

THERMAL DECOMPOSITION OF 1,2-DICHLOROBENZENE

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ABSTRACT

Incineration is emerging as the best long term solution to the management of hazardous waste. One problem of incineration is that compounds surviving the combustion process are emitted from the combustion chamber and can be emitted to the environment. Much of the public opposition to incineration is based on the fear that the combustion process will produce a more toxic by-product than the original wastes. To study this problem, tests were conducted in a laboratory scale test system that allows the establishment of a steady state combustion environment. The tests were run with 1,2-dichlorobenzene while varying the temperatures of the reaction zone, the residence time, and the oxygen concentration. The various tests produced different product distributions. The tests with excess oxygen and a moderate temperature of 750°C produced a small number of compounds at trace levels. Tests using 1,2-dichlorobenzene that were low in oxygen concentration produced as many as thirty compounds. The organic compounds identified from the thermal decomposition of 1,2-dichlorobenzene were unsaturated chlorinated aliphatic hydrocarbons, chlorinated cyclopentadienes, chlorinated benzenes, chlorinated phenols, chlorinated naphthalenes, and chlorinated benzoic acids.

INTRODUCTION

Modern society depends upon chemicals in nearly every aspect of life. This dependence is not available to us without costs. Every time a chemical is manufactured, it produces a waste stream at one step or another. In the past, these wastes have been dumped without regard to their effect on the environment. The first approach used to solve this problem was burial of the wastes. This has proven to be a tenuous solution at best with cases being reported every day where organic chemicals are reaching the ground water supplies. A more permanent solution to this problem is the incineration of these organic hazardous chemicals to produce water, carbon dioxide, and acid gases.

Incineration is not without its problems as well. Compounds containing halogens, sulfur, and nitrogen produce acid gases when combusted. These acid gases must be removed from the combustion

gas stream before they are emitted to the environment. Principal Organic Hazardous Constituents (POHCs) that survive the combustion process can still be emitted to the environment. Other compounds can be formed during the combustion process which are called products of incomplete combustion (PICs). These compounds could be more toxic than the original compounds being disposed of. Concern over the later two types of compounds led to the need for this research.

Dichlorobenzene (DCB) is a typical industrial organic compound. It is used in the manufacture of consumer products and as an intermediate for the production of dyes. Therefore, it was proposed to study the thermal decomposition of dichlorobenzene as a model compound to determine the extent of the production of products of incomplete combustion and under what conditions these products are produced.

Emission of PICs from Combustion Process

The evaluation of the POHC emission from hazardous waste incinerators has created an awareness of the total emissions from these combustion processes. Researchers who have tried to determine the identity and concentration of all of the organic compounds emitted during combustion have met with limited success. The possibilities of the compounds which can be formed are nearly endless. These studies have resulted in the identification of certain PICs that are of greatest environmental concern and have been listed as hazardous compounds in CFR 40, Part 261, Appendix VIII.¹ Some of the other more common compounds not listed in Appendix VIII have also been identified in these emissions.

Trenholm and Lee have evaluated the total mass emissions from several combustion processes. Their study evaluated nine industrial boilers that co-fired hazardous wastes, eight hazardous waste incinerators, five mineral processing kilns that fired hazardous wastes as a part of their fuel requirements and two municipal solid waste incinerators. They were able to identify 55 different compounds in the combustion gas stream from these units. About one-third of these compounds are listed in Appendix VIII.²

Wyss, Castaldini, and Murray published an EPA report on two different incineration sites and the PIC and POHC emissions produced. They reported that the PIC emissions were associated with high emissions of the POHCs. The ratio of the total PIC emissions to the total POHC emissions at the two sites were about 25 % and 80 %. The PICs identified were mainly chlorinated methanes, ethane, ethylenes, and propanes.³

