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Effect of Gamma Irradiation on a PCB Mixture in Organic Solvent

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Gamma irradiation is a food preservation process that can alter the relative proportions of PCB congeners in a PCB mixture. Gamma irradiation induced dechlorination of PCBs in organic solvents was first studied by Sawai and co-workers (1972, 1974). Zabik and co-workers (1979) also investigated the effects of gamma irradiation on PCB residues in fish and observed a 40% reduction of the PCB levels at 1 Mrad, which is the maximum dose recommended by the FAO/IAEA/WHO for food processing. In both studies, the lack of chromatographic resolution of the packed columns used did not allow the investigation of the degradation of specific congeners in a complex PCB mixture.

The objectives of this study were two folds. First, to assess the effects of small doses of gamma irradiation on the PCB mixture profile in various organic solvents used as model systems for PCB residues in food irradiated with gamma rays. Second, to investigate the fate of some toxic congeners such as congener 77, 126 and 169 (according to Ballschmiter nomenclature (1980)) and some of their toxic mono-ortho substituted congeners.

MATERIALS AND METHODS

All the solvents used were glass distilled. PCB mixture and standards were purchased from Analab (Norwalk, CT). The irradiation experiments were performed in a Gammacell 220 using a Cobalt 60 source delivering 253.5 rad/min. The irradiations were performed using 0.5 mL of Aroclor 1260 solutions at a concentration of 4 ppm in a 1.5 mL vial closed with a screw cap. Five samples were irradiated simultaneously, and one sample was removed at 250 Krad intervals up to 1.25 Mrad. Decachlorobiphenyl was then added (2 ng) and used as a reference standard. The area of each PCB peak was measured with respect to that of the internal standard.

Gas chromatography was performed with a Varian 3500 interfaced to a DS 654 computer. A 30 m DB-5 capillary column (0.32 mm I.D.,

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0.25 µm film thickness) was connected to a Ni-63 electron-capture detector with nitrogen as make up gas. The initial flow of helium was 1.4 mL min^{-1} at 70°C. Injection was performed at 270°C in the splitless mode and the temperature program was as follows: the initial temperature (70°C) was successively increased to 150°C at 20°C min^{-1}, then to 235 at 2°C min^{-1} and finally to 320°C at 5°C min^{-1}.

Peak assignation of the PCB congeners was done using the data reported by Safe and co-workers (1984). The percentage of the various congeners in Aroclor 1260 mentioned below were taken from the publication of Albro et al. (1981). The area of the peaks listed in Table 1 are the mean of three injections and were calculated for each of the five irradiation doses and linear regression analysis was performed. The area under each peak varies linearly with the irradiation dose with a correlation coefficient $r > 0.97$ for most peaks.

RESULTS AND DISCUSSION

As shown in Figure 1, gamma irradiation of Aroclor 1260 modifies the PCBs profile in a manner similar to that previously reported (Sawai et al. 1972). Indeed, the proportion of the more chlorinated congeners decreases whereas that of the less chlorinated increases. Only congener 123, which was not originally present in the PCB mixture was detected upon irradiation at a dose as low as 250 Krad.

Table 1 summarizes the peak area variation of selected congeners after a 1.25 Mrad treatment in various organic solvents. These congeners were selected on the basis of their reactivity, toxicological interest and mostly on their chromatographic behavior, in order to avoid any coeluting congeners as described by Safe et al. (1984). The solvents used cover a large range of polarity from petroleum ether to a methanol/water mixture, in order to study the effects of the medium polarity on the dechlorination rate so as to mimic to a certain extent the heterogenous food matrices. Petroleum ether mimics the hydrophobic environment in which PCBs tend to concentrate whereas the methanol/water mixture mimics the hydrophilic moiety of food. The PCB concentration was set at 4 ppm in order to obtained a PCB level similar to that generally encountered in fish which is the main source of dietary PCBs for man. The average PCB concentration in fish ranges from 0.1 to 1 ppm taking into account that these hydrophobic residues are mostly concentrated in the fatty tissues which approximately account for 5 to 10% of the animal weight. Concentration of more than 40 ppm have been reported in lake trout captured in the Great Lakes (Zabik et al. 1979).

