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Agency

Hazardous Waste Engineering
Research Laboratory
Cincinnati OH 45268

Research and Development

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EPA

Project Summary

Interim Report on Non-Flame Hazardous Waste Thermal Destruction

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The thermal decomposition of toxic organic compounds is being investigated in a laboratory system dedicated to the non-flame mode/zone of the combustion process. The early phase of this study has focused on three compounds: pentachloronitrobenzene (a fungicide), chloroform (a ubiquitous industrial compound) and heptane.

The results of the third compound, heptane, are preliminary to those sought for a mixture of two or more compounds such as chloroform, a toxic substance, and heptane, a combustion process fuel.

The data of this report were collected during the period January - June 1985.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In the thermal destruction of hazardous organic waste material; the interactions of the gaseous components in the post-flame or the non-flame zone of the combustion process make an important contribution to the overall results. The thermal decomposition in those zones can range from simple pyrolysis in an oxygen-deficient atmosphere as might occur in a boiler, to a thermal-oxidative treatment with a considerable excess of oxygen as can occur in a liquid injection incinerator supported by a secondary combustion zone or supply of air.

A laboratory unit, identified as the Thermal Decomposition Unit-Gas Chromatograph (TDU-GC), has been used to investigate key thermal decomposition factors of the post-flame zone, such as time of exposure and temperature, and their impact upon the effluent decomposition products. The TDU-GC was developed at the University of Dayton Research Institute (UDRI) and has been applied by Institute personnel over the past several years to study many different organic compounds.

The TDU-GC at the U.S. Environmental Protection Agency (EPA) Center Hill Facility has been used thus far to investigate pentachloronitrobenzene (PCNB) and also chloroform in order to determine the level of reproducibility as measured by the comparison of these findings to those reported by the UDRI for the same compounds.

The thermal decomposition of heptane was also investigated in a preliminary step to determine the effect of its presence upon chloroform decomposition; this simulates the use of heptane as a co-fired fuel or solvent for a hazardous waste constituent such as chloroform.

Experimental Procedure

The principal equipment used in this study was the TDU-GC system, a closed in-line system consisting of two basic units, the thermal reactor and the analyzer, a gas chromatograph. These units are shown in Figure 1.

1. The thermal reactor incorporates a capillary quartz tube within a furnace with three heating zones that are inde-

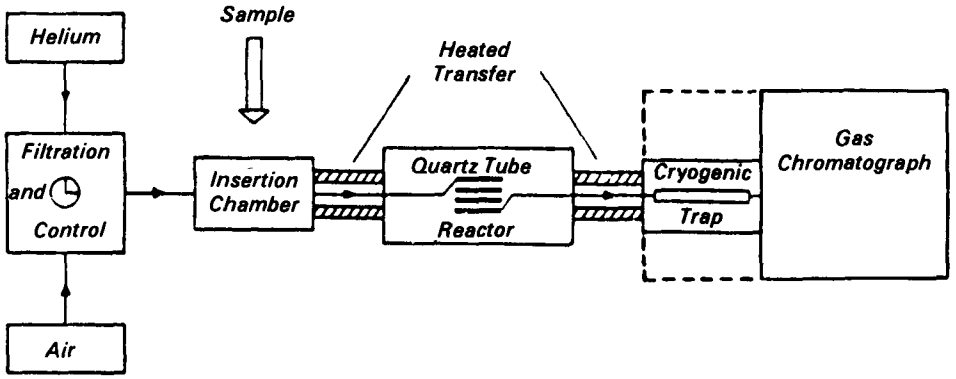

Figure 1. Basic schematic of TDU-GC system.

pendently controlled to produce temperatures up to 1150°C in the central zone for thermally decomposing the sample compound in its gaseous state.

A tubular quartz extension at the entrance of the furnace transfers the feed gas from the larger-bore sample insertion chamber. That chamber is fitted with any one of several probes adapted to handle gas, liquid or solid samples. A temperature programmer controls the heating jacket on the insertion chamber, for converting the liquid and solid samples to the vapor phase at selected elevated temperatures. The vapor or gas is conveyed to the reactor by a controlled flow of carrier gas which is selected according to the nature of the atmosphere required in the high-temperature zone of the reactor. According to the temperature and pressure measured in the reactor tube, the carrier gas flow is regulated at the instrument console to result in a precise residence time of the vaporized/gaseous sample in the closely-controlled high-temperature zone.

