Thermal Degradation of Chlorophenoxy Acid Herbicides

Maria José Gomez, Christian Bruneau, Noël Soyer,* and Auguste Brault

Vapor-phase pyrolysis and combustion of three chlorophenoxy acid herbicides were studied in the range 200–1000 °C in laboratory flow reactors. The identification and quantitative determination of most gaseous and condensed products by means of gas chromatography, liquid chromatography, and mass spectrometry made possible the suggestion of a general thermal degradation scheme. The risks arising from accidental burning or incineration of chlorophenoxy acids resulted from the presence of corrosive or explosive gases, carcinogenic polyaromatics, and caustic phenol derivatives.

The thermal behavior of widely distributed industrial organic compounds is the main purpose of our research (Bruneau et al., 1981, 1982; Lhomme et al., 1984). The indentification and quantitative determination of products resulting from thermal degradation provide useful information on the toxicological hazards that could arise from accidental burning during manufacturing, storage, and use or from incineration of residues. The thermal behavior of organic pesticides has already been investigated, especially for the disposal of waste pesticides by incineration (McPherson and Johnson, 1956; Kennedy et al., 1972; Holloman et al., 1976; Ahling and Wiberger, 1979). In previous papers, we gave the results of our work on the thermal degradation of diuron and iprodione (Gomez et al., 1982a), oxadiazon (Gomez et al., 1982b), and phosalone (Bruneau et al., 1986). The present investigation deals with the analysis of the products resulting from pyrolysis in an atmosphere of helium of three widely used chlorophenoxy acid herbicides [(2,4-dichlorophenoxy)acetic acid (2,4-D), (2,4-dichlorophenoxy)propionic acid (2,4-DP), (2-methyl-4-chlorophenoxy)acetic acid (MCPA)] in the range 200–1000 °C. The degradation of these compounds in the presence of air was also studied, essentially through the analysis of the carbon oxides and hydrochloric acid.

MATERIALS AND METHODS

Materials. The three herbicides studied (2,4-D, 2,4-DP, MCPA) were 99%+ pure.

Procedure for Pyrolysis. The pyrolyses were carried out in an inert atmosphere of helium in a flow reactor. The apparatus consisted of a ceramic tube containing baffles placed in a horizontal tubular furnace (inner diameter of the reactor, 2.7 cm; length of the hot zone, 33 cm). A stream of helium swept the tube at a flow rate of 4 L/h, which gave a residence time located in the range 30–90 s according to the experimental temperature. The solid samples of herbicides (0.5 g) were powdered (particle size, 0.04–0.08 mm) and propelled into the hot zone by means of a rubber bulb filled with helium. The effluent gas stream was directed into a gas sampling system, a cold trap cooled with ice, and bubblers containing 1 N sodium hydroxide.

The gaseous hydrocarbons, carbon oxides, hydrogen, and water were identified by their GC retention times on stainless-steel columns packed with Porapak Q (100–120 mesh, 1.5 m × 2.2 mm) or with 5-Å molecular sieves (40–60 mesh, 3 m × 2.2 mm). The chromatograph was a Girdel 3000 unit equipped with a thermal conductivity detector,

Laboratoire de Chimie Organique et de l'Environnement, Ecole Nationale Supérieure de Chimie de Rennes, 35700 Rennes-Beaulieu, France.

the temperature of the column was 60 °C, and the carrier gas was helium.

The acidic gases soluble in sodium hydroxide were collected in the bubblers, and the corresponding ions (carbonate and chloride) were titrated respectively by pH-metry with a glass electrode with 0.1 N HCl and by potentiometry with a silver electrode using 0.05 N $AgNO_3$.

The condensate in the cold trap was dissolved in diethyl ether, dried over calcium chloride, and concentrated, and the compounds were analyzed by GC-MS. A 25-m vitreous silica capillary column coated with Carbowax 20 M and a VG Micromass 7070 F mass spectrometer were used. The structures of the products were assigned by comparison of their mass spectra with data from the literature (Heller and Milne, 1978), and some of them were confirmed by comparison of their retention times with those of standards eluted under the same chromatographic conditions.

