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Project Summary

Catalytic Dehydrohalogenation: A Chemical Destruction Method for Halogenated Organics

Dehydrohalogenation shows potential as a means for converting certain halogenated organics in wastes to inorganic salts and gaseous aliphatic compounds.

Dehydrohalogenation is a dehalogenation/elimination reaction that is initiated by a strong base. The resulting products are the halide salt, water, and an elimination compound.

A novel reagent, sodium or potassium hydroxide mixed with a polyethylene glycol, is a very effective dehydrohalogenation agent. This reagent is shown to dehalogenate six organic compounds that are representative of low molecular weight compounds encountered in hazardous wastes: CCl_4, $CHCl_3$, CH_2Cl_2, $C_2H_4Br_2$, and CCl_3NO_2. Kinetics data for the reactions of this reagent with the six compounds is given to allow reactor design and calculation of destruction efficiency.

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 full documented in a separate report of the same title (see Project Report ordering information at back).
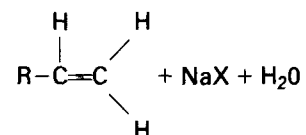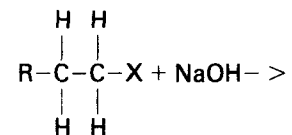
Introduction

Background

Halogenated organic compounds account for a major portion of toxic and persistent hazardous wastes. Various techniques have been proposed for destroying these constituents. Incineration is a widely used destruction techniques, but has limitations.

There have been other methods proposed and used for destroying halogenated species, such as ultraviolet (UV) and UV/ozone degradation, biotreatment with specially adapted microorganisms, and sodium metal reduction. Each of these techniques has shown promise for destruction (or transformation) of the halogenated species, and each of these technologies has certain applications wherein it is the method of choice.

Preliminary work has been initiated toward development of an alternate method for the destruction of halogenated organics that is based on a classical organic chemistry technique for dehalogenation. It involves reaction of the halogenated species with caustic to produce an elimination reaction. The products of the reaction are the halide salts, water, and a multiple bond on the organic molecule at the site of the dehalogenation.

$$
\begin{array}{cc}
H & H \\
| & | \\
R-C-C-X + NaOH-> \\
| & | \\
H & H
\end{array}
$$

$$
\begin{array}{cc}
H & H \\
| & / \\
R-C=C & + NaX + H_2O \\
& \backslash \\
& H
\end{array}
$$

This reaction mechanism is referred to as dehydrohalogenation.

Typical dehydrohalogenation reactions are carried out in an initially anhydrous system in the presence of solid caustic, or a small amount of water may be used as a catalyst. These conditions lead to very vigorous, and even uncontrollable, reactions. In order to make this technology useful for the treatment of hazardous waste, the following criteria must be met:

1. The reaction system must accommodate wastes containing water.
2. The reaction must be smooth and controlled.
3. The methodology must provide treatment efficiency equivalent to or exceeding existing treatment techniques.

The full report documents an experimental program to validate the treatment of halogenated waste compounds by means of a novel dehydrohalogenation reagent that meets the above listed criteria. This reagent, composed of caustic mixed with a relatively small quantity of polyethylene glycol, has been shown to be effective in rapid yet controlled dehydrohalogenation in organic syntheses. The polyethylene glycol acts as a catalyst in the reaction. In this program, the reagent mixture chosen for experimentation was potassium hydroxide (KOH) and tetraethylene glycol (TEG). This reagent will be referred to subsequently as KTEG.

Objectives

There were four objectives in this program:

1. Validation of the efficacy of KTEG to destroy ethylene dibromide,
2. General, qualitative observation of the reactivity of KTEG with a series of halogenated and nonhalogenated compounds to determine those showing promise for treatment with KTEG,
3. Determination of reaction kinetics data to allow design of treatment systems and calculation of treatment efficiencies, and
4. Conceptual design of a possible treatment system.

