

Short communication

Amine promoted, metal enhanced degradation of Mirex under high temperature conditions

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Abstract

In this study, zero-valent metal dehalogenation of mirex was conducted with amine solvents at high temperatures. Mirex was treated with excess amine in sealed glass tube reactors under nitrogen. The amines used were *n*-butyl amine (l), ethyl amine (l), dimethyl amine (g), diethyl amine (l), triethyl amine (l), trimethyl amine (g) and ammonia (g). The metals used were copper, zinc, magnesium, aluminum and calcium. The most suitable amine solvent and metal were selected by running a series of reactions with different amines and different zero-valent metals, in order to optimize the conditions under which complete degradation of mirex takes place. These dehalogenation reactions illustrated the role of zero-valent metals as reductants, whereas the amine solvents acted as proton donors. In this study, we report that mirex was completely degraded with diethyl amine (l) in the presence of copper at 100 °C and the hydrogenated products accounted for more than 94 of the degraded mirex.

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1. Introduction

Mirex (C₁₀Cl₁₂) is a man made compound, hence all environmental contamination is attributed to the manufacture and use of this compound. Mirex is a white crystalline, free flowing, odorless solid with a molecular mass of 545.6 g/mol and a melting point of 485 °C at which temperature decomposition occurs [1,2]. Mirex is insoluble in water, but is soluble in organic solvents such as benzene, carbon tetrachloride, dioxane, methyl ethyl ketone and xylene [1,2]. This compound is non-flammable and is unaffected by sulfuric, nitric or hydrochloric acid and has a density of 2.002 ± 0.005 g/cm³ at 24.3 °C. In the early 1960s, mirex was used as a fire ant bait in nine southeastern states including Florida, Georgia, South Carolina, North Carolina, Alabama, Mississippi, Louisiana, Texas and Arkansas [3]. In addition, it has also been used against leaf cutter ants in South America and harvester termites in South Africa [3]. As a consequence, environmental contaminations resulted from using the

compound in pesticide formulations on large areas of land [3]. Mirex is readily adsorbed on suspended solid particles that may be ingested by aquatic organisms, thereby ultimately entering the human food chain [4]. Mirex will usually migrate to portions of biological organisms that are high in fats and oils. This bioaccumulation, along with non-biodegradability [4], make this compound of special concern for ecological and health considerations. This compound has been found to be quite stable in the environment and may have a half-life of a decade or more [4].

Although mirex is known to have a high degree of chemical and biological stability, different dehalogenating methods have been developed in which mirex loses one or more chlorine. It was shown by Alley et al. [5] that irradiation of mirex in hydrocarbon solvents like cyclohexane or isooctane with a Hovonia 450 W, medium pressure mercury lamp, produced monohydro and dihydro products. Also, it was shown [6] that mirex degraded under anaerobic conditions using sewage sludge microbes to give a monohydro product. Studies of degradation of mirex with an iron(II) porphyrin model were conducted by Holmstead [7] and showed that mirex reacts with reduced hematin to yield products formed from reductive dechlorination which included mono-,

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di-, tri- and tetrahydro derivatives. Pittman and Tabei conducted a study for dechlorinating mirex showing that polyethylene glycol (PEG) or tetraethylene glycol (TEG)/KOH can be used with either sodium borohydride or alkoxyborohydrides to provide a very powerful reducing medium, which destroys mirex [8]. Nevertheless, these investigations did not indicate whether mirex degraded completely or not. Also, they did not account quantitatively either for the mirex destroyed or the hydrogenated products obtained.

The goal of this investigation was to develop a system to remediate mirex completely. The dehalogenation of mirex was conducted at high temperatures over metals such as copper, zinc, etc. in sealed glass tubes (reactors) in the presence of amine solvents under inert conditions. The relative dehalogenating abilities of the solvent amines used were compared by calculating the percentage of mirex destroyed in each case and the percentages of the dechlorinated products obtained. The identities of the dechlorinated products were confirmed using gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS).

2. Methods and material

2.1. Dechlorination procedure

The amounts of metal and mirex used were 0.156 and 0.092 mmol, respectively. Mirex (high degree of purity >96%) was obtained from Mississippi State Chemical Laboratory (MSCL). Five different metals were used in the reaction, four of which were powder like, flammable, corrosive, solids namely zinc, aluminum, magnesium and copper. The fifth metal used was calcium, which was a granular, flammable, corrosive solid. All metals were obtained from Sigma–Aldrich, USA and were of high purity (>99%). The amounts of mirex and metal were inserted inside a glass tube 0.6 cm inner diameter, around 20 cm in length and sealed at one end. The volume of the glass tube was around 5–6 cm³. The volume of the liquid amine solvent used was 0.5 mL. The amines used for this dehalogenation reaction were *n*-butyl amine (l), diethyl amine (l), dimethyl amine (g), triethyl amine (l), trimethyl amine (g) and ammonia (g). All were obtained from Sigma–Aldrich, USA and were of high purity (>99%). These amines are considered to be dangerous and toxic if swallowed, inhaled or absorbed through the skin by affecting the cardiovascular system, central nervous system, liver and kidneys. They are also corrosive, causing burns to skin, eyes and respiratory tract. Thus, working under a chemical fume hood and wearing chemical resistant and impervious gloves is a must. The glass tube was flushed with nitrogen gas to insure an inert medium. Rotating the glass tube (reactor) uniformly above the flame, it was sealed. The sealing of the glass has to be done symmetrically with no accumulation of glass at any point; otherwise, the accumulation of glass will cause weak spots in the glass tube causing the tube to burst due to pressure build up inside the tube upon heating. The contents of the reactor tube were mixed by shaking the reactor tube after which it was placed inside a metal pipe, which had two pin holes drilled symmetrically at its end caps. Finally, the metal pipe contain-