In each case, the main condensed product was the phenol corresponding to the initial pesticide. The quantitative determination of these phenols and the undegraded herbicides were effected by high-pressure liquid chromatography with a stainless steel column (i.d. 0.46 cm, length 25 cm) packed with Lichrosorb RP 18; the eluent consisted of a CH_3OH/H_2O mixture (60/40) + reagent B 7 Waters (heptanesulfonic acid); the UV detection was assumed at 254 nm. The chromatograph was a Varian 5000 unit and the detector an UV LDC Spectromonitor II followed by a Hewlett-Packard 3390 A integrator.

At high temperature an insoluble residue was collected, the elementary analysis of which was 90% carbon and 2% hydrogen. This residue was dried and weighed, but no further analysis was performed.

Procedure for Combustion. Our experiments were carried out in an apparatus consisting of a quartz tube (i.d. 6 cm, length 135 cm) passing through two tubular furnaces placed in series. The first was a preheating furnace where the herbicide was volatilized and homogeneously mixed with the gaseous phase. The oxidation reactions took place in the second oven containing carborundum baffles. The temperatures of the two furnaces were programmed separately.

Herbicide (0.1 g) was placed in a ceramic dish and pushed into the preheating zone, the temperature of which corresponded to the total volatilization of the sample (300 °C for 2,4-D and 2,4-DP; 350 °C for MCPA).

A stream of air swept the tube at a flow rate of 10 L/min, the corresponding residence time was within the range 2–5 s according to the temperature, and the amount of oxygen was 8.3×10^{-2} mol/min.

Carbon monoxide and carbon dioxide were detected and quantitatively determined at each temperature with Cosma Rubis 3000 CO and CO_2 analyzers. Hydrochloric acid was

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Table I. Moles of Gases Formed/Mole of Herbicide Submitted to Pyrolysis

temp, °C	compound	main gases, mol/mol					
		CO	CO_2	CH_4	C_2H_4	H_2	HCl
300	2,4-D	0.01	0.12				
300	2,4-DP	0.32	0.07				
300	MCPA	0.02	0.07				
400	2,4-D	0.23	0.31	tr	tr		0.08
400	2,4-DP	0.55	0.17	tr	tr		0.06
400	MCPA	0.07	0.22	tr	tr		tr
600	2,4-D	0.42	0.54	0.01	0.01	tr	0.54
600	2,4-DP	1.26	0.36	0.34	0.06	tr	0.36
600	MCPA	0.38	0.47	0.09	0.02	tr	0.16
700	2,4-D						
700	2,4-DP	1.32	0.41	0.37	0.12	0.17	0.69
700	MCPA	0.66	0.51	0.26	0.04	0.43	0.34
800	2,4-D	1.32	0.60	0.06	0.02	0.70	1.40
800	2,4-DP	1.47	0.35	0.36	0.12	0.58	1.00
800	MCPA	0.97	0.52	0.31	0.05	0.80	0.48
900	2,4-D	1.50	0.63	0.05	0.01	0.88	1.70
900	2,4-DP	1.63	0.34	0.32	0.13	0.82	1.16
900	MCPA	1.34	0.57	0.43	0.06	1.60	0.69
1000	2,4-D	1.40	0.58	0.03	0.01	1.00	1.86
1000	2,4-DP	1.60	0.34	0.25	0.10	1.26	1.33
1000	MCPA	1.72	0.50	0.36	0.05	1.98	0.76

trapped in bubblers containing 1 N sodium hydroxide and titrated with 0.05 N AgNO$_3$ by potentiometry with a silver electrode.

RESULTS AND DISCUSSION

Pyrolysis. In the inert atmosphere of helium 2,4-DP began to decompose below 200 °C, whereas the first degradation of 2,4-D and MCPA appeared in the range 250–300 °C. The determination of the first degradation temperature was possible by the analysis of the effluent gas phase and was probably more sensible than the analysis of the solid residue that contained almost quantitatively the initial pesticide (Stojanovic et al., 1972).