Experimental Program

The experiments for both the qualitative observations and the kinetic studies were carried out in a bench scale reactor system (Figure 1). The reactor vessel was a 1 L three-neck flask. Attached to the flask were a thermometer, a chilled reflux condenser, a sample withdrawal system, and a mechanical stirrer. The mechanical stirrer was used instead of a
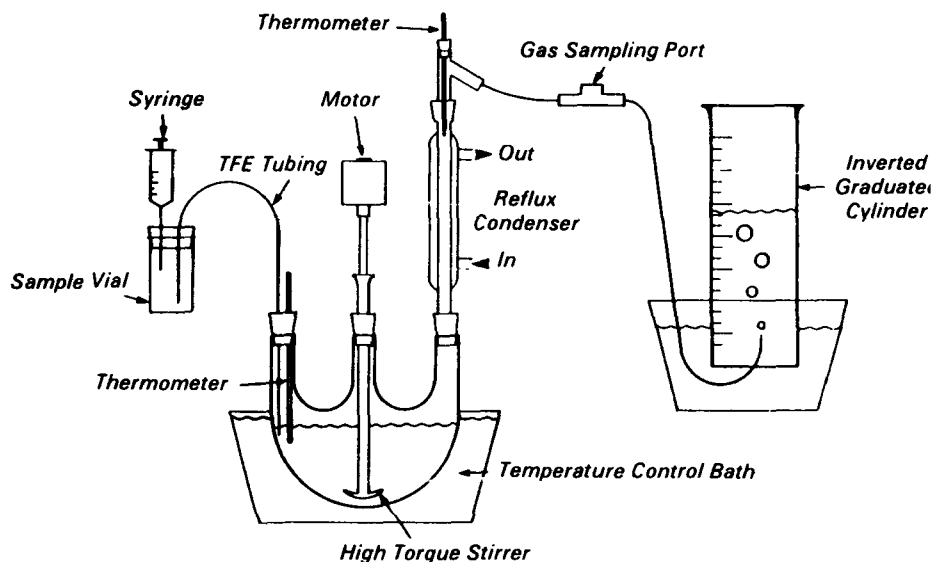

Figure 1. Experimental set-up.

magnetic stirrer because the density of the reaction mixture increased with time; if a magnetic bar were used it would become stalled in the slurry.

A typical run is outlined below: 280 g of potassium hydroxide (KOH) was dissolved in 180 mL water in the 500 mL 3-neck flask. A 5 mL portion of n-nonane was added to the flask as an internal standard. A 5 mL portion of ethylene dibromide (EDB) was added, the system was closed, and stirring was initiated. The system was observed closely for several minutes to assure that no reaction was taking place. An initial sample was taken from the reaction vessel, and then 10 mL of tetraethylene glycol (TEG) was added to the vessel.

Reaction began immediately, as evidenced by vigorous bubbling, and gas displacement versus time was plotted. Gas samples and liquid samples were taken at several intermediate reaction times and at the end of the reaction. After the gas evolution had stopped, an additional 5 mL portion of EDB was added to the reaction mixture, and the reaction resumed. The sampling and gas displacement readings were taken as before. The entire process was repeated until the mixture became too thick to stir and the reaction showed signs of slowing.

The reflux condenser was chilled to 0°C (±5°C) to prevent escape of the moderate boiling point halogenated species. Gases generated in the reaction passed through the reflux con-

denser and into the inverted graduated cylinder by means of a $\frac{1}{4}$" ID flexible tube. Gas samples were taken at the top of the reflux column through a septum closed sample port by means of a gas tight syringe.

Liquid samples were removed from the reactor through the suction mechanism shown in Figure 2. The empty sample vial was retained in place solely to prevent system pressure loss. Three mL of water was placed in a 5 mL sample vial and frozen. To remove a sample from the reacting mixture, the empty vial was removed and the syringe was filled with approximately $\frac{1}{2}$ mL of air. Static pressure within the sample tube would usually prevent any leakage of reactor contents during the sample via transfer. The vial containing the deionized ice was transferred to the syringe assembly, the $\frac{1}{2}$ mL of air pushed through to clear the sample line, and the syringe withdrawn 1 mL to create a suction and draw sample from the reaction flask into the ice vial. The sudden cold and dilution from the melting ice halted the reaction. This facilitated a reasonable delay in actually getting the sample to analysis. The samples were then refrozen for preservation. Such samples taken at intervals during the reaction provided process "snapshots" and enabled detailed determination of the reaction kinetics. Analyses of the gas and liquid samples were performed by GC FID.
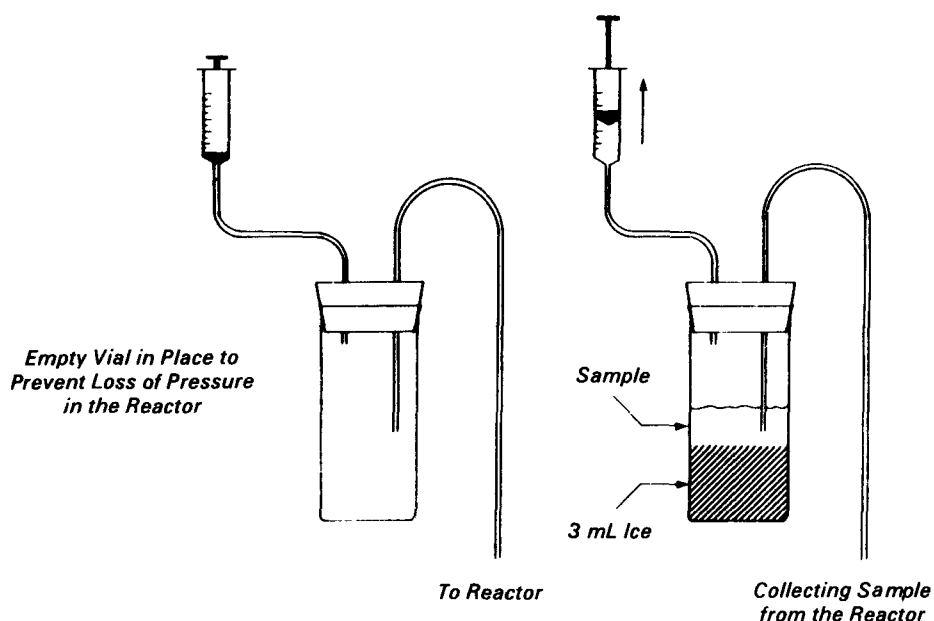
Figure 2. *Liquid sample collection.*