Tiernan and co-workers sampled combustion gas streams from incinerators burning hazardous wastes for total mass emissions and found that the chlorophenols and chlorobenzenes were higher in concentration than the polychlorodibenzofurans (PCDFs),

polychlorodibenzo-p-dioxins (PCDDs), and the polychlorobiphenyls (PCBs). The PCDFs, PCDDs, and PCBs were present at only trace quantities. The tetrachloro dibenzo-p-dioxins were carefully examined for 2,3,7,8-TCDD and found it to be present at only a small percentage of the other TCDDs.⁴

Recent studies by the research group at the University of Dayton have shown a correlation of the ranking of organic compounds by thermal stability in low oxygen conditions with the destruction and removal efficiencies (DREs) observed in actual field studies.⁵ This group of researchers has also tested mixtures of six different compounds for thermal stability. They found that the relative thermal stability of compounds can change when they are present in mixtures as compared to testing the compounds alone.⁶ The six compounds carbon tetrachloride, chlorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, trichloroethylene, and toluene were present in the mixture. From the thermal treatment of these compounds, they were able to identify 58 different PICs. This testing was done in different atmospheres and at different temperatures. Not all 58 compounds were present in any of the individual tests. The PICs ranged from benzene to several polynuclear aromatic compounds and from chloroform to chlorinated benzenes and naphthalenes.

EXPERIMENTAL

Test Apparatus

The test combustion system has a sample introduction system, a preheater section, the high temperature reaction section, and the absorber section. The sample introduction system is composed of a pump, gas flow meters, and a spray nozzle. The pump delivers the test compounds to the introduction system at a set rate that can be adjusted to the desired level. The pump consists of a stainless steel reservoir that is pressurized with nitrogen. The outlet of the vessel is a fine metering valve that controls the flow of chemicals to the system. The gas flow meters are two sets of gas proportioning valves that allow for adjusting flows of up to three different gases in any proportion that is necessary to achieve the desired atmosphere for testing. The spray nozzle is used to atomize the test compounds into the preheater section. This is used to help evaporate the compounds and insure that the compounds are in the gas phase before entering the reaction zone. The preheater and reaction sections are tubes packed with an aluminosilicate fire brick material. The reaction tube has a section of coiled tube following the packed bed section. Tubes with two different lengths of coiled tube allowed the residence time of the system to be varied without changing the velocity through the system. The temperatures of the two heated zones can be controlled separately. The absorber section is a series of impingers containing solvents to condense and absorb organic compounds as they exit the heated zones.

Analysis Methods

The solvent used in the absorber section for these tests was methanol. Methanol would allow water and organic compounds to be dissolved in the solvent. The absorbing solutions were analyzed directly using GC/MS to determine the concentration of those compounds present at higher concentrations. The solutions from the first impinger were also concentrated by extraction into methylene chloride. The methylene chloride was then evaporated to a small volume and analyzed by GC/MS.

RESULTS

The decomposition system used in this research allowed the temperature, oxygen concentration, and residence time to be varied. These parameters were determined to have the highest probability of affecting the production of PICs and the survival of POHCs in the feed. These parameters were varied in an effort to determine the formation chemistry of the PICs.

The variation of the oxygen concentration had the most dramatic effect on the distribution of products. The tests where there was a calculated excess of oxygen in the system resulted in very few compounds being formed at temperatures of 750°C or higher. An intermediate number of compounds were formed in tests using a stoichiometric concentration of oxygen. In those tests where the oxygen concentration was at a substoichiometric concentration, there was a large number of compounds formed. Table I lists the compounds that were formed or that remained after combustion as a function of the oxygen concentrations. These three tests were performed under identical conditions on the same day with only the oxygen concentration being varied. The temperature of the tests was 750°C with about 2 seconds residence time in the system. The gas flow rate through the system was maintained at the same rate by the addition of more nitrogen to the system to make up for the decrease in oxygen flow in the system.