Gaseous Pyrolysis Products. The first gases resulting from pyrolysis of the three chlorophenoxy acids were carbon monoxide and carbon dioxide. When the temperature was increased to 350–400 °C, hydrochloric acid and light hydrocarbons (methane, ethane, ethylene) were formed. Above 600 °C, the production of hydrogen increased rapidly. The evolution of these main gases can be seen in Table I. To the gases noticed in this table must be added for 2,4-DP trace amounts of propene, which were detected between 600 and 900 °C, and for the three herbicides trace amounts of ethane above 400 °C (the detection limit of these light hydrocarbons being 0.01 mol/mol of herbicide submitted to pyrolysis).

Condensed Products. The yield of condensed products soluble in diethyl ether decreased with temperature (Table II). Above 600 °C, the formation of an insoluble residue containing 90% carbon was noticed for each pesticide, the amount of which increased regularly as the pyrolysis temperature was increased (the yield obtained at 1000 °C was about 0.10–0.15 g of carbon/g of herbicide). As already indicated, the amounts of undegraded feedstocks and the main phenols (2,4-dichlorophenol for 2,4-D and 2,4-DP; 2-methyl-4-chlorophenol for MCPA) were determined by liquid chromatography; the corresponding results are shown in Table II.

The amounts of herbicide recovered at the end of the pyrolysis apparatus decreased as the temperature was increased. On the other hand, the yields in the major phenols reached a maximum around 500 °C. Above this temperature they were also degraded into gases and condensed aromatics. Besides these phenols, which were the major products in the range 200–600 °C, other products were also formed. At 300 °C, the pyrolysis of 2,4-D and 2,4-DP led to 5,7-dichlorobenzofuran, which was one of the

Table II. Condensed Products Formed during Pyrolysis of the Chlorophenoxy Acids (Gram of Product/Gram of Herbicide Submitted to Pyrolysis)

temp, °C	compound	condensed products	undegraded herbicide	phenol formed	carbon in insol residue
300	2,4-D	0.74			
300	2,4-DP	0.76	0.34	0.40	
300	MCPA	0.86	0.36	0.09	
400	2,4-D	0.65	0.36	0.21	
400	2,4-DP	0.69	0.13	0.49	
400	MCPA	0.81	0.20	0.16	
600	2,4-D	0.52	0.08	0.40	0.01
600	2,4-DP	0.42	0.01	0.30	tr
600	MCPA	0.75	0.13	0.18	tr
800	2,4-D	0.41	0.01	0.04	0.08
800	2,4-DP	0.40	0.00	0.08	0.04
800	MCPA	0.45	0.13	0.06	0.04
1000	2,4-D	0.26	0.00	0.02	0.14
1000	2,4-DP	0.25	0.00	0.04	0.10
1000	MCPA	0.10	0.04	0.02	0.11

most important compounds. Above 500 °C, its degradation gave the monochlorinated benzofurans (essentially 5-chlorobenzofuran) and benzofuran. The homologue compounds were detected during the pyrolysis of MCPA. At the beginning of the degradation, the formation of benzaldehydes, benzylic alcohols, and acetophenone (2,4-DP) substituted by the corresponding Cl or CH$_3$ groups was noticed. The relative yields in these compounds depended on the initial herbicide and the temperature. The presence of organic acids (acetic, propionic, propenoic acids) was also displayed at low temperature (Figure 1).

When the temperature was increased above 600 °C, the degradation reactions also led to 4-chlorophenol, dibenzofurans, and aromatic compounds especially naphthalene and some chlorinated derivatives (Figure 2).
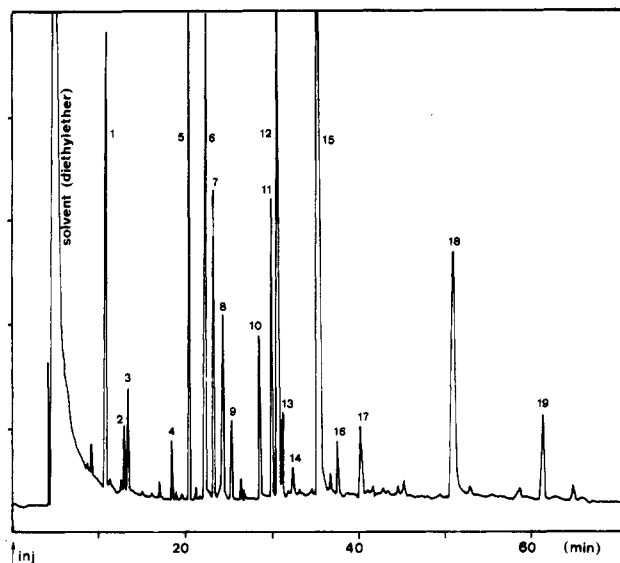
General Scheme for Pyrolysis. The first thermal degradation that occurred during the mild pyrolysis of the chlorophenoxy acids led essentially to the formation of the corresponding 2,4-disubstituted phenols. This type of splitting leading to phenols had already been described in the degradation of similar structures such as phenyl ethers (Bowman et al., 1957; Colussi et al., 1977; Daly et al., 1981). The mechanism generally admitted involves the homolytic splitting leading to the phenoxy radical. In our case, the influence of the substituant in the position 2 was a stabilization of this radical, probably more active with a Cl atom than with a CH$_3$ group.