Labels in figure: *Empty Vial in Place to Prevent Loss of Pressure in the Reactor*; *Sample*; *3 mL Ice*; *To Reactor*; *Collecting Sample from the Reactor*

Results and Conclusions

General and Qualitative Observations

A total of seven compounds were tested in the dehydrohalogenation system. These compounds are listed in Table 1 along with qualitative descriptions of the results of the dehydrohalogenation. It should be noted that several chemicals appeared to react with the tetraethylene glycol (TEG) catalyst under the reaction conditions. The mechanisms for these non-catalytic TEG reactions are not known at this time, but such reactions always resulted in an overall slowdown of the desired dehydrohalogenation. Carbon disulfide, for example, a nonhalogenated test compound, stoichiometrically reacted with the TEG to form a sticky brown sludge; this reaction prevented all further reaction of the reagent with any halogenated compounds. Carbon tetrachloride and chloropicrin both showed evidence of slight consumption of the catalyst, but this did not seriously impair their dehalogenation. The effects of such compounds in real world situations can be overcome by addition of excess reagent.

Chloroform showed an unusual reaction with the TEG. The chloroform reacted vigorously when added to the system, and it evolved a large volume of gas very quickly. If a large volume of chloroform was added to the reactor, a gray-colored foam formed, and this foam solidified into a stable open-celled spongy material. A portion of this foam was cleaned with a series of solvents and analyzed by infrared spectroscopy (IR). From this cursory analysis, the foam appeared to be a substituted form of the TEG.

Chloroform could be added in small portions to the reactor without foam formation. However, under these conditions, the chloroform reacted smoothly and consumed a small amount of the TEG in a similar manner to CCl_4 and chloropicrin.

The reactions with ethylene dibromide and ethylene dichloride were fast, controlled, and showed no consumption of the TEG. The reaction products consisted of vinyl bromide or vinyl chloride, acetylene, and the halogen salt as a reactor residue.

Determination of Reaction Kinetics

The reaction rate constants for dehydrohalogenations by the KTEG reagent vary by temperature. Table 2 shows rate constants for six compounds over the temperature range of 21°-50°C.

These rate constants may be used to design reactors and to determine the reaction efficiencies for KTEG systems. Since this particular dehydrohalogenation reaction is a first order (or pseudo first order), nonreversible reaction, the level of destruction is dependent only upon time of contact of the halogenated compound and the KTEG reagent. This means that any desired level of destruction may be accomplished by designing the reaction system for proper residence times.

The values of k_a in Table 2 may be easily converted to other units as needed. For example, the rate constant for EDB at 21°C on a molar basis is:

$$90.2 \frac{\text{mL EDB}}{\text{mole TEG} \cdot \text{min}} \times \frac{2.179 \text{ g EDB}}{\text{mL EDB}} \times$$

$$\frac{1 \text{ mole EDB}}{187.87 \text{ g EDB}} = 1.05 \frac{\text{mole EDB}}{\text{mole TEG} \cdot \text{min}}$$

Reactor Design

Conceptual designs of reactors for treatment of halogenated wastes were developed by utilizing the kinetics data described above and the parameters listed below:

WASTE COMPOSITION	- 95% CCl_4, 5% EDB (V/V)
REACTOR TYPE	- (A) Plug flow, tubular (B) Batch
OPERATION TEMPERATURE	- 50°C
FEED RATE	- (A) 1 gal/min (B) 60 gal/hr
DESTRUCTION EFFICIENCY	- 99.999% of the EDB

Table 3 shows the necessary lengths for a tubular, plug-flow reactor according to the tubular inner diameter.