The gaseous emissions from the reactor pass through a capillary tube into an in-line tubular trap controlled to sub-ambient temperatures as low as −50°C and colder. The trap is located inside the wall of the gas chromatograph (GC) and is very short (several mm) section of the extension of the GC capillary column into the 30:1 splitter tubing.

2. The gas chromatograph is fitted with a fused silica capillary column leading to a flame ionization detector (FID). Heating the trap transfers, via the 30:1 splitter, the smaller stream of trapped emissions sample to the front end of the capillary column which itself is at the sub-ambient temperature. Upon injection of the sample into the GC, as initiated by the switch on the supporting computer, the temperature program for the capillary column controls the separation of the components of the reactor emissions sample and their ensuing detection and measurement by the FID.

The computer coupled with a recorder provides a means of storing the output from the FID and of depicting it in a chromatogram as well as in a tabulation of the various peak areas.

3. The Principal Organic Hazardous Constituent (POHC) material under investigation was introduced into the insertion chamber as a gas, liquid or solid.

The more volatile, low molecular weight compounds were generally fed by syringe to the TDU-GC system as gaseous samples prepared at known concentrations.

For various organic liquids, nanoliter quantities were injected directly into the insertion chamber where the sample was converted to the vapor form by a programmed temperature increase that provided transfer by the carrier gas into the thermal reactor.

4. Samples of organic solids were deposited as measured amounts in solution onto the end of the "solids" probe. Evaporation of the solvent left a residue which in the confines of the insertion chamber was transformed to the vapor state for transfer into the thermal reactor by the carrier gas.

Results

TDU-GC test run series were made on (1) pentachloronitrobenzene (PCNB) as a single component feed, (2) chloroform, also as a single component feed, and (3) chloroform in solution with "fuel" heptane constituting the bulk of the organic feed.

The results for PCNB are presented in Figure 2 as a plot of reactor effluent concentrations vs. exposure temperature. Curve A in that figure shows the increase in decomposition of the POHC material, the feed PCNB, in an oxidative atmosphere with increasing temperature. Curves B, C, D present the concentrations for the more abundant PICs that were produced in the thermal treatment process. PIC component B was subsequently identified as hexachlorobenzene (HCB).

Chloroform in the predominantly oxidative atmosphere produced major quantities of several PICs. These are identified in Figure 3 as hexachloroethane (C_2Cl_6), tetrachloroethylene (C_2Cl_4) and carbon tetrachloride (CCl_4). The highest reactor temperature investigated was 625°C, at which level essentially total destruction (≥99.99% DE) of the POHC (chloroform) had occurred.

Chloroform as one of several organic compounds that might be found in a feed mixture in an actual incinerator, was selected for mixture (solution) in "fuel" heptane to undergo thermal decomposition treatment. Initially, heptane alone was investigated at various temperatures to characterize its decomposition, Figure 4. The high temperature of 675° was considered adequate to bracket the high for total chloroform decomposition, namely the 625°C observed in Figure 3. When a three weight percent of chloroform was added to the heptane, its products, as observed for pure chloroform in Figure 3, were completely masked by the peaks of "pollutant" components present in the heptane. Those pollutants were dominant even at a low, non-decomposing temperature, 300°C, for heptane.

Discussion

The test runs with PCNB and with pure chloroform were made primarily to check for inter-laboratory reproducibility.

The PCNB results from the present study yielded a decomposition curve for PCNB that closely matched that reported by the University of Dayton Research Institute (UDRI). The hexachlorobenzene formation/decomposition profile, Curve B of Figure 2 also closely matched that reported by UDRI.

The results for pure chloroform showed very good agreement with those presented by UDRI in some of

