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HIGH-TEMPERATURE DEGRADATION CHARACTERISTICS OF HAZARDOUS ORGANIC WASTES - A LABORATORY APPROACH

by

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ABSTRACT

The safe disposal of highly toxic organic wastes is vitally important, and controlled high-temperature incineration is one of the most promising methods for permanent disposal of such materials. However, there is a serious lack of basic experimental data concerning the thermal decomposition behavior of these organic materials. This research program was initiated with the overall objective being to determine the thermal destruction characteristics in the laboratory for a wide assortment of hazardous organic waste materials.

A sophisticated laboratory system has been designed and assembled with the objective being to provide fundamental thermal decomposition data on a wide variety of organic materials. This thermal decomposition analytical system (TDAS) is a closed system consisting of a versatile, highly instrumented thermal decomposition unit which is connected to a gas chromatograph-mass spectrometer-computer. With the TDAS, gases, liquids, and solids (including polymers) can be subjected to thermal decomposition studies.

In the TDAS, precisely controlled thermal decompositions are conducted in a narrow-bore quartz tube reactor. The various ensuing thermal decomposition products are subsequently collected using a cryogenic adsorptive trap. After thermal desorption, the products are subjected to high-resolution gas chromatographic analysis and identification of the various decomposition products is accomplished using in-line coupled mass spectrometry. A dedicated minicomputer is used for reducing the analytical data. From the product analyses obtained through a sequence of thermal exposures, the thermal decomposition properties for a given organic sample can be readily obtained.

Thermal decomposition tests conducted with the TDAS include work done with polychlorinated biphenyls (PCBs), "Hex" wastes, polybrominated biphenyls (PBBs), and Kepone. The PCBs were found

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to have high thermal stability in air. Furthermore, in oxygen-starved atmospheres their thermal stability is increased by at least 200°C over that experienced in air. "Hex" wastes also demonstrated a high degree of thermal stability. Several chlorinated, aromatic compounds were still present after exposure to 800°C. Further increases in temperature to 1000°C decomposed all compounds except for low levels of hexachlorobenzene.

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SECTION 6
THERMAL DECOMPOSITION INVESTIGATIONS

6.1 POLYCHLORINATED BIPHENYLS (PCBs)

6.1.1 Summary of Findings

A selected group of PCB isomers were subjected to a series of experiments using the thermal decomposition analytical system (TDAS). It was anticipated that PCBs would be very thermally stable, and this was found to be the case. Specific observations made during the course of this work are as follows:

(1) PCBs volatilized in an atmosphere of air (~21% O_2), and exposed to high-temperature destruction in a laminar flow regime, and a residence time of 2 sec were more than 99.95% destroyed at 800°C.

(2) However, bear in mind that this was true when the PCBs were gas phase molecules in a controlled air environment (Oxygen level was ~21% throughout the test). At oxygen - starved conditions, temperatures required to decompose the PCB were about 200°C. higher.

(3) At intermediate temperatures in air and in nitrogen, where only partial decomposition took place, significant quantities of toxic chlorinated compounds were formed.

6.1.2 Background

The introduction of PCBs to the world market came in 1929. Because of their unique chemical properties, particularly their good thermal and chemical stability, industrial usage of PCBs grew rapidly through the years. However, it was not until about 1966 that PCBs were recognized as widespread environmental contaminants. Now the extremely serious problem of global environmental contamination by PCBs has been well documented. Comprehensive reviews have reported the existence of significant quantities of PCBs in atmosphere, soil, water, sediment, fish, wildlife, and even in samples of human blood and tissue.[20]

PCBs are persistent toxic pollutants. Once they enter the environment, they degrade extremely slowly. PCBs are

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only sparingly soluble in water, but they readily accumulate in fatty tissues, and can cause reproductive failures in fish-eating birds.[21] In April 1979, the EPA issued final rules[22] prohibiting the manufacture of PCBs.

6.1.3 Experiments with PCBs

A selected group of PCB isomers were subjected to a series of thermal decomposition experiments using the thermal decomposition analytical system. Experiments were conducted with 2,2',5,5'-tetrachlorobiphenyl; 2,2',4,5,5'-pentachlorobiphenyl; and 2,2',4,4',5,5'-hexachlorobiphenyl. These isomers were obtained from the RFR Corporation, Hope, Rhode Island, and were used without further purification.