Alternately, a batch reactor sized to handle a feed rate of 60 gallons per hour would have a volume of 550 to 600 gallons. The batch reactor could operate at atmospheric pressure, and it could be fitted with manual or automatic valves for filling and discharging the reactor contents.

A practical design for any dehydrohalogenation waste treatment reactor must be based on realistic considerations of material costs and reactor size as well as its capability for achieving the desired treatment efficiency. The ultimate cost of treatment of a unit volume of waste is determined by adding all associated costs (system construction, operation, waste disposal, etc.), and dividing that sum by the volume of waste treated. Thus, even though operating costs of a continuous feed process are generally lower than those of a batch feed process, the high initial cost of the tublar reactor might never be offset, if there were relatively small volumes of waste to be treated.

Table 1. Compounds Investigated

Chemical	Results
Carbon disulfide (CS$_2$)	Quantitatively reacts with the TEG to form a brown sludge.
Methylene chloride (CH$_2$Cl$_2$)	Reacts slowly. Consumes some TEG.
Chloroform (CHCl$_3$)	Rapid, uncontrollable reaction if added too quickly. Forms a stable, open-celled foam. Slow addition produces a controlled reaction without foam formation. Consumes some TEG.
Carbon tetrachloride (CCl$_4$)	Moderate reaction rate. Consumes some TEG.
Ethylene dichloride $\left(\begin{array}{c} Cl\ Cl \\ \vert\ \vert \\ -C-C- \\ \vert\ \vert \end{array}\right)$	Fast but controlled reaction. No evidence of reaction with TEG.
Ethylene dibromide $\left(\begin{array}{c} Br\ Br \\ \vert\ \vert \\ -C-C- \\ \vert\ \vert \end{array}\right)$	Slightly faster rate than with EDC, but still controlled. No TEG consumption.
Chloropicrin $\left(\begin{array}{c} Cl \\ \vert \\ Cl-C-NO_2 \\ \vert \\ Cl \end{array}\right)$	Moderate reaction rate. Consumes some TEG.

Table 2. Reaction Rate Constants by Temperature

Compound	k_a (mL Constituent/mole TEG · min)			
	21°C	30°C	40°C	50°C
Ethylene dibromide (EDB)	90.2	153	267	449
Ethylene dichloride (EDC)	102	163	265	419
Carbon tetrachloride	16.0	22.3	31.6	43.7
Chloroform	9.8	21.3	48.0	103
Methylene chloride	0.10	0.36	1.36	4.78
Chloropicrin	5.72	N/D	N/D	N/D

N/D = no data.

Table 3. Representative Tubular Reacto Lengths

Diameter (in.)	Length (ft
2	1,056
4	264
6	117
8	86
10	42
12	29

Modification of key design param ters, such as temperature of operatio or feed rate, could change the size re quirements of the tubular reactor suff ciently to make it more cost effective a a treatment system design. The desig parameters of a dehydrohalogenatio reactor system must be derived on case-by-case basis for the specifi wastes to be treated. This may be don by using techniques similar to those de scribed in the full report.

Recommendations

Dehydrohalogenation technology i to be developed and evaluated as a pos sible alternative treatment of halocai bon wastes. In determining the relativ advantages and disadvantages of thi technique, it is necessary to compare to existing treatment methods.

The potential advantages of dehydro halogenation include cost, energy sav ings, materials recovery, and the nor production of harmful by-product Dehydrohalogenation by-products ten to be hydrolysis products of the parer molecule; it is highly unlikely that com plex aromatic species will be produce in these reactions. The potential disac vantages of dehydrohalogenation in clude the production of waste gases, or ganics, and brine that may requir disposal.

Future research with this techniqu should explore its practicality for treat ment of contaminated soils and fo scrubbing halocarbons from gaseou streams. The technique should b tested on actual wastes, such as distilla tion bottoms from chlorinated solven recycle, to determine the effects of com plex waste matrices on the treatmen efficiency of the technique.