

SOLVENT EFFECTS ON THE THERMAL
DECOMPOSITION OF 1,2-DICHLOROBENZENE

Craig M. Young
Waste-Tech Services, Inc., Golden, CO 80401

Kent J. Voorhees
Department of Chemistry and Geochemistry, Colorado School of
Mines, Golden, CO 80401

ABSTRACT

The incineration of hazardous wastes is emerging as a positive solution to the management of hazardous organic containing wastes. To better understand the formation of products of incomplete combustion (PICs), a study of the thermal decomposition of dichlorobenzene in the presence of several organic solvents was studied. Experiments have been conducted in a laboratory scale test system using a steady state combustion environment to study the effects of co-solvents on product distribution. The introduction of chlorinated solvents resulted in an increase in the number and concentration of chlorinated compounds being formed. Conversely, the introduction of chlorophenol into the system had little effect on the product distribution. The introduction of methanol, hexane, and water into the system lowered the number of chlorinated compounds being formed.

INTRODUCTION

The incineration of hazardous organic wastes is gaining acceptance as a technique for the management of these materials. The placement of wastes containing hazardous organic chemicals in landfills represents a potential hazard to the water supplies of future generations. For this reason, landfilling of wastes is meeting with greater resistance from the public and tighter restrictions from regulating agencies.

Incineration offers a more permanent solution to handling organic compounds. During the combustion process, organic compounds are converted to carbon dioxide, water, and acid gases. A public concern to incineration is the survival of compounds from the combustion environment and the products of incomplete combustion (PICs) that are formed during the combustion reaction. This study was undertaken to define the parameters that affect the formation of PICs during combustion.

Dichlorobenzene (DCB) was selected for this study as a model of a typical industrial organic compound found in hazardous

wastes. The thermal decomposition of DCB was reported earlier.¹ The present study expands the previous work by investigating the effect of solvents on the decomposition products from DCB.

PIC Formation in Mixtures.

Others have reported that thermal treatment of mixtures of organic compounds produce more PICs than when these compounds are treated individually. The University of Dayton Research Institute has done extensive work on the thermal stability of organic compounds. They tested a six-component mixture and found that the relative thermal stability of compounds changed when they were present in mixtures as compared to testing the individual compounds.² The compounds studied were divided into two classes. One class was the compounds whose decomposition was independent of the reaction atmosphere. The other class of compounds were those species that increased in stability with decreasing oxygen concentration. From the thermal treatment of these compounds, the Dayton group identified 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 polynuclear aromatic (PNA) compounds and from chloroform to chlorinated benzenes and naphthalenes. Many of these compounds were seen primarily from oxygen deficient conditions. It was proposed that a substantial portion of these products were formed in the initial reaction, but they are destroyed by oxidative pathways when they are available leaving only the compounds insensitive to oxidative pathways. Under oxygen deficient conditions, the competing oxidative pathways are no longer available and the PNAs show up as PICs.²

Taylor and Dellinger³ reported on a study conducted on the thermal decomposition of chloromethane mixtures. They studied the decomposition of CCl_4 , CHCl_3 , CH_2Cl_2 , and CH_3Cl . This group reported that the thermal stability of these compounds was dependent on the oxygen concentration and the other compounds present in the feed to the system. The evaluation of the decomposition of mixtures indicated that the degradation of CHCl_3 initiated the generation of a radical pool that lead to the decomposition of the other compounds.

EXPERIMENTAL

Test Apparatus

The test combustion apparatus has a sample introduction system, a preheater section, the high temperature reaction section, and the absorber section. The sample introduction device 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

using a fine metering valve. The tests that added water to the system used a second pump and a spray nozzle with two tubes for delivering compounds to the system. The gas flow meters were two sets of gas proportioning valves for adjusting flows of oxygen and nitrogen to achieve the desired atmosphere for testing. The spray nozzle atomized the test compounds into the preheater section to assist evaporation of the compounds. The preheater and reaction sections were tubes packed with an aluminosilicate fire brick material. The reaction tube had a coiled tube following the packed bed section which can be adjusted in length to change the reaction time. The temperatures of the two heated zones were controlled separately. The absorber unit was a series of impingers containing methanol to condense and absorb organic compounds as they exit the heated zones.

Analysis Methods

The solvent used in the impingers for these tests was methanol. The absorbing solutions were analyzed directly using GC/MS. In addition, 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 for the detection of compounds present at lower concentrations.

RESULTS

The tests conducted had only two variables: the oxygen concentration and the feed mixture composition fed to the system. The oxygen concentration caused a large variation in the number and concentrations of compounds formed. The type of compounds added to the system also affected the product distribution and the concentrations of PICs. The presence of a highly chlorinated solvent in the system led to the formation of more chlorinated compounds. The presence of a non-halogenated solvent in the system tended to suppress the formation of chlorinated species.