Thermal decomposition profiles were obtained for these isomers in a flowing air environment with a 2.0 sec residence time at the exposure temperature. These data are listed in Table 1, and depicted in a logarithmic plot in Figure 2.

TABLE 1

EFFECT OF TEMPERATURE ON DECOMPOSITION

Compound	Exposure Temperature (°C)						
	550	650	675	700	725	750	775
Tetrachlorobiphenyl (2,2',5,5')	100*	92	74	57	21	0.14	---
Pentachlorobiphenyl (2,2',4,5,5')	100	98	80	53	9.3	0.05	0.007
Hexachlorobiphenyl (2,2',4,4',5,5')	100	100	73	26	---	----	<0.005

*Values are wt.% remaining after exposure

There was very little difference in thermal stability noted between the tetrachlorobiphenyl and the pentachlorobiphenyl. However, the hexachlorobiphenyl did exhibit a sharp break in stability at a temperature 25-50°C. lower than the other two.

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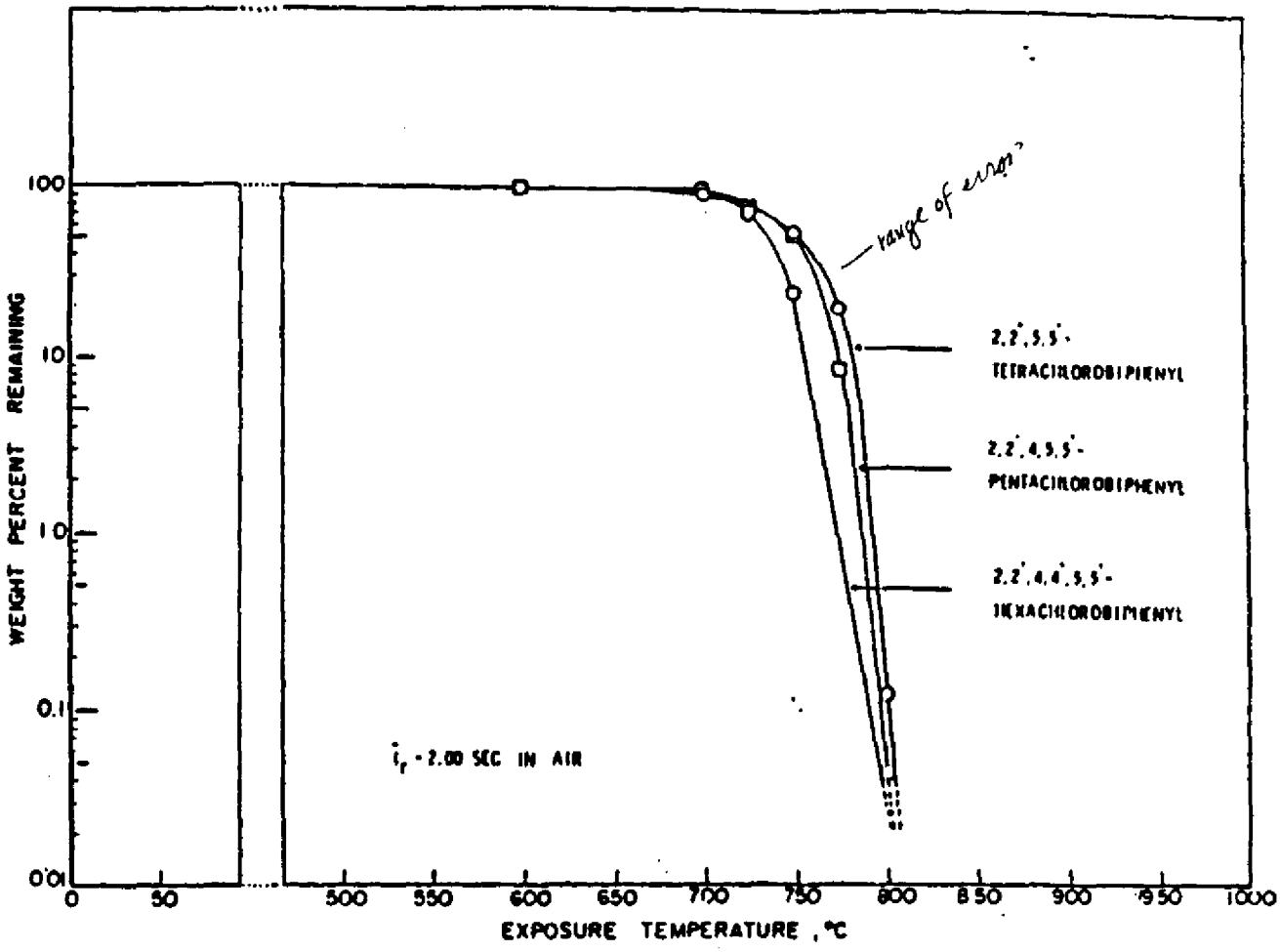