The variation of the temperature also produced a dramatic effect in the number of compounds being produced. Figure 1 shows the total ion chromatogram for a concentrated sample that was run at 700°C with a residence time of about one second. Figure 2 shows a sample that was run at 800°C with a residence time of about 2 seconds. Both samples were from tests that had an excess oxygen concentration. Figure 3 also illustrates the effect of temperature on the amount of DCB surviving the combustion process as a function of temperature and of oxygen concentration. At a temperature of 700°C, a relatively high concentration of DCB remained even with excess oxygen present. Increasing the temperature to 800°C lowered the concentration of DCB remaining by nearly two orders of magnitude even with a substoichiometric oxygen concentration.

The variation of the residence time had the smallest effect on the product distribution of the parameters studied. There was a slight enhancement of the amount of more highly chlorinated compounds formed as illustrated in Table II. Table II lists the relative amounts of PICs formed and the amount of DCB remaining for two tests that varied only in the length of time the compounds remained in the high temperature section of the system. The residence time in the high temperature region was varied by using two tubes with different lengths of post packed bed tube coils. This allows the residence time to be varied without altering the gas velocity in the packed bed section.

CONCLUSION

These studies have shown that factors such as temperature, oxygen concentration, and residence time can have an affect on the product distribution from a combustion reaction. In cases where moderate temperatures and excess oxygen are available, there is generally low levels of PICs formed as well as low concentrations of POHCs surviving the combustion reaction.

REFERENCES

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Table I
EFFECT OF OXYGEN CONCENTRATION ON PRODUCT DISTRIBUTION

<u>Compound Present</u>	<u>Oxygen Concentration in Test</u>		
	<u>Excess</u>	<u>Stoic.</u>	<u>Substoic.</u>
Chlorobenzene	X	X	X
Dichlorobenzene	X	X	X
Trichlorobenzene	X	X	X
Tetrachlorobenzene	X	X	X
Pentachlorobenzene	X		
Hexachlorobenzene	X		
Chlorophenol			
Dichlorophenol		X	X
Trichlorophenol		X	X
Tetrachlorophenol		X	X
Pentachlorophenol		X	X
C ₄ H ₆ Cl ₂	X		
C ₅ H ₁₀ Cl ₂	X		
C ₅ H ₁₀ OCl	X		
Hexachlorobutadiene	X		
Dichlorobutetetraene			X
Propanedioic acid, Dimethyl ester			X
1-Chloro-4-ethynyl-Benzene		X	X
Methyl Benzoate			X
Tetrachlorobutene			X
C ₈ H ₄ Cl ₂		X	
Chlorobenzofuran		X	X
Dichloro-(chloromethyl)-benzene		X	
Naphthalene			X
C ₈ H ₆ Cl ₂			X
Chlorobenzoic Acid methyl ester		X	X
Chloronaphthalene			X
Dichlorobenzofuran		X	X
C ₈ H ₇ Cl			X
Dichlorobenzoic acid methyl ester		X	X
Acenaphthalene			X
C ₁₀ H ₈ Cl ₂		X	X
Dichloronaphthalene		X	X
C ₁₂ H ₇ Cl			X
C ₁₀ H ₇ Cl ₃			X
Chlorodibenzofuran			X
Trichloronaphthalene		X	X
Tetrachlorobenzofuran			X
Dichlorodibenzofuran		X	X
Tetrachloronaphthalene		X	X
Trichloro-diphenyl ether			X
Trichloro-1,1'-Biphenyl		X	X
Trichlorodibenzofuran			X
Tetrachloro-1,1'-Biphenyl		X	X
Tetrachlorodibenzofuran		X	X
Dichloronaphthol			X
Tetrachloronaphthol			X