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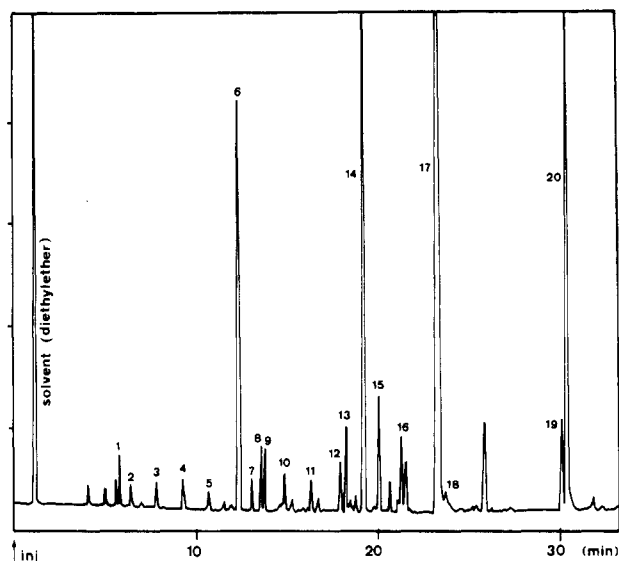
Figure 1. Pyrogram of 2,4-DP. Products collected in the cold trap at 600 °C. Conditions: capillary column, 25 m long, coated with Carbowax 20 M; temperature programmed from 110 to 200 °C at 4 °C/min; nitrogen carrier gas inlet pressure, 0.6 atm. Peaks: 1, propionic acid; 2, isobutyric acid; 3, propenoic acid; 4, dichlorostyrene; 5, naphthalene; 6, 5-chlorobenzofuran; 7, 7-chlorobenzofuran; 8, 2,4-dichlorobenzaldehyde; 9, dichlorophenetole; 10, methylchlorobenzofuran + dichloroanisole; 11, ethylchlorobenzofuran; 12, 2,4-dichloroacetophenone; 13, chloronaphthalene; 14, 5,7-dichlorobenzofuran; 15, ethyldichlorophenol; 16, chloronaphthol; 17, 2,4-dichlorophenol; 18, dichloronaphthalene; 19, 2-methyl-4-chlorophenol; 20, 4-chlorophenol. Compounds at peaks 1–4, 6, 7, 9–13, 15, 16, and 18 were identified by MS data. Compounds at peaks 5, 8, 14, 17, 19, and 20 were identified by MS data and retention times.

Figure 2. Pyrogram of 2,4-D. Products collected in the cold trap at 800 °C. Conditions: capillary column, 25 m long, coated with Carbowax 20 M; temperature programmed from 100 to 200 °C at 2 °C/min; nitrogen carrier gas inlet pressure, 0.6 atm. Peaks: 1, 1,3-dichlorobenzene; 2, benzofuran; 3, 2,4-dichlorotoluene; 4, dichlorostyrene; 5, naphthalene; 6, 5-chlorobenzofuran; 7, 7-chlorobenzofuran; 8, benzyl alcohol; 9, methylchlorobenzofuran; 10, phenol; 11, chloronaphthalene; 12, 5,7-dichlorobenzofuran; 13, dichlorobenzyl alcohol; 14, chloronaphthol; 15, 2,4-dichlorophenol; 16, dichloronaphthalene; 17, dibenzofuran; 18, 4-chlorophenol; 19, chlorodibenzofuran. Compounds at peaks 1–4, 6–9, 11, 13, 14, 16, and 19 were identified by MS data. Compounds at peaks 5, 10, 12, 15, 17, and 18 were identified by MS data and retention times.