Figure 2. Thermal Decomposition Profile of PCB Isomers

6.1.4 Decomposition Products

The major decomposition products formed from the thermal stressing of 2,2',5,5'-tetrachlorobiphenyl, 2,2',4,5,5'-pentachlorobiphenyl, and 2,2',4,4',5,5'-hexachlorobiphenyl at 725°C in flowing air for 2 seconds residence time are itemized in Table 2. The general fragmentation pattern of PCB isomers features successive expulsion of both clorine atoms and molecules.[23] Due to the known variability of ion intensities produced with different mass spectrometers, no attempt was made to distinguish between various isomers by their primary ion mass spectra. Thus, the names used to identify the products indicate the total number of chlorine atoms present rather than their positional notation. The various PCB species were readily identified on the basis of intense molecular ions (M^+), intense $(M-70)^+$ ions, and unusually abundant doubly-charged molecular ions.

A major concern of this work was to confirm the formation of chlorinated dibenzofurans (PCDFs) from the thermal oxidation of PCBs. As is seen in Table 2 several PCDFs were generated. These include dichlorodibenzofuran and trichlorodibenzofuran from the tetra-PCB isomer, trichlorodibenzofuran and two isomers of the tetrachlorodibenzofuran from the penta-PCB isomer, and pentachlorodibenzofuran from the hexa-PCB isomer. These results agree with those obtained by other workers[24,25] except in the case of the hexa-PCB isomer. Other workers have shown the formation of a tetrachlorodibenzofuran and two isomers of the pentachlorodibenzofuran from the hexa-PCB isomer. The chlorinated dibenzofurans were identified on the basis of calculated chlorine isotope ratios,[26] intense molecular ions (M^+), molecular ions minus the loss of the COCl group $(M-63)^+$, and minor characteristic fragment losses.

All of the PCB samples were directly analyzed by repetitive scanning of complete mass spectra (mass range 30-492 amu) utilizing a computer data system. After data acquisition the mass spectra (up to 800/run) were searched for PCBs, PCDFs, and other possible reaction products by examining individual mass spectra and by plotting single ion chromatograms of known fragment ions. It can be noted that under the test conditions employed, no dioxin

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TABLE 2

COMPOUNDS FORMED FROM DECOMPOSITION OF PCB ISOMERS

Compounds*	Isomers 2,2',5,5'	2,2',4,5,5'	2,2',4,4',5,5'
trichlorobenzene	+	+	-
biphenyl	+	-	-
tetrachlorobenzene	+	2 isomers	+
monochlorobiphenyl	+	+	-
chlorinated compound MW204+	+	-	-
dichlorobiphenyl	+	+	-
pentachlorobenzene	-	+	+
chlorinated compound MW230+	2 isomers	-	-
trichlorobiphenyl	2 isomers	+	+
dichlorodibenzofuran	+	-	-
tetrachlorobiphenyl	2 isomers	+	-
pentachlorobiphenyl	2 isomers	+	-
trichlorodibenzofuran	+(3)	+(1)	-
hexachlorobenzene	-	+	+
chlorinated compound MW264+	-	3 isomers	-
tetrachlorodibenzofuran	-	2 isomers(1)	-(2)
hexachlorobiphenyl	-	+	+
heptachlorobiphenyl	-	-	+
pentachlorodibenzofuran	-	-	+(2)
chlorinated compound MW288+	-	-	+

\+ = tentative identification

\- = not found

*Flowing air, 725°C, and residence time of 2 sec.

(1) Predict formation of 1,4,6,7-TCDF, 1,2,4,6-TCDF and 2,3,7-T_3CDF

(2) Predict formation of 2,3,7,8-TCDF, and 1,2,4,7,8-P_5CDF

(3) Predict formation of 1,4,6-T_3CDF.

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structures were observed. Individual mass spectra were compared with reference library spectra if available. Otherwise, manual interpretation of the spectra was performed.