The extent of dechlorination for most congeners decreases with respect to the solvent used in the following order: tetrahydrofuran (THF) > isopropanol > dimethoxyethane (DME) > methanol ≥ methanol/water ≥ petroleum ether. These data are in agreement with the findings of Sawai et al. (1972). These authors reported

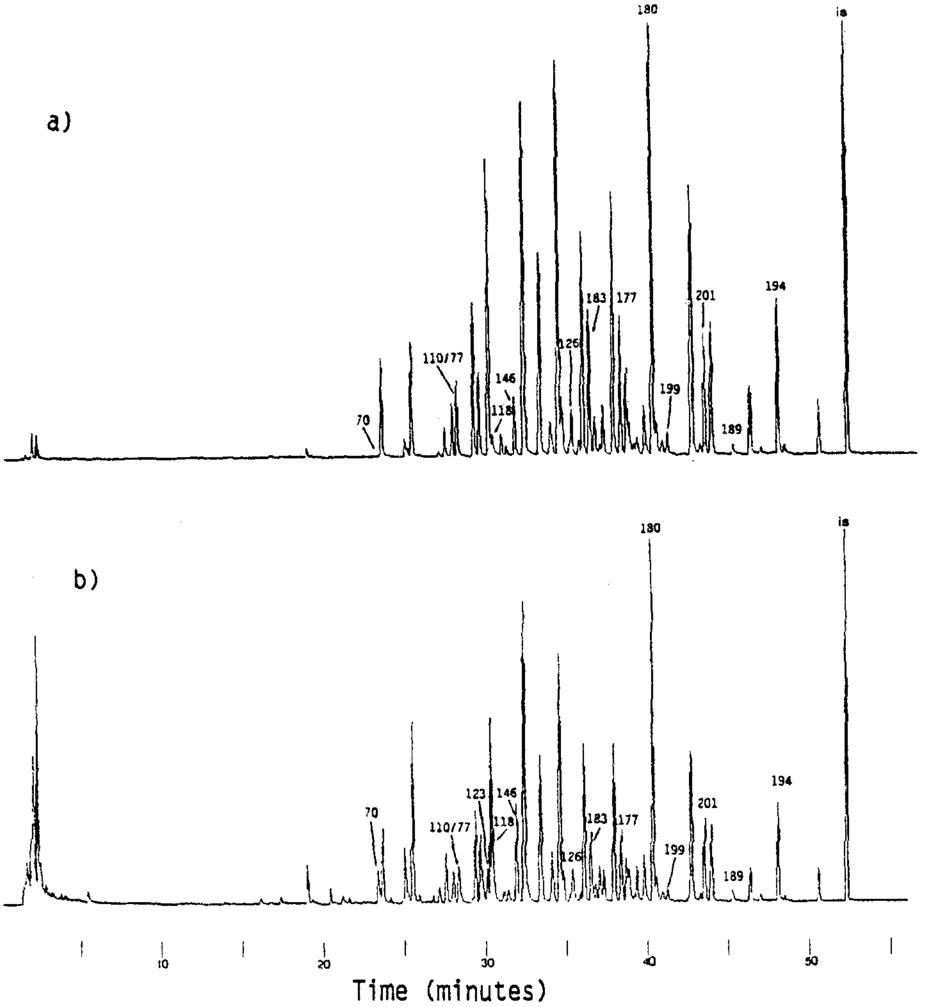

Figure 1. Gas chromatograms of Aroclor 1260 a) in petroleum ether b) after 1.25 Mrad. Peaks identified are those reported in Table 1.

a greater dechlorination rate in polar than in nonpolar solvents. This probably reflects the larger G values of solvated electrons in polar solvents, since dechlorination occurs through dissociative attachment of those electrons on PCBs. The resulting chlorinated biphenyl radical appears to react by abstracting a hydrogen from the solvent since no addition or dimerization products were detected by GC/MS analysis.

The mono-ortho substituted analogs of congeners 77, 126, and 169 which presents some toxicological concerns are 105, 118, 156, 167, 157, and 189 (Safe et al. 1985). Upon irradiation congener 118 showed a 5.4-, 19.1- and 8.4- fold increase in pet. ether, THF and DME, respectively. The large increase of congener 118 was expected because its potential precursors 153 and 138 account for 8.2

Table 1. Effect of 1.25 Mrad irradiation on Aroclor 1260 in organic solvent: percent variations of relative peak area of selected congeners[a]

ISOMER NUMBER	PET ETHER	THF	DME	ISOPROPANOL	METHANOL	METHANOL +20% H_2O
201	0.68	0.37	0.57	0.51	0.67	0.64
199	0.61	0.50	0.67	0.46	0.63	0.57
194	0.83	0.45	0.63	0.48	0.66	0.62
189	1.43	2.60	1.84	0.79	1.08	1.13
185	0.70	0.34	0.62	0.52	0.64	0.63
183	0.77	0.62	0.64	0.60	0.74	0.76
180	0.87	0.48	0.62	0.53	0.69	0.71
177	0.63	0.44	0.66	0.77	0.70	0.68
167	3.58	6.59	4.50	1.78	2.30	3.09
146	1.87	1.96	1.42	1.43	1.67	2.26
128	0.51	0.81	0.75	0.55	0.70	0.88
126	1.14	1.54	1.11	0.73	0.87	1.06
123[b]	4.2	3.14	2.65	1.03	2.92	3.83
118	6.42	20.1	9.44	1.73	2.26	2.7
110/77	0.95	1.46	1.00	0.74	0.86	1.01
70	16.0	31.9	18.7	9.03	8.40	2.72