The phenoxy radical may provide the phenol directly by abstraction of a hydrogen radical from another molecule or may react with other radicals present in the gas phase through its mesomeric forms and give alkyl-substituted phenols as proposed by Mulcahy and Williams (1963, 1965) or Daly et al. (1981). Such components (chlorocresols, ethyl or methylphenols) were not important in our experiments, but with 2,4-DP and MCPA where methyl radicals could be formed easily, some of them were detected. The formation of the phenoxy radical by homolytic scission also led to the radical RĊHCO$_2$H (R = H, CH$_3$). The evolution of this entity was the formation of acetic, propionic, or butyric acid by addition of a methyl or hydrogen radical and propenoic acid (R = CH$_3$) through the loss of a hydrogen radical. These organic acids submitted to higher temperatures essentially led to light hydrocarbons, carbon oxides, and water (Dele and Louw, 1972; Bigley and Weatherhead, 1978).

The direct decarboxylation of the initial chlorophenoxy acids was another way of degradation that gave carbon dioxide and the radical ArOĊHR (Ar = 2,4-dichlorophenyl, 2-methyl-4-chlorophenyl; R = H, CH$_3$). From this radical, the formation of a phenyl ether was possible and effectively detected in our experiments. The thermal behavior of anisole has been described in previous papers by Freidlin et al. (1949a,b), Schlosberg et al. (1983), and Vuori et al. (1985); the products found were phenol, benzaldehyde, benzyl alcohol, benzene, toluene, cresols, and unidentified higher products. The authors generally considered that phenol was formed through the homolytic breaking of the methyl C–O bond and addition of hydrogen to the phenoxy radical. The formation of benzyl alcohol and benzaldehyde was the result of the rearrangement of a phenoxymethyl radical to a benzyloxy radical via a spiranic oxiran

(Schlosberg et al., 1983). In our experiments, chlorinated and methylated benzaldehydes and benzyl alcohols substituted in the ortho position were also detected. We also investigated the degradation of 2-chloroanisole and 2-methylanisole under our conditions (in the range 500–600 °C) and exhibited clearly the formation of 2-chlorobenzaldehyde and 2-methylbenzaldehyde besides the major ortho-substituted phenols. These compounds probably resulted from an initial scission of a methyl C–H bond leading to the radical Ar–OCH$_2$· which rearranged via a spiranic oxiran as proposed by Schlosberg et al. (1983). Another rearrangement with a vicinal aromatic carbon atom would have led to the meta-substituted benzaldehydes. The intermediate radical ArOĊHR may also undergo a cyclization reaction to a benzofuran, by direct means or through the formation of 2-ethylphenol (Daly et al., 1981; Givens and Venuto, 1969).

The dechlorination began around 400 °C and became more effective when the temperature was increased. The main product formed was hydrochloric acid, but the condensates also contained chlorinated compounds (Figures 1 and 2). When the temperature was increased, the amounts of condensate collected in the cold trap decreased and some very stable compounds such as phenol, dibenzofuran, and polyaromatic hydrocarbons (naphthalene, biphenyl) were formed, resulting from the thermal degradation of the chlorinated phenols, benzofurans, and benzaldehydes generated at lower temperature (Braekman-Danheux and Heyvaert, 1972; Gräber and Hüttinger, 1980; Schaden, 1980).

All these remarks made possible the suggestion of the following scheme for the degradation of the chlorophenoxy acids (Figure 3).