Examples of the data compiled in Table 2 are plotted in Figures 3 and 4. The formation profile of the trichlorodibenzofuran from the decomposition of 2,2',5,5'-tetrachlorobiphenyl is shown in Figure 3, and the quantities produced are significant - exceeding 0.1 wt. % through a 50-75°C range before the PCB itself is destroyed. Again, the toxic products of intermediate temperature decomposition are demonstrated.

In Figure 4, are plotted the chlorinated aromatics which were formed from the decomposition of 2,2',4,4'5,5'-hexachlorobiphenyl. These were formed in large quantities approaching 1% by weight. The formation of these chlorinated aromatics is alarming, not only from the toxicity standpoint, but from the fact that their thermal stability is such that they remain intact, even efter the parent PCB has been destroyed.

Figure 5 illustrates the type of products found when 2,2'4,5,5'-pentachlorobiphenyl is decomposed in nitrogen. A major share of decomposition products are formed by dechlorination to the tetra-isomers. Also, a chlorinated aromatic is shown in significant quantities. Note that the temperatures required for decomposition are much higher than in air. This is discussed more fully in subsection 6.1.5.

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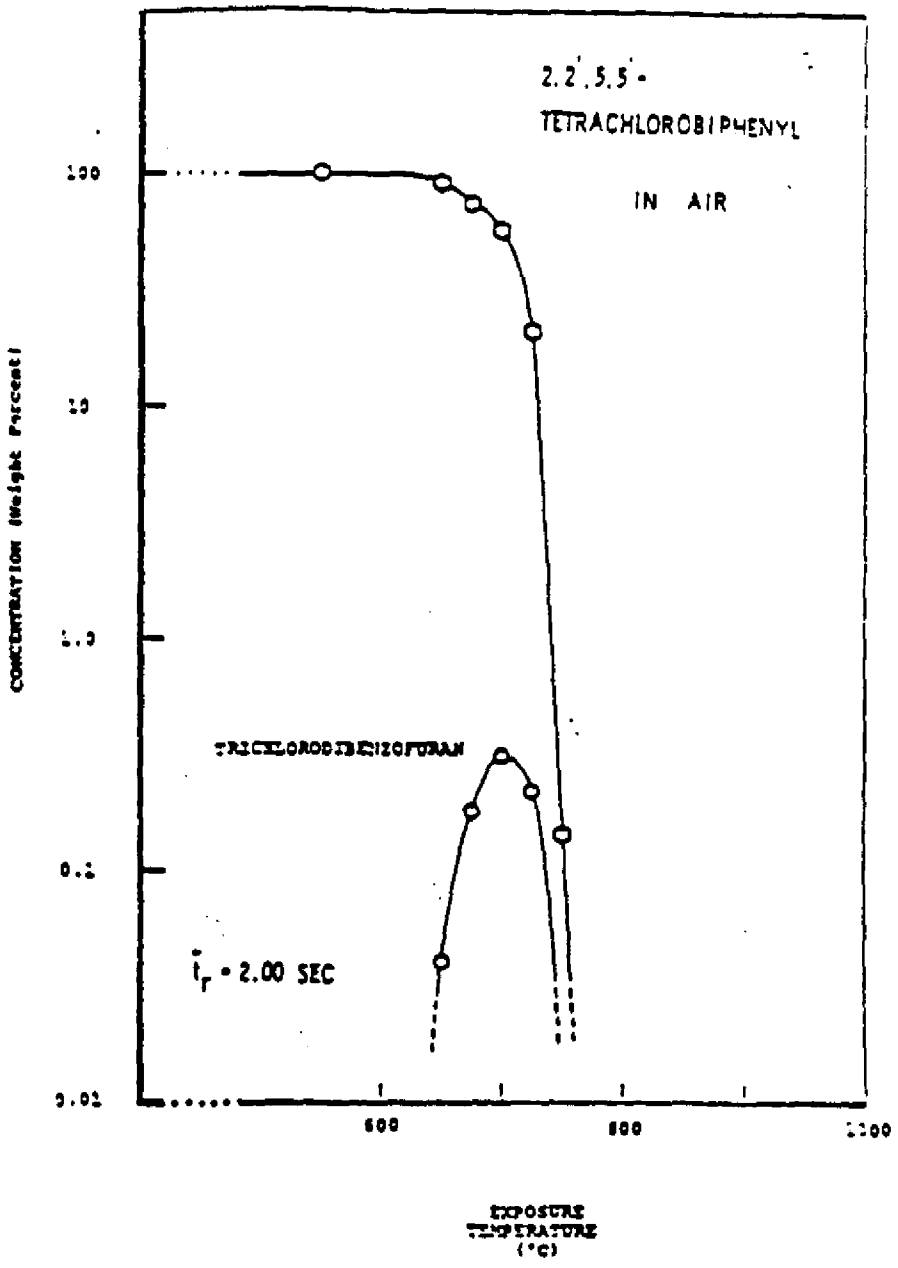
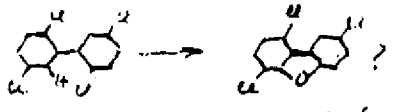