[a] Compared to the relative peak area of congener in the unirradiated solution

[b] Relative to the peak area observed at 0.25 Mrad

and 5.0 %, respectively, of Aroclor 1260. Irradiation of the Aroclor solution fortified with these congeners in two separate experiments confirmed that they are both immediate precursors of 118. Interestingly, in both cases formation of congener 118 occurred through ortho dechlorination of its precursors. The levels of congener 167 also increased considerably in pet. ether, THF and DME (3.5-, 6.6- and 4.5- fold, respectively). Congener 167 is likely to arise from the degradation of the very abundant congener 180 (accounting for 7.2% of Aroclor 1260) through specific elimination of an ortho chlorine atom. This was confirmed in an experiment where the Aroclor mixture was fortified with congener 180. Finally, congener 189 levels also increased, but to a smaller extent (1.4-, 2.6- and 1.8- fold, respectively) when irradiated in the above mentioned solvents. This congener arises from ortho dechlorination of congener 194 as confirmed by fortification experiment. The three other mono-ortho substituted congeners of interest 105, 156 and 157 coelute with congeners present in large amounts in Aroclor 1260, and thus were not investigated in this study.

Variations in the relative peak areas of congeners 70, 118, 146, and 167 were much smaller in protic solvents than in DME, THF and pet. ether, contrary to what was observed for the other congeners. In addition, the formation of these congeners do not vary linearly with the irradiation dose and level off at around 750 Krad. For all other congeners the variations are linear with a correlation coefficient >0.97. These data can be rationalized on the basis that acetone and formaldehyde, the main radiolytic products of isopropanol and methanol, are electron scavengers (Anbar et al. 1967) that are likely to compete with the precursors of these congeners to inhibit their formation at higher irradiation doses. Mass spectrometric analyses failed to reveal any PCB solvent adducts.

Congener 169, one of the three very toxic ortho unsubstituted congeners (Tanabe 1987) is not generated upon irradiation. Isomer 126 did not vary significantly in petroleum ether but increased slightly in DME and THF and decreased slightly in MeOH and isopropanol. The variations in congener 77 levels could not be quantitated because it coeluted with congener 110. However, the corresponding peak area varied only slightly and in a way similar to that of congener 126. Since congener 77 is present in trace amount in Aroclor 1260 and since any increase of its relative amount could occur concomitantly with a decrease of congener 110, it was not possible to assess the extent of congener 77 increments in the irradiated PCB mixture. The relative amounts of congeners 105, 126 and 118, which are potential precursors of 77, represents 2.0 and 1.59 % of Aroclor 1260 for congeners 118 and 126, respectively, whereas congener 105 is not present in this mixture. Fortifying the Aroclor solution with 0.2 ppm of the pure 118 congener increased the area of the 110/77 congener's peak after irradiation. Because there is a considerable increase in the amount of congener 118 upon irradiation, it is likely to cause an increase in the amounts of 77 in the PCB mixture. The small variations of the area under the 110/77 peak in the initial experiment can likely result from the concomittant degradation of 110 and the small response of 77 to the ECD detector (Safe et al. 1984).

The generation of congener 123 is of prime interest since it is the sole congener not originally present in the PCB mixture prior to irradiation. It is probably generated through ortho dechlorination of congener 168 which accounts for 0.69% of the total PCBs in Aroclor 1260. It could also be produced from congener 167 through loss of a meta chlorine atom but it accounts only for 0.17% of the total PCBs in Aroclor 1260. Congener 70 is the one that exhibited the largest variations upon irradiation. Its peak area increased by 8- to 9- folds in hydroxylic solvents, and by 18- and 32- folds in DME and THF, respectively. Although congener 70 could coelute with congener 76, the latter cannot be generated by dechlorination upon irradiation of Aroclor 1260 since its precursors 86, 122, 123, 124 and 125 are not detected in Aroclor 1260. The potential precursors of 70 are: 118, 110, 101 and 87 which account for 2.0, 3.6, 5.0 and 1.1%, respectively, of the total PCBs. Of these four compounds, 110, 101 and 87 could yield 70 through the loss of an ortho chlorine atom, whereas its formation from congener 118 would require the loss of a meta chlorine. However, the latter degradation pathway appears to be minor since a very small increase of peak 70 was observed when the Aroclor mixture was fortified with congener 118 and irradiated as mentioned previously. Fortifying with congener 101 confirms that it is a precursor of congener 70.

The data summarized in Table 1 also indicate that the rate of dechlorination is not substantially affected by the total number of chlorine atoms on the biphenyl nucleus. The degradation rates of the octachlorinated congeners 194, 201 and 199 are similar to those of the heptachlorinated congeners 180, 177, 185 and 183.

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