



The University of Dayton

May 10, 1984

Dr. Fred D. Hileman
Senior Research Chemist
Monsanto Research Corporation
1515 Nicholas Road
Dayton, OH 45418

Dear Fred:

I have enclosed a preliminary cost estimate for the work we discussed on the phone concerning the determination of the thermal degradation properties of 1,2,4-trichlorobenzene (1,2,4-TCBz). I have outlined a fairly comprehensive program which may be broken down into three experimental tasks.

Task 1 is designed to determine the thermal properties of 1,2,4-TCBz under conditions that could be encountered in a transformer fire. We would determine the degree of destruction of the parent compound and the identity of combustion products at a minimum of six temperatures. This work would be performed at a mean gas phase residence time ($\bar{t}_r$) of 1.0 seconds in three possible reaction atmospheres (pyrolysis, oxygen starved, and oxidation). We feel this residence time is representative of that encountered in the high-temperature zone of a transformer fire; however, the three reaction atmospheres are necessary to identify all possible formation products.

The determination of possible dibenzodioxins and dibenzofurans is clearly of interest. We would propose that Monsanto furnish the standards for these analyses. We would also propose to trap a few samples of the thermal reactor effluent and deliver them to you for confirmatory analysis. We may want to trap additional samples for your analysis if our initial research findings indicate further analysis to be desirable.

Tasks 2 and 3 represent a detailed study of the pyrolysis and oxidation reaction kinetics of 1,2,4-TCBz. A minimum of six gas-phase residence times ($\bar{t}_r$ ranging from 0.25 to 2.0 seconds) and

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six temperatures will be necessary for each task. The kinetic data should be sufficient to predict the rate of destruction of 1,2,4-TCBz under the range of conditions experienced in a transformer fire.

As I am not aware of your budget for this program, I have attempted to provide something of a "shopping list" for your inspection. We feel a detailed complete kinetics and mechanistic study, which would be the result of this proposed total program, will be of immense value. The kinetics studies outlined under tasks 2 and 3 in combination with product identification should clarify many questions concerning the mechanism of formation of dibenzodioxins and dibenzofurans from chlorobenzenes (if indeed they are formed).

We are most interested in performing this work and are willing to be as flexible as possible in arriving at final arrangements. If you decide to proceed with the program, I would point out that we can also accept grants or possibly an equipment donation as full or partial payment for our research. Such options may be more practical or economically advantageous to Monsanto.

We would be in position to initiate this program by no later than September of this year. Allowing for other scheduled activities, I would estimate the full program would be completed 8 to 10 months following program initiation.

I have also included some literature which describes the equipment and facilities which would be used to perform this work. Please do not hesitate to contact me if you have additional questions or identify some points in need of clarification.

Sincerely,

Barry Dellinger

Barry Dellinger, Ph.D.
Group Leader
Environmental Sciences

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Enclosures

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PRELIMINARY COST ESTIMATE

MONSANTO

THERMAL DEGRADATION PROPERTIES OF 1,2,4-TRICHLOROBENZENE

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1.	Thermal Decomposition Profiles and Product Identification for 1,2,4-TCBz	\$39,985
1.1	Pyrolysis	
1.2	Oxygen starved	
1.3	Oxidation	
2.	Pyrolysis Kinetics	\$18,960
2.1	Reaction Order determination	
2.2	Determination of Pyrolysis rate constants, activation energy, and Arrhenius coefficient	
3.	Oxidation Kinetics	\$21,443
3.1	Reaction order determination w.r.t. 1,2,4-TCBz	
3.2	Reaction order determination w.r.t. oxygen	
3.3	Determination of oxidation rate constants, activation energy, and Arrhenius coefficient	
	Total	<u>\$80,388</u>

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Capabilities

Incineration and Thermal Degradation

The success of the Kepone and other related thermal degradation studies resulted in the establishment of the Environmental Chemistry Laboratory at the University of Dayton Research Institute. Using state-of-the-art equipment developed by Research Institute personnel, thermal degradation data has been generated on a range of samples from pesticides to complex industrial mixtures and chloromethanes to dibenzo-p-dioxins.

The Environmental Chemistry Laboratory contains two proven instrumentation systems that determine the high-temperature thermal degradation properties of virtually any organic substance. The Thermal Decomposition Analytical System (TDAS) consists of a controlled high-temperature decomposition unit with a dedicated in-line LKB 2091 gas chromatography-mass spectrometer to measure destruction efficiency and analyze products of incomplete combustion. The Thermal Decomposition Unit-Gas Chromatographic system (TDU-GC) is a similar thermal decomposition unit, which uses a high-resolution capillary gas chromatography system with cryogenic capabilities to perform the necessary analyses. Both systems allow a prediction of the temperature at which, for example, 99.99 per cent of the parent compound has been destroyed for a given set of incinerator conditions. These systems can also be used to identify thermally stable products of incomplete combustion which also may be hazardous.

There are many advantages to generating fundamental thermal degradation data in the laboratory. First, such thermal degradation experiments are conducted safely, using microgram quantities of the sample in a properly equipped laboratory with an experienced staff. Second, data generated in the laboratory are much more precise and comprehensive than thermal degradation data generated in field-scale studies. Third, in the laboratory, thermal degradation data can be obtained quickly and economically.