Figure 3. Decomposition Products of Tetrachlorobiphenyl



1,4,6-trichlorofuran 19

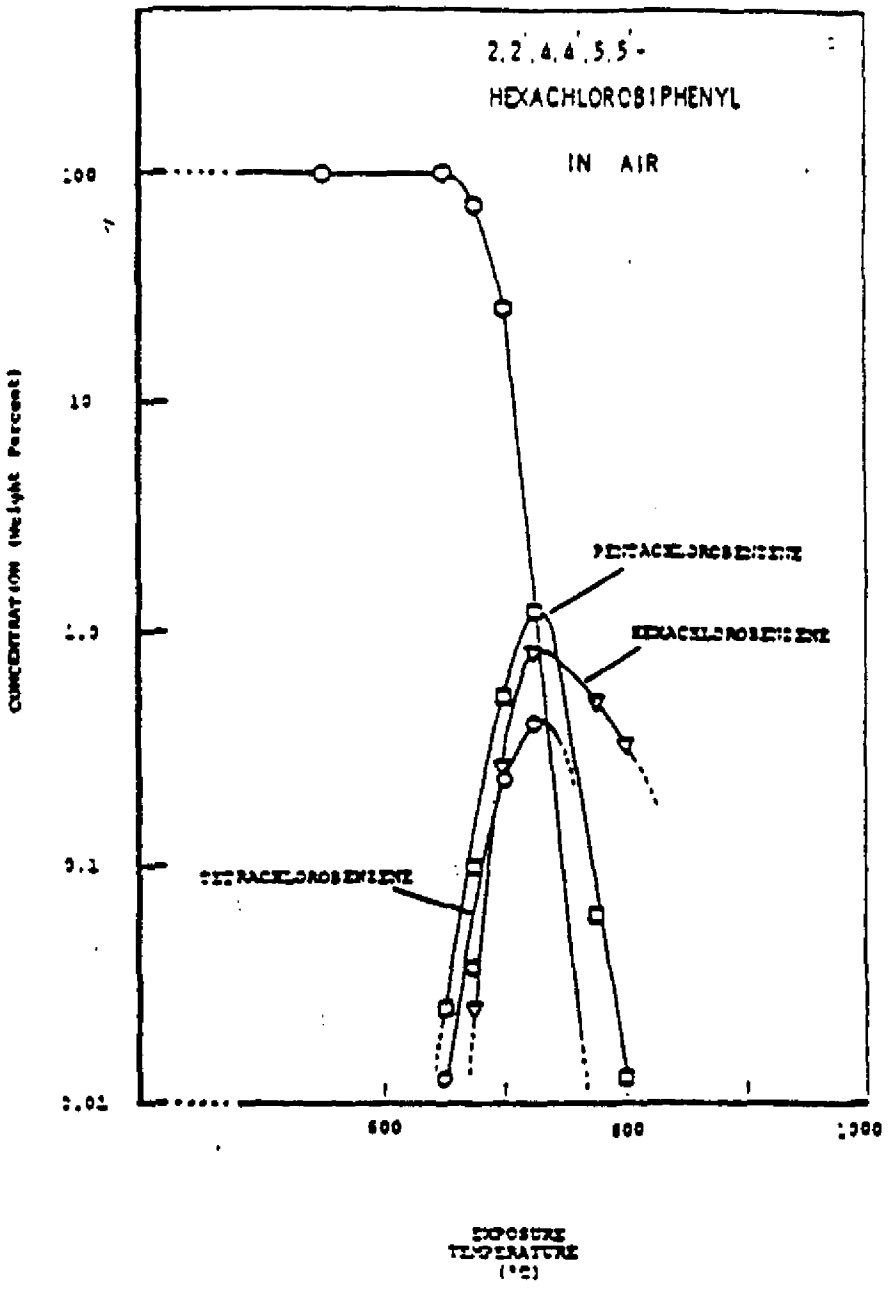


Figure 4. Decomposition Products of Hexachlorobiphenyl

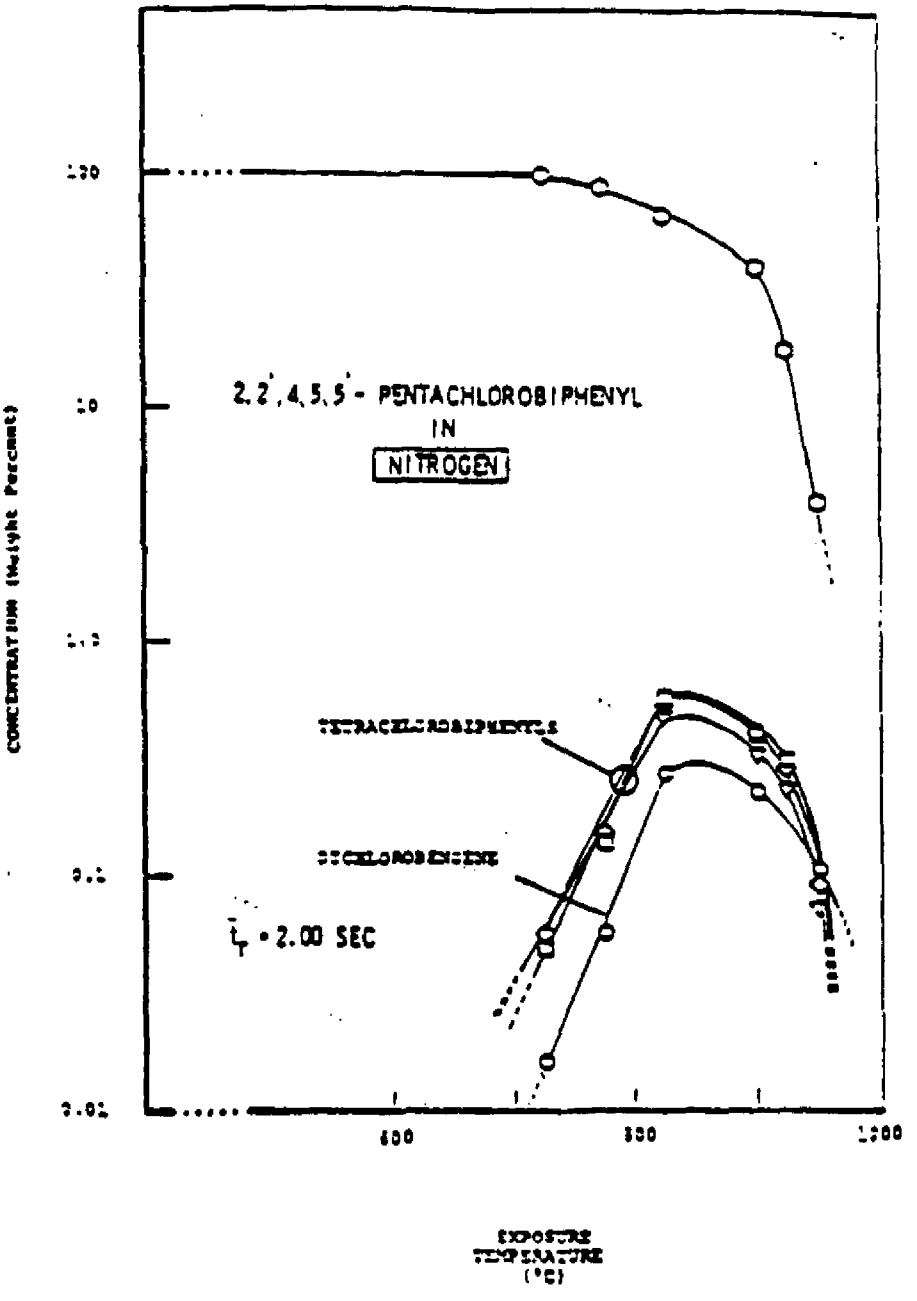


Figure 5. Decomposition Products of Pentachlorobiphenyl

6.1.5 Effect of Atmospheres

Some of the most interesting work with the PCBs involved results obtained when the flowing gaseous atmospheres were varied. These particular experiments were conducted with the 2,2',4,5,5'-pentachlorobiphenyl and are shown graphically in Figure 6, and tabulated in Table 3. Selection of this isomer was made because it is commonly found in most of the commercial PCB mixtures and is still a prevalent contaminant in the environment. Thermal decomposition profile experiments were conducted using a variety of gaseous atmospheres: (1) 40 percent oxygen in nitrogen; (2) compressed air; (3) 2.5 percent oxygen in nitrogen; and (4) nitrogen. Two tests were also conducted in helium, and these are also reported as they presented some interesting results. All tests were made at a residence time of 2 seconds.

These experiments showed the profound effect that the oxygen level has on the thermal decomposition of PCBs. Differences noted between air (~21% O_2) and 40% O_2 were quite small; however, when proceeding in the direction of oxygen starvation, or pyrolytic decomposition, temperatures required for decomposition exceeded those in air by more than 200°C.

If the oxygen levels are plotted in a different manner, one can view their effect on thermal stability as illustrated in Figure 7. In this figure, exposure temperature is plotted versus the oxygen content of the reactor atmosphere. The plotted 100 ppm oxygen value is an approximate level of trace oxygen in nitrogen gas. (This value agrees with our previous experience with bottled nitrogen carrier gases.) When this 100 ppm data point is plotted along with the other oxygen concentrations, it can easily be seen that the semi-logarithmic graphing is linear. It is evident from these experimental data that this PCB isomer is very thermally stable in oxygen-deficient atmospheres. Further, the oxygen content of the flowing gas seems to dictate on an orderly basis the extent of thermal decomposition at temperatures above 600°C.