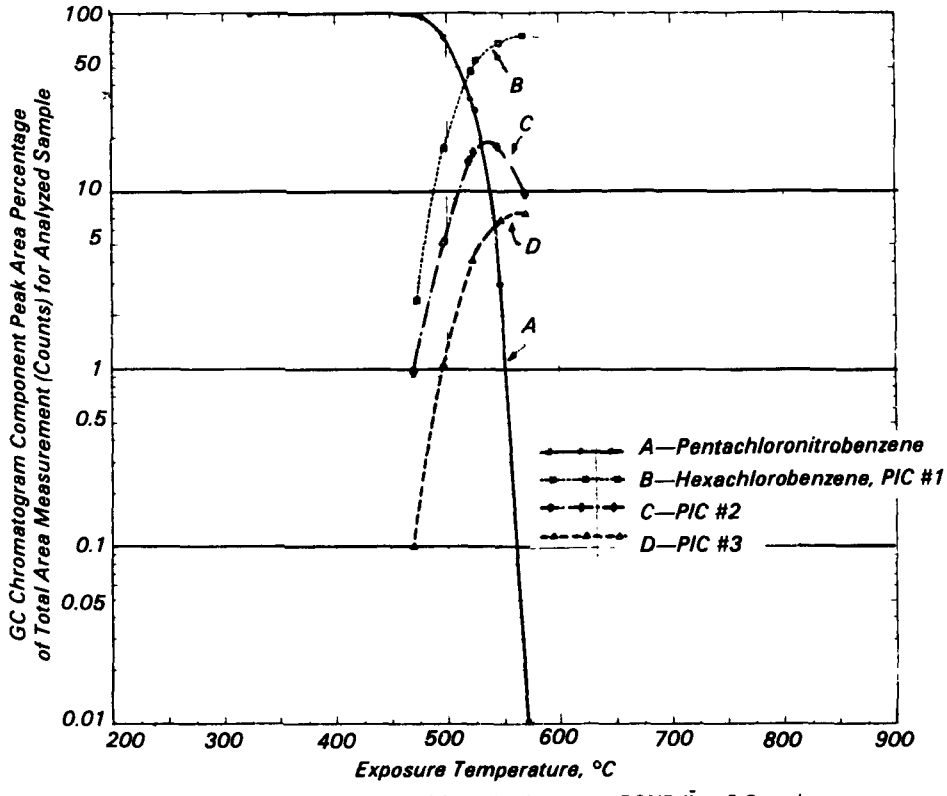

Figure 2. Thermal treatment of pentachloronitrobenzene, PCNB ($\bar{t}_r$ = 2.0 sec).

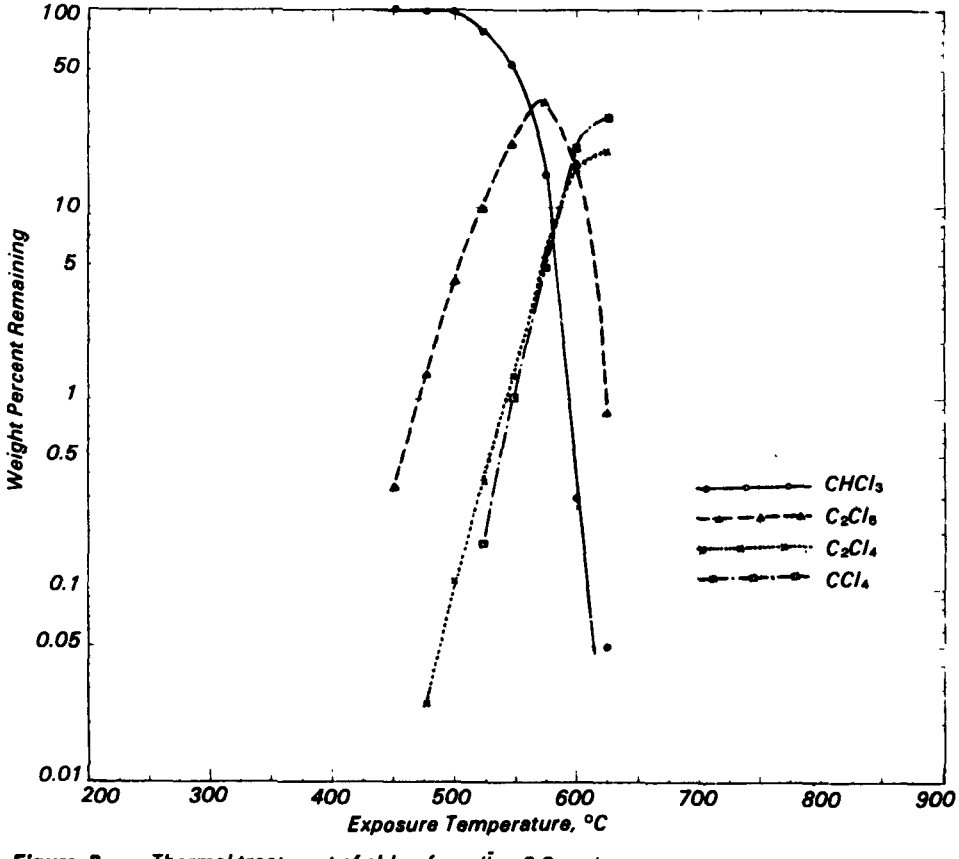

Figure 3. Thermal treatment of chloroform ($\bar{t}_r$ = 2.0 sec).