Combustion. We were especially interested in the formation of carbon oxides and hydrochloric acid during
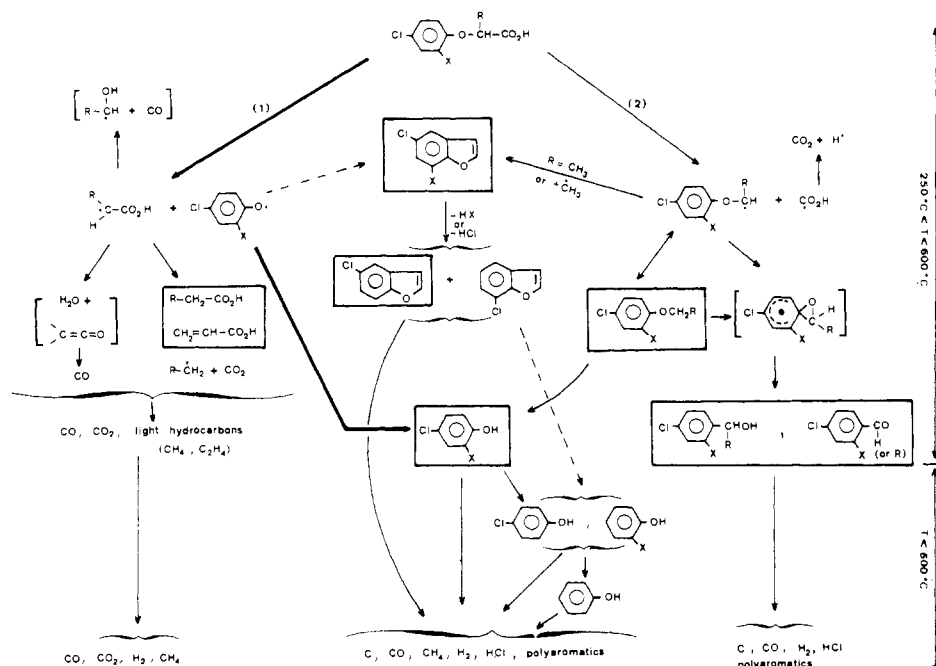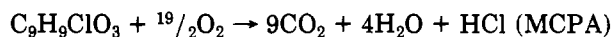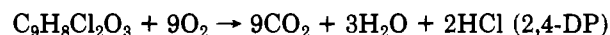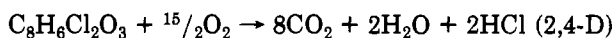
Figure 3. General pyrolysis scheme of chlorophenoxy acids.

Table III. Moles of HCl Formed/Mole of Herbicide Submitted to Thermal Degradation in the Presence of Air

temp, °C	HCl emitted, mol/mol		
	2,4-D	2,4-DP	MCPA
300	tr	tr	tr
350	0.34	0.26	0.10
400	0.73	0.71	0.25
450	0.75	0.90	0.45
500	0.98	0.90	0.53
550	1.12	1.18	0.55
600	1.16	1.12	0.60
675	1.47	1.34	0.65
750	1.55	1.61	0.75
850	1.84	1.77	0.90
1000	1.79	1.82	0.91

the thermal degradation of the herbicides in the presence of a large excess of air. The stoichiometric quantities of oxygen according to the reactions

$$C_8H_6Cl_2O_3 + {}^{15}/_2O_2 \rightarrow 8CO_2 + 2H_2O + 2HCl \text{ (2,4-D)}$$

$$C_9H_8Cl_2O_3 + 9O_2 \rightarrow 9CO_2 + 3H_2O + 2HCl \text{ (2,4-DP)}$$

$$C_9H_9ClO_3 + {}^{19}/_2O_2 \rightarrow 9CO_2 + 4H_2O + HCl \text{ (MCPA)}$$

were respectively 3.4×10^{-3}, 3.9×10^{-3}, and 4.7×10^{-3} mol/0.1 g of herbicide.