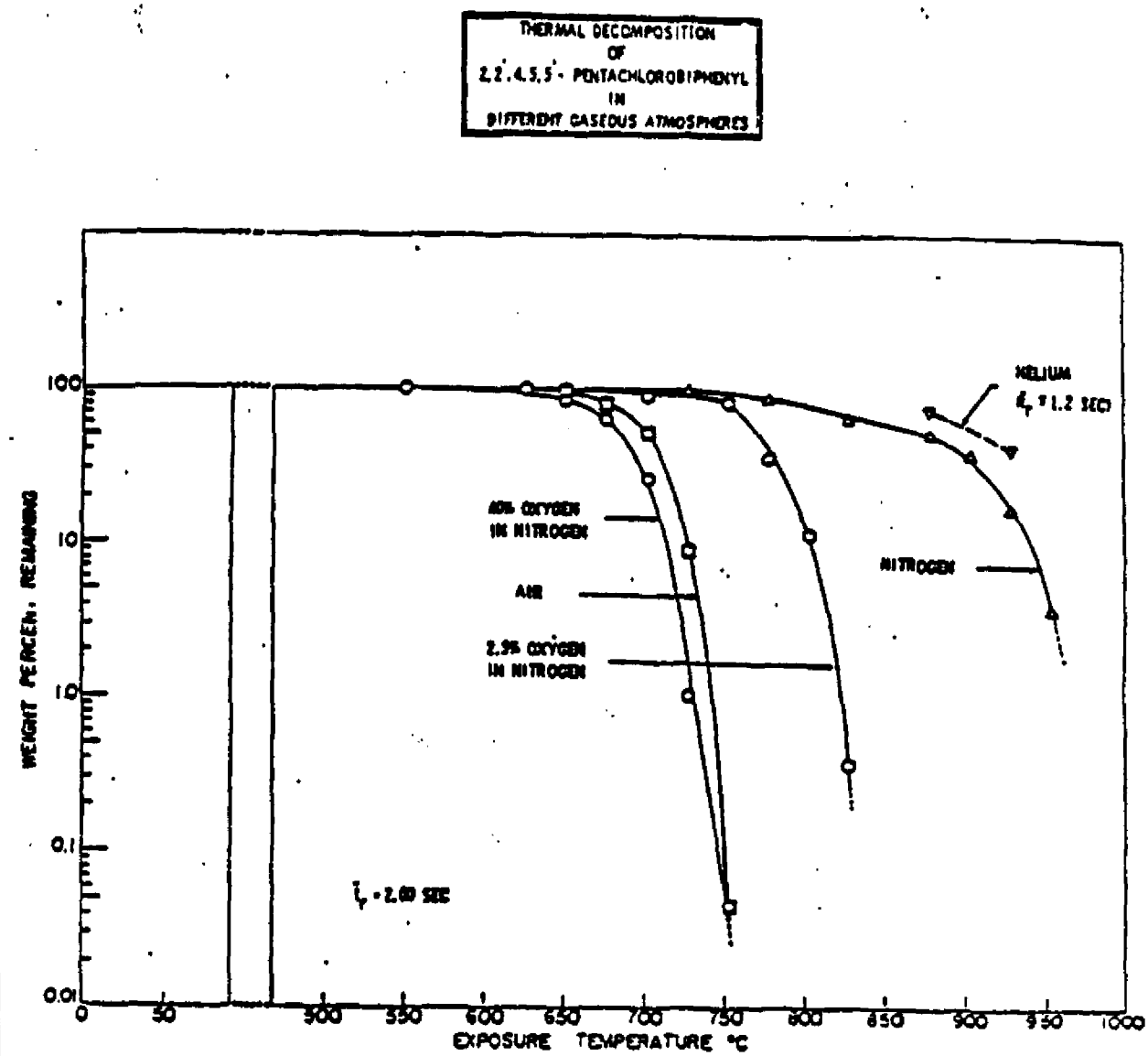


Figure 6. Effect of Atmospheres with Pentachlorobiphenyl.

TABLE 3

EFFECT OF ATMOSPHERE ON THERMAL
DECOMPOSITION OF 2,2'4,5,5'-PENTACHLOROBIPHENYL

..owing Atmosphere	Exposure Temperature* (°C)														
	550	600	650	675	700	725	750	775	800	825	850	875	900	925	95C
40% Oxygen in Nitrogen	100+	---	85	65	27	1.1	0.05	---	---	---	---	---	---	---	---
Air (~ 21% O_2)	---	---	98	80	53	9.3	0.05	0.007	---	---	---	---	---	---	---