their earlier work with toxic organic compounds, not only for the feed material but also for the three major PICs shown in Figure 3. It is evident, from the chlorine-saturated state of each of the PIC molecules (CCl_4, C_2Cl_4, C_2Cl_6) identified in major concentrations, that the hydrogen atom present in the parent chloroform molecule is being thoroughly eliminated from the organic product species. Figure 5 presents the data for chloroform on a linear scale, in contrast to the semi-log scale of Figure 3; it readily shows the comparative amounts of compounds present in the emissions from the thermal reactor. It is evident from Figure 5 that the concentration of the hexachloroethane (C_2Cl_6) has peaked at a temperature (~570°C) where the tetrachloroethylene (C_2Cl_4) and carbon tetrachloride (CCl_4) are only beginning to form.

In light of the effective masking of the GC peaks for chloroform and its products by the heptane source pollutants, the results are limited to a decomposition profile for heptane, Figure 4. The moderate slope of the decomposition curve at the high temperatures indicates the more refractory nature of the compound, so that by 675°C, a full 125°C after the start of decomposition at 550°C, a little more than one percent of the heptane still persists in the effluent stream from the reactor.

Conclusions and Recommendations

The Thermal Decomposition Unit-Gas Chromatograph (TDU-GC) system has been used in obtaining thermal decomposition profiles for several organic compounds associated with the incineration of toxic/hazardous organic waste substances.

The system has been used successfully to demonstrate reproducibility of results consistent with the findings of other investigations using similar equipment.

From the experience with heptane as a component in the feed, it appears necessary, for accurate measurement of the effects of feed composition, to limit mixtures to a very few, perhaps only two, compounds that are individually "clean" in any GC analysis.

For more fully characterizing the thermal reactor emissions with respect to PICs, more extensive procedures involving additional instrumentation is needed to identify and quantify PIC compounds. A Mass Selective Detector

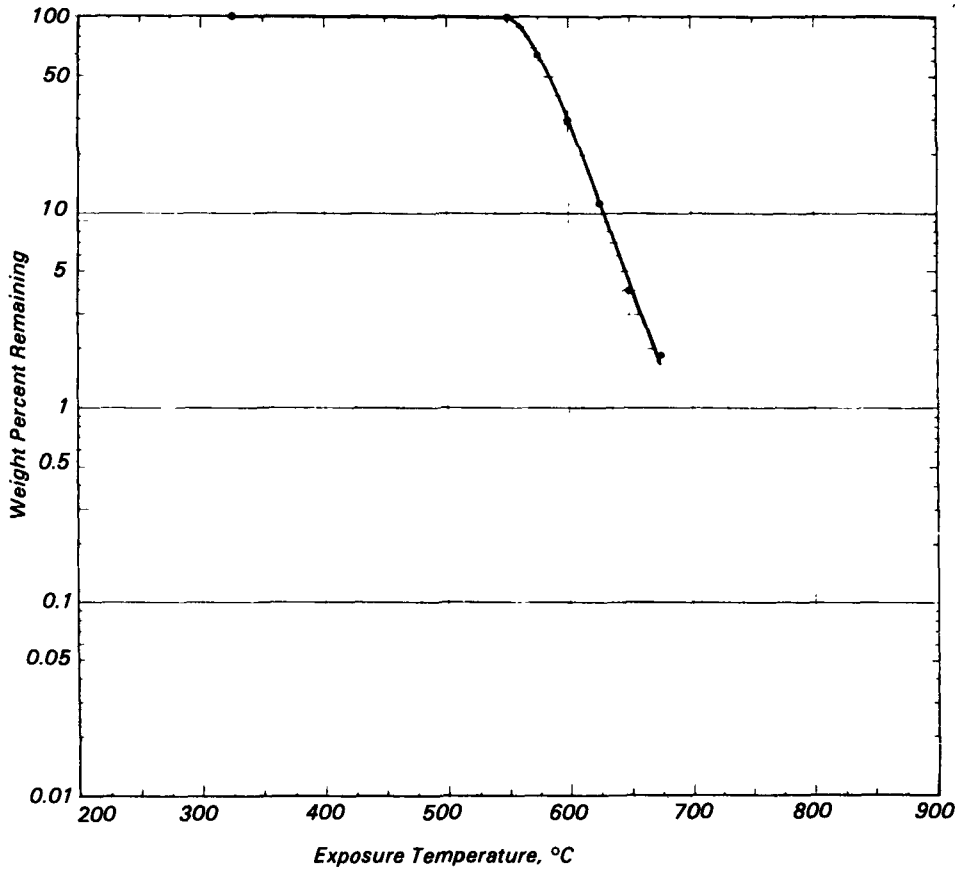

Figure 4. Thermal treatment of heptane ($\bar{\tau}_r$ = 2.0 sec).