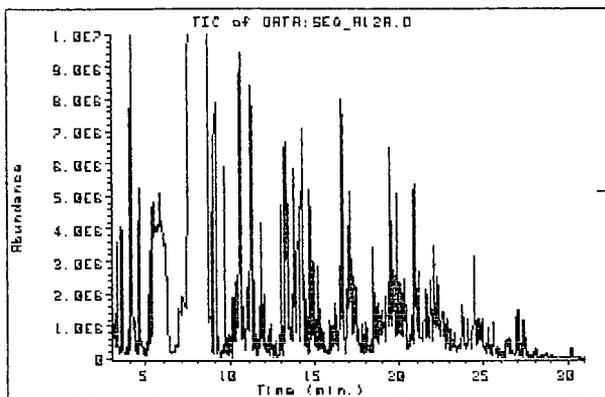


Figure 1. Chromatogram of Concentrated Sample ran at 700°C, 1 second residence time.

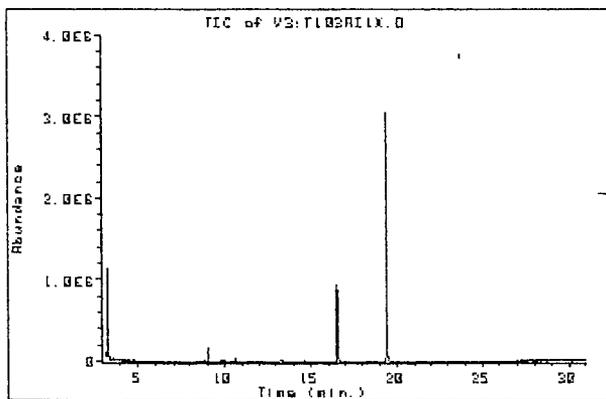


Figure 2. Chromatogram of Concentrated Sample ran at 800°C, 2 second residence time.

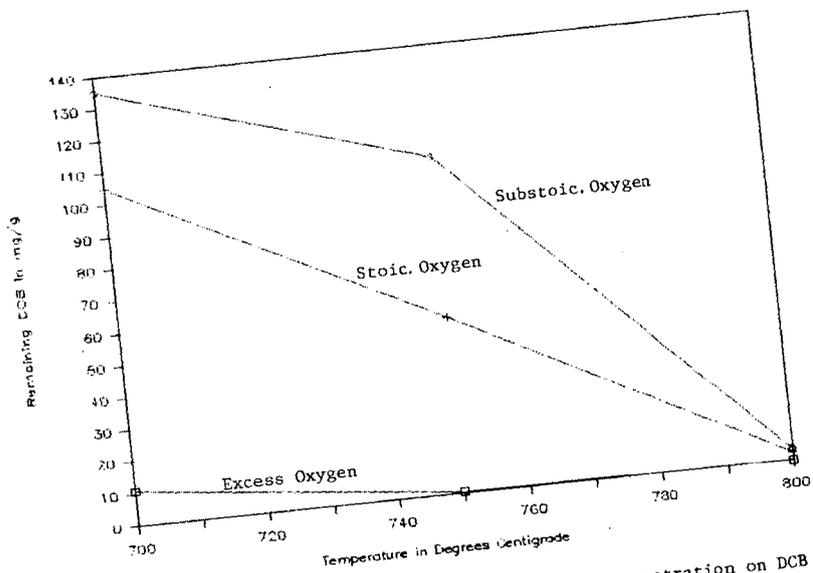


Figure 3. Effect of temperature and oxygen concentration on DCB surmising combustion.

Table II
EFFECT OF RESIDENCE TIME ON PRODUCT DISTRIBUTION

Compounds Present	Amount/g of Parent Material	
	1 Second	2 Second
Chlorobenzene	7.5 ug/g	17.7 ug/g
Dichlorobenzene	62 ug/g	372 ug/g
Trichlorobenzene	173 ug/g	0.78 ug/g
Tetrachlorobenzene	113 ug/g	0.30 ug/g
Pentachlorobenzene	79 ug/g	1.42 ug/g
Hexachlorobenzene	32 ug/g	7.48 ug/g