Solvents were tested with DCB alone or in combination with other solvents. The other solvents tested were hexane, methanol, chloroform, carbon tetrachloride, chlorophenol, and water. The chlorinated solvent tests were performed to determine if their decomposition would increase the available chlorinating species and increase the number of chlorinated compounds formed. The non-halogenated solvent tests allowed determination of their effect on the chlorinating species produced by the decomposition of DCB.

The multi-solvent combinations studied were DCB/chloroform/methanol, DCB/chloroform/water, and DCB/carbon tetrachloride/water. Tests with the non-halogenated solvents mixed with the halogenated solvents were conducted to determine if the chlorination caused by the halogenated solvents could be suppressed by a hydrogen donor solvent. The results of the tests

indicated that fewer highly chlorinated compounds were formed when a hydrogen donor solvent was present.

The tests with hexane present were complicated by the low autoignition temperature of hexane. The temperature of the reaction chamber was set at 750°C, which caused auto ignition of the hexane. The flame front was observed to move back into the preheater section where it turned the last 1.5 inches of the bed bright red. This resulted in a non-controlled temperature for the tests with hexane.

The comparison of the results of DCB alone, DCB with hexane and DCB with methanol are shown in Table I. These results show a marked decrease in the amount of DCB remaining for those tests where a non-halogenated solvent was added to the system. The introduction of methanol into the feed resulted in the largest decrease in the number and concentration of chlorinated compounds formed. The test with hexane reduced the concentration of chlorobenzene, DCB, and hexachlorobenzene. It also reduced the number of compounds formed from 10 to 6. The tests with methanol reduced the concentration of DCB two orders of magnitude and reduced the number of compounds formed to 4.

Table II lists the product distribution of PICs formed for the tests of DCB, DCB/chloroform and DCB/carbon tetrachloride. The PICs were largely chlorinated compounds of various chemical classes. The chlorinated benzenes and chlorinated phenols show a general trend of increasing concentration with increasing number of chlorine atoms on the molecule. The compounds having the highest concentrations after combustion in the tests with the chlorinated solvents are the tetra- to hexachlorobenzenes. These compounds were three orders of magnitude higher in concentration than with DCB alone. The concentration of DCB remaining decreased in the tests with the chlorinated solvents, but this effect was overwhelmed by the much higher concentrations of the higher chlorinated benzenes. The tests with CCl₄ converted about 1 % of the dichlorobenzene to hexachlorobenzene. Crystals of hexachlorobenzene were also noted between the preheater and the reaction chamber indicating that some chlorination was taking place at the preheater temperatures of around 400°C.

The thermal decomposition of DCB in the presence of chlorophenol was studied to determine if this combination would lead to the formation of fused ring heterocyclic compounds. The excess oxygen test produced very few compounds and resulted in low levels of DCB or chlorophenol surviving the thermal decomposition. The compounds identified were similar to the thermal decomposition products of DCB by itself. The chlorophenol tests did follow the trends of other tests in that the decrease in the oxygen concentration produced a marked increase in the number of compounds formed and the amount of DCB remaining. The amount of chlorophenol did not necessarily follow this trend. Only small amounts of chlorophenol remained in any

of the tests. No fused ring heterocycles were formed except in the oxygen deficient test.

The studies conducted to this point had shown that increasing the chlorine content of the feed increased the number of chlorinated compounds formed. The addition of a non-halogenated solvent decreased the number of chlorinated compounds. The next investigations were designed to determine if the addition of a non-halogenated solvent to the feed could reduce the number of chlorinated compounds produced by acting as a scavenger for the chlorinating species present.

The use of methanol as a non-halogenated solvent was chosen to avoid the temperature increases caused by the ignition and burning of hexane with a flame front. To test this theory, DCB was mixed with chloroform and methanol in two different ratios. The methanol concentration was doubled in the second set of tests. Table III summarizes the results of these tests as compared to the DCB/chloroform test. The methanol showed some effectiveness at reducing the amount of chlorination with the largest reductions being in the amount of hexachlorobenzene being produced.

The addition of water into the system had a similar effect of reducing the amount of chlorination that takes place in the system. Table IV summarizes the data from the tests where water was added as a separate feed to the system. The water clearly reduced the concentrations of higher chlorinated compounds, but increased the amount of DCB that remained in the system.