The laboratory approach is particularly economical in that the guesswork and complexity involved in a trial burn are significantly reduced, thus greatly decreasing the probability of having to conduct a second burn. Furthermore, Environmental Protection Agency regulations require the identification of the principle organic hazardous constituents, those components of the waste streams that are most highly concentrated, toxic, and thermally stable. Such identification usually requires a costly chemical analysis of the waste sample. However, by first subjecting the sample to high temperatures, the most stable components can be identified, thus reducing the required chemical analysis from hundreds of compounds to less than a dozen. Their identity can be determined on the Thermal Decomposition Analysis System (TDAS) without additional analysis.

Instrumentation Development

The proficiency of the Environmental Sciences Group in ascertaining thermal degradation properties of organic compounds is the result of innovative application of state-of-the-art technology from a variety of technical disciplines. Since 1969, researchers in the Group have designed and assembled thermal instrumentation systems that are used to study the thermal degradation properties of hazardous wastes and other organic materials. Initially, thermal analysis systems were designed to obtain simultaneous analytical data on the thermal decomposition characterization of polymeric organic substances. As the Environmental Sciences Groups' ability to design thermal instrumentation became known, requests grew for the development of additional thermal systems that would determine thermal decomposition properties of pesticides, industrial organic wastes, and various environmentally sensitive organic materials.

In these thermal systems, high-resolution gas chromatography is the major technique used to analyze products or effluents. For example, the TDAS is a versatile system that incorporates a gas chromatography-mass spectrometer-computer downstream of a thermal decomposition unit, while the TDU-GC sys-

tem uses an in-line high-performance multifunctional gas chromatograph. With both laboratory systems, toxic organic substances can be studied and products of decomposition identified and quantified. These systems are designed so that the major thermal decomposition variables — exposure temperature, composition of atmosphere, mean residence time, residence time distribution, and reactor internal pressure — can be varied and experimentally evaluated.

Although these relatively sophisticated systems are the workhorses for the Environmental Chemistry Laboratory, other thermal systems are currently being developed to address more routine thermal degradation problems. Research grade systems being developed can be used to address very specific and complex questions associated with incineration and thermal degradation.

Chemical Analysis

The Environmental Chemistry Laboratory contains several systems which aid in the chemical characterization of complex organic samples. The LKB 2091 gas chromatograph-mass spectrometer and the Vista 44 gas chromatographic systems are used for surveying chemical analysis and identification of principal organic hazardous constituents and products of incomplete combustion in hazardous waste samples. Other gas chromatographic, analytical, and research grade systems are used to study specific problems in the analysis of very complex systems.

The Environmental Science Groups' proficiency in routine and survey chemical analysis is complemented by research activities in the analysis of highly complex mixtures of volatile organic compounds. Work being done in the Environmental Chemistry Laboratory includes research experiments and methods development work with high-resolution gas chromatographic columns and associated system components. In addition to using gas chromatographic techniques to analyze hazardous organic compounds of various types, sophisticated techniques for the chemical analysis of jet fuels and shale oil samples for the Air Force are being developed.

Facilities

Environmental Sciences Laboratories

The activities of the Environmental Sciences Group are performed in seven different laboratories which are located within the Eugene W. Ketterling Engineering and Research Laboratories. This building was constructed in 1969 on the University of Dayton campus, and an annex built in 1978 added laboratory and office space to the Research Institute's main facilities, bringing the total floor space in this facility to approximately 56,000 square feet. In addition, the Research Institute occupies slightly more than 58,000 square feet in other buildings of the University.

The seven laboratories of the Environmental Sciences Group are located in one interconnected complex and constitute approximately 2,100 square feet of floor space. Three of these laboratories are

dedicated to conducting thermal decomposition studies with special analytical instrumentation that has been designed and developed at the University of Dayton. Also, there is an Environmental Chemistry Laboratory and an Environmental Engineering Laboratory that are used for a variety of different tasks associated with experimental activities. In addition, there is a laboratory that is devoted to analytical instrumental research in the fields of high resolution gas chromatography and thermal instrumentation system development. The hub of this laboratory complex consists of a hazardous materials handling facility, which is fully equipped for dealing with toxic organic substances as it has a minimum of five levels of containment. This hazardous materials handling facility enhances our capability to prepare and analyze highly toxic organic substances.

EQUIPMENT LIST

Thermal Decomposition Equipment
Thermal Decomposition Analytical System

Thermal Decomposition Unit-Gas Chromatograph
Packaged Thermal Reactor System

Analytical Equipment

LBK Model 2091 GC-Mass Spectrometer

Varian Model 1800 Gas Chromatograph

Varian Model 2400 Gas Chromatograph

Varian Model 3700 (Modified)

Varian Model Vista 44 (Modified)

Tracor Model 550 (Modified)

Special Purpose Detectors

Tracor Model 310 and 550/700 A ECD

Computer Support

Digital Vax 11/780 (Accessible)

Univac 90/80-3 (Accessible)

Digital PDP 11/04

Versatec Printer

Tektronix 4012 Graphics Terminal

TI Silent 700 ASR Terminal