In our experiments, the gas emission during the thermal degradation lasted about 5 min; during that time the amount of available oxygen was about 415×10^{-3} mol (approximately the stoichiometric amount × 100). The constant level of CO_2 and the zero concentration of CO obtained at high temperature indicated the complete oxidation of the chlorophenoxy acids. The concentrations of CO and CO_2 at each temperature have been compared to the maximum CO_2 level; the results are given in Figure 4. The formation of CO appeared between 300 and 400 °C and increased regularly with temperature up to 700 °C, and then carbon monoxide was oxidated into CO_2 and disappeared around 900 °C. Carbon dioxide was formed at low temperature, as soon as the degradation began, which was in agreement with the general thermal behavior of organic acids (Chevalier and Dupoux, 1976). This was probably due to decarboxylation reactions rather than oxidation reactions.
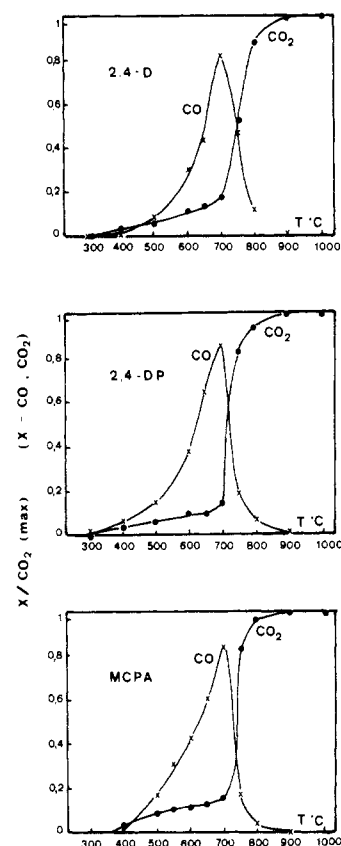

Figure 4. $CO/CO_2(max)$ and $CO_2/CO_2(max)$ as a function of temperature for each herbicide.

In comparison with the thermal degradation in helium, the presence of air induced the formation of HCl at lower temperature. The yields in hydrochloric acid as a function of temperature are shown in Table III. At 1000 °C, the recovery of Cl atoms as HCl was about 90%, and traces amounts of Cl_2 were detected in the gaseous effluent in the range 650–1000 °C as observed by Kennedy et al. (1972).

CONCLUSION

The three chlorophenoxy acids that we studied began to decompose in the range 200–250 °C. The main splitting

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involved the ether bond O–aliphatic C that led to a phenoxy radical stabilized by the substituted aromatic cycle. The disubstituted phenol corresponding to the initial molecule was formed through this intermediate and was the major product of the pyrolysis.

Decarboxylation was a secondary way of degradation that led to substituted anisoles, benzofurans, and benzaldehydes.

At higher temperature, all those compounds were decomposed, leading to gaseous products (CO, HCl, H_2, ...) and condensed aromatics.

The complete thermal degradation of the chlorophenoxy acids was possible in the presence of air beyond 900 °C. The formation of hydrochloric acid and chlorine as corrosive substances must be noted.

The main undesirable gases formed were carbon monoxide, hydrochloric acid, and Cl_2. In case of incomplete degradation (lack of oxygen or too low temperature), the injurious aspect of the condensed aromatics must be pointed out.

Registry No. 2,4-D, 94-75-7; 2,4-DP, 120-36-5; MCPA, 94-74-6; CO, 630-08-0; CO_2, 124-38-9; CH_4, 74-82-8; CH_3CH_3, 74-84-0; H_2, 1333-74-0; HCl, 7647-01-0; propionic acid, 79-09-4; isobutyric acid, 79-31-2; propenoic acid, 79-10-7; dichlorostyrene, 50852-77-2; naphthalene, 91-20-3; 5-chlorobenzofuran, 23145-05-3; 7-chlorobenzofuran, 24410-55-7; 2,4-dichlorobenzaldehyde, 874-42-0; dichlorophenetate, 62973-52-8; methylchlorobenzofuran, 104593-59-1; dichloroanisole, 54518-15-9; ethylchlorobenzofuran, 113220-56-7; 2,4-dichloroacetophenone, 2234-16-4; chloronaphthalene, 25586-43-0; 5,7-dichlorobenzofuran, 23145-06-4; ethyldichlorophenol, 113220-57-8; chloronaphthol, 34390-12-0; 2,4-dichlorophenol, 120-83-2; dichloronaphthalene, 28699-88-9; 2-methyl-4-chlorophenol, 1570-64-5; 4-chlorophenol, 106-48-9; 1,3-dichlorobenzene, 541-73-1; benzofuran, 271-89-6; 2,4-dichlorotoluene, 95-73-8; benzyl alcohol, 100-51-6; phenol, 108-95-2; dichlorobenzyl alcohol, 12041-76-8; dibenzofuran, 132-64-9; chlorodibenzofuran, 42934-53-2.

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