CONCLUSION

The formation of products of incomplete combustion are influenced by the compounds in the combustion feed system, the temperature of the oxidizing system, and the oxygen available for combustion. The presence of highly chlorinated solvents in the feed can result in a chlorinating environment that leads to the production of more highly chlorinated PICs. The presence of non-halogenated solvents in the system produces an environment that suppresses the chlorination processes. When both types of solvents are introduced into the feed system, there is a moderate suppression of the chlorination. One possible explanation of this phenomena is that the hydrocarbon solvents produce water during combustion which acts as a hydrogen source for scavenging the chlorinating species present. Commercial scale incineration systems that use hydrocarbon fuels for maintaining combustion temperatures can actually lead to environments that suppress the formation of PICs by providing a pool of hydrogen donors to react with the released chlorine from the combustion of chlorinated compounds.

REFERENCES

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2. Graham, J.L.; Hall, D.L.; Dellinger, B.; Environ. Sci. Technol., 1986, 20, 703-710.
3. Taylor, P.H.; Dellinger, B.; Environ. Sci. Technol., 1988, 22, 438-447.

Table I
EFFECT OF CoSolvents ON PRODUCT DISTRIBUTION AT 750°C
Hydrocarbon Solvents

<u>Compound Present</u>	<u>Solvent System Additions</u>		
	<u>None</u>	<u>Hexane</u>	<u>Methanol</u>
Chlorobenzene	18	7.7	1.1
Dichlorobenzene	372	137	1.5
Trichlorobenzene	0.8	1.4	<0.1
Tetrachlorobenzene	0.3	1.8	<0.1
Pentachlorobenzene	1.4	0.3	3.0
Hexachlorobenzene	7.5	<0.5	1.5
Additional Compounds	4	1	0

* Concentrations are in ug/gram of Mixture input.

Table II
EFFECT OF CoSolvents ON PRODUCT DISTRIBUTION AT 750°C
Chlorinated Solvents

<u>Compound Present</u>	<u>Solvent System Additions</u>		
	<u>None</u>	<u>CHCl₃</u>	<u>CCl₄</u>
Chlorobenzene	18	<10	3.17 mg
Dichlorobenzene	372	40	12
Trichlorobenzene	0.8	40	1.4
Tetrachlorobenzene	0.3	1.42 mg	3.1
Pentachlorobenzene	1.4	1.24 mg	130
Hexachlorobenzene	7.5	1.67 mg	11.3 mg
Chlorophenol	<0.1	<0.1	4.0
Dichlorophenol	<0.1	0.7	0.9
Trichlorophenol	<0.1	0.4	1.5
Tetrachlorophenol	<0.1	6.9	<0.1
Pentachlorophenol	<0.1	5.3	<0.1
Additional Compounds	4	23	23

* Concentrations are in ug/gram of Mixture input, unless noted.

Table III
EFFECT OF CoSolvents ON PRODUCT DISTRIBUTION AT 750°C
Chlorinated Solvents with Methanol

<u>Compound Present</u>	<u>Solvent System Additions</u>		
	<u>CHCl₃</u>	<u>Ratio #1</u>	<u>Ratio #2</u>
Chlorobenzene	<10	14	167
Dichlorobenzene	40	806	589
Trichlorobenzene	40	850	748
Tetrachlorobenzene	1.42 mg	1.15 mg	1.19 mg
Pentachlorobenzene	1.24 mg	869	748
Hexachlorobenzene	1.67 mg	212	261
Chlorophenol	<0.1	1.2	0.4
Dichlorophenol	0.7	8.4	1.1
Trichlorophenol	0.4	8.9	0.6
Tetrachlorophenol	6.9	15	0.7
Pentachlorophenol	5.3	5.4	0.9
Additional Compounds	23	50	30

* Concentrations are in ug/gram of Mixture input, unless noted.

Table IV
EFFECT OF CoSolvents ON PRODUCT DISTRIBUTION AT 750°C
Chlorinated Solvents with Water

<u>Compound Present</u>	<u>Solvent System Additions</u>		
	<u>None</u>	<u>CHCl₃</u>	<u>CCl₄</u>
Chlorobenzene	6.61 mg	88	214
Dichlorobenzene	51.1 mg	1.76 mg	5.07 mg
Trichlorobenzene	334	1.37 mg	1.11 mg
Tetrachlorobenzene	0.7	2.49 mg	3.61 mg
Pentachlorobenzene	0.9	2.02 mg	4.18 mg
Hexachlorobenzene	2.1	2.44 mg	4.72 mg
Chlorophenol	694	0.4	13
Dichlorophenol	381	6.0	8.6
Trichlorophenol	1.2	4.0	0.9
Tetrachlorophenol	0.9	6.6	1.7
Pentachlorophenol	6.3	3.8	4.5
Additional Compounds	4	18	38

* Concentrations are in ug/gram of Mixture input, unless noted.