Degradation of pure malathion solution was 9.1×10^{-6} (mol L⁻¹)/kGy, while for the commercial mixture it was only 5.1×10^{-6} (mol L⁻¹)/kGy. The only exception was for technical methyl parathion solution from which a 8.6×10^{-6} (mol L⁻¹)/kGy degradation was obtained, while, in commercial preparation, 1.2×10^{-5} (mol L⁻¹)/kGy was observed.

Because of the limited number of studies dealing with degradation of pesticides in food, it is difficult to evaluate the importance of the "protective" effect of the food matrix due to scavenging of the reactive species. Unfortunately, there are no data available on the degradation of Mirex in irradiated solutions to compare with the data of Lane et al. (1976) and those of Cin and Kroger (1982) obtained in food. In both studies Mirex degradation yields were 7.2×10^{-6} and 1.1×10^{-7} (mol kg⁻¹)/kGy at 45 and 50 kGy, respectively. The very high concentration of Mirex in the former study (233 ppm) is probably the cause of this higher degradation yield, and the second figure of 1.1×10^{-7} (mol kg⁻¹)/kGy obtained at a 8 ppm concentration is probably more representative of the degradation yield to be expected in "naturally" contaminated food products. In all of the studies where a comparison can be made, degradation of a pesticide irradiated in food was smaller than that in pure aqueous solution. In the publication by Solar et al. (1971), on a weight basis, a 1.3×10^{-7} (mol kg⁻¹)/kGy degradation of aldrin was observed in potatoes irradiated at 8.7 kGy, and a value of 1.0×10^{-6} (mol kg⁻¹)/kGy was obtained by Shastri and Rao (1980) in aqueous solution at 2.0 kGy. Solar and co-workers (Solar et al., 1971) obtained, again on a weight basis, a 1.9×10^{-7} (mol kg⁻¹)/kGy reduction of heptachlor epoxide at 8.7 kGy, while Shastri and Rao (1980) obtained a 1.1×10^{-6} (mol kg⁻¹)/kGy reduction in aqueous solution at 10 kGy. In Bachman's publication (Bachman and Gieszczyńska, 1982), a 2.6×10^{-8} (mol kg⁻¹)/kGy degradation of lindane residues in food was observed at 50 kGy, while Shastri and Rao (1980) obtained a 1.8×10^{-4} (mol kg⁻¹)/kGy degradation at 0.15 kGy in water and Cappadona et al., (1975) a 7.4×10^{-6} (mol kg⁻¹)/kGy degradation at 3 kGy (Table I). It should be pointed out, however, that at the radiation dose used in Bachman's work 99% of the initial amounts of lindane were degraded and that, in this nonlinear portion of the degradation curve, degradation yields are underestimated. The degradation yields of aldrin and lindane in food seem to be closer to the values obtained in hexane, which were 4.9×10^{-8} (mol L⁻¹)/kGy at 5 kGy and 1.5×10^{-8} (mol L⁻¹)/kGy at 25 kGy, respectively, as described by Ceurvels et al. (1974). This could indicate that for these hydrophobic pesticides an aliphatic solution mimics the fate of these pesticides in irradiated food better than aqueous solution. But this can also be explained by the scavenging of the reactive species by the other constituents of the food matrix.

Finally, the extent of the degradation of pesticide upon irradiation is proportional to the applied dose. The maximum radiation dose recommended by the Food and

Agriculture Organization of the United Nations (FAO) for food processing is 10 kGy. At this radiation dose in solutions, almost every author mentioned previously reported significant pesticide degradations, especially in aqueous solutions. For most food products, however, the radiation doses used industrially are smaller than 10 kGy and the effect on pesticide residues should decrease proportionally.

Degradation Products. The nature of the degradation products obtained upon γ irradiation of pesticide solutions will obviously depend on the nature of the pesticide and the solvent. For chlorinated pesticides, the main decomposition products identified were products in which one or more chlorine atoms were replaced by hydrogen. For compounds such as aldrin and Mirex the γ -radiation-induced degradation products were found to be generally identical to those produced by ultraviolet radiations. Solvent addition products were also detected. These compounds were hexyl adducts of aldrin (Vollner and Korte, 1974) and thioether (Buser, 1985) and cyclohexyl adducts of PCBs (Lépine et al., 1990). Formation of addition products between DDT and fatty acid derivatives was also observed by Kimbrough and Gaines (1971) and by Lépine et al. (1991). Formation of hydroxyl adducts of organochlorinated pesticides have been postulated by some authors, but these substances were not formally identified in the above-mentioned literature. Little information exists on the nature of the degradation products for other classes of pesticides but for the work of Grant et al. (1969), who formally identified oxidation products at the thioether linkage of phorate analogues and formation of oxo derivatives.

Toxicity of the Degradation Products. The small number of studies dealing with the toxicity of irradiated pesticides does not allow definite conclusions to be drawn on this subject. No long-term chronic toxicity studies have been reported for irradiated pesticides. The acute toxicities of PCBs irradiated in water and of DDT irradiated in triglycerides were either reduced or unaffected, as shown by LD₅₀ experiments performed with shrimps and rats, respectively. Toxicological data obtained from enzymatic assays of irradiated organophosphorus insecticides did show an increased toxicity at 1 kGy in some organic solvents. The toxicity to seedlings of some irradiated herbicides varied depending on the nature of the herbicide.

CONCLUSION

Considering the small number of studies dealing with the effects of γ irradiation on pesticides in food products, it is difficult to draw conclusions about the extent of pesticide degradation, the nature of the byproducts, and the overall toxicological effects of radiation on these compounds. Because pesticide levels normally occurring in food are low, it is further difficult to evaluate the toxicological effects of food irradiation with respect to pesticides.

However, within the maximum dose range recommended by the FAO, pesticide degradation was found to be significant in pure solution models and in some food products. There are still unexplained discrepancies in the results reported by some authors about the degradation yields of some pesticides even in the same solvent. More important, there have been few formal identifications of the byproducts of irradiated pesticides even in pure solutions. This leaves plenty of room for comparative studies on the destruction yields and degradation products of pesticides irradiated in solution and in food. These

data would be very useful to evaluate the toxicological implications of food irradiation with respect to pesticides.

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Received for review March 5, 1991. Revised manuscript received July 15, 1991. Accepted September 23, 1991.