2.5% Oxygen in Nitrogen	---	100	97	---	91	---	83	37	12	0.40	---	---	---	---	---
Nitrogen	---	---	---	---	---	100	---	89	---	66	---	54	40	18	4.0
Helium	---	---	---	---	---	---	---	---	---	---	---	76	---	44	---

* - All determinations at 2 sec residence time (except helium which was 1.2 sec)

+ - Values are weight % remaining after exposure

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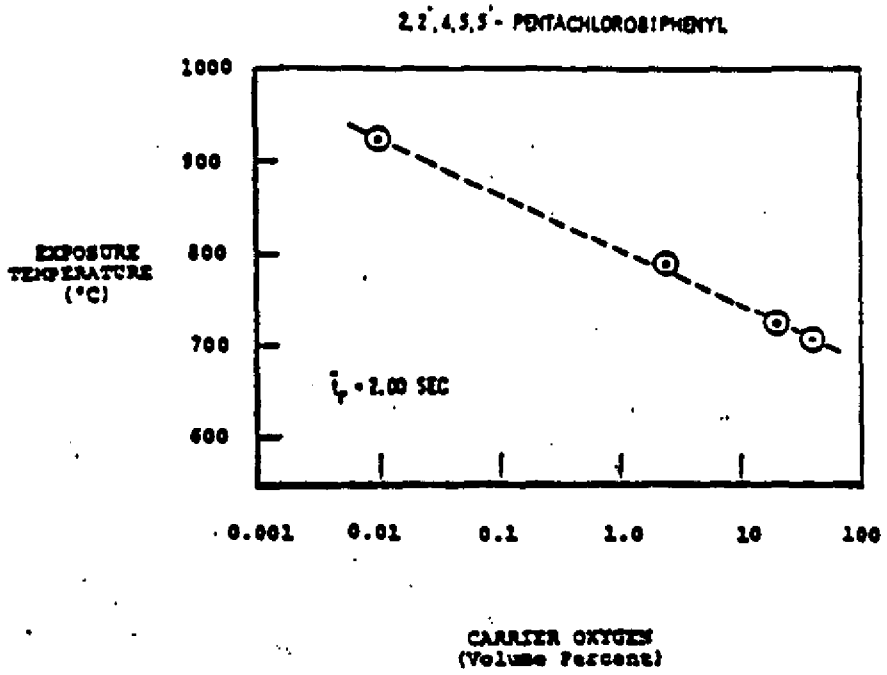

Figure 7. Effect of Oxygen Content.

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