(MSD) dedicated to the TDU-GC system is the instrument of choice, both for accuracy of determinations and for volume of work that can be expedited.

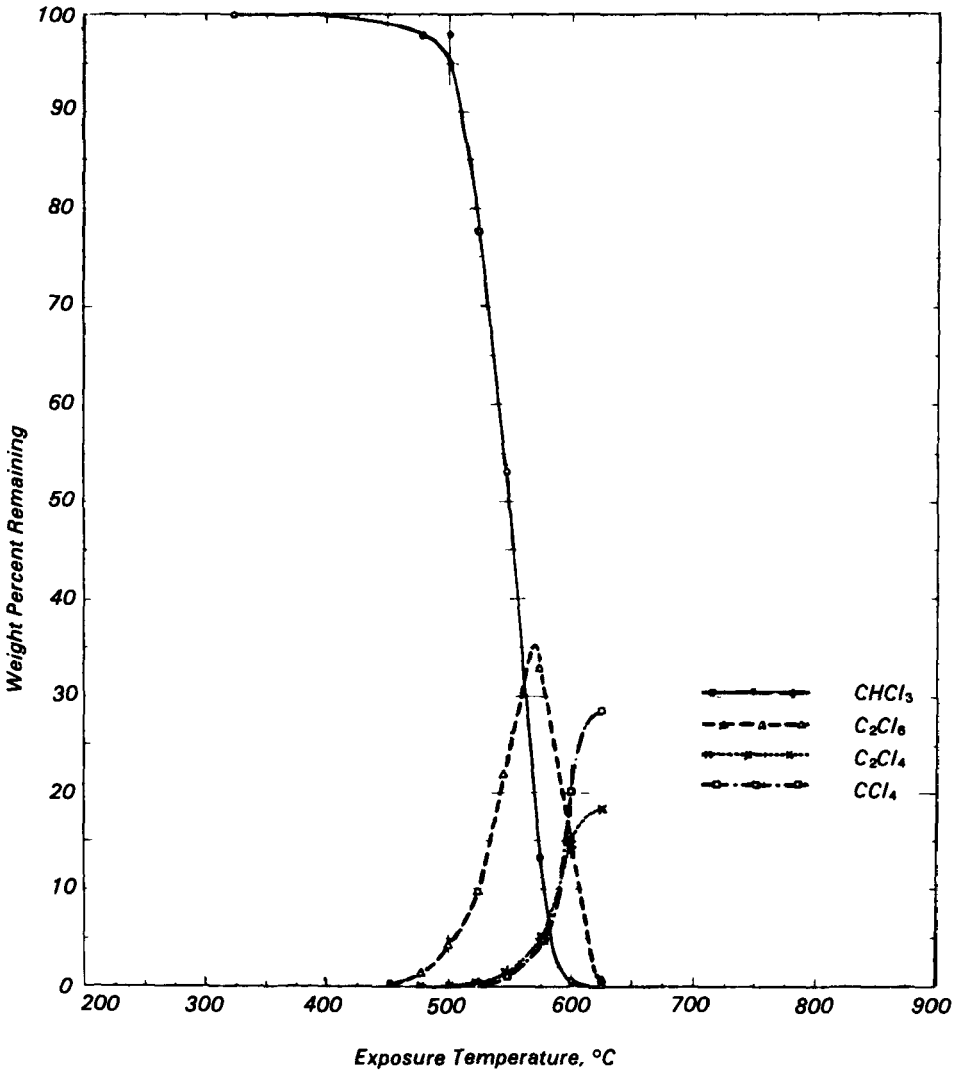

Figure 5. *Thermal treatment of chloroform ($\bar{\tau}_r$ = 2.0 sec).*

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The complete report, entitled "Interim Report on Non-Flame Hazardous Waste Thermal Destruction," (Order No. PB 86-176 435/AS; Cost: $9.95, subject to change) will be available only from:

National Technical Information Service
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