ing the glass reactor tube was placed in an oven at the desired temperature for the desired time. When the time of the reaction was over, the metal pipe was removed cautiously from the oven. After cooling, the reactor glass tube was removed from the metal pipe. Breaking the glass tube at one end, the ingredients were emptied into a separatory funnel; the glass tube was washed with 5 mL of water followed by 5 mL of methylene chloride. Separation was done using this separatory funnel where the organic layer was drained into a 10 mL volumetric flask and the aqueous layer was discarded. By adding methylene chloride to the volumetric flask, the solution was brought up to the 10 mL mark, and the sample was analyzed by gas chromatography.

Certain precautionary steps had to be followed when working with gaseous amines. The glass tube (reactor), already containing the amounts of mirex and metal, was placed in a dewar filled with dry ice and methylene chloride. By using a mini bore Teflon tubing connected to the gaseous amine cylinder, the amine gas condensed in the glass tube (0.5 mL). The glass tube was transferred directly to another dewar flask filled with liquid nitrogen where the gaseous amine solidified (prevent evaporation of amine). Keeping two thirds of the glass tube (reactor) in liquid nitrogen and rotating uniformly, it was sealed. After which, the same steps described before were followed.

2.2. Analytical procedure

There are well-established methods in the literature for analysis of chlorocarbons and chlorinated hydrocarbons [9]. Gas chromatography using a capillary column and flame ionization detector (FID) was the analytical technique used in this study. Concentrations of analytes were relatively high in this study; therefore, FID was sufficiently sensitive for this purpose. Internal standard techniques were routinely employed. The internal standard tetradecane was obtained from Sigma–Aldrich, USA. In addition, the following compounds were used as standards for identification and calibration (10 monohydro mirex; 5,10 dihydro mirex; 10,10 dihydro mirex; 2,8 dihydro mirex; 8 monohydro mirex). All of these compounds were obtained from MSCL and mirex derivatives had a high degree of purity (>96%).

Quantitative calculations were done in this study in order to account for the amount of mirex destroyed and the amount of mirex derivatives formed. For this purpose, a solution of internal standard in methylene chloride of concentration 1.0 mg/mL was prepared and used for extraction. The internal standard was tetradecane. To determine the amount of each desired component in the sample, a standard solution was prepared by dissolving a known weight (around 0.050 g) of the standard (mirex and mirex derivatives) in 10 mL of internal standard solution (1.0 mg/mL). The response factor, *F*, of the desired component was calculated from the standard solutions prepared and the following equation was used [10]

$$F_c = \frac{\text{weight of standard/weight of internal standard}}{\text{peak area of standard/peak area of internal standard}} \quad (1)$$

Table 1
Statistical calculations of response factors

Standard	Average F_c	Relative standard deviation (RSD, %)	Times
Mirex	0.664	0.50	20
10 Monohydro mirex	0.674	0.52	10
8 Monohydro mirex	0.662	0.56	10
2,8 Dihydro mirex	0.666	0.51	10
5,10 Dihydro mirex	0.672	0.45	10
10,10 Dihydro mirex	0.676	0.59	10

Then the weight of the desired component, W , in the unknown can be calculated using

$$W = \frac{\text{area of component} \times \text{weight of internal standard}}{\text{area of internal standard} \times \text{response factor}} \quad (2)$$

Standard solutions were injected to recalibrate the system before, during and after every series of analyses to insure the response factors being employed were accurate and not fluctuating. The statistical calculations of the response factors corresponding to each component are shown in Table 1.

2.3. Instrumentation

A Varian model 3300 temperature programmed GC equipped with a fused-silica bonded-phase capillary column (30 m, 0.53 mm i.d., DB-5) and an FID detector was used to analyze the experimental samples. In addition, a Finnigan GC Quadrupole MS model 4500 instrument was used. Product identification was based on retention times and MS spectra. The temperature program used to separate the analytes on the GC was set as follows: the temperature of the column was set at 80 °C and held at this temperature for 2 min, then heated to 300 °C at rate of 15 °C/min. The injector was set at 280 °C. Carrier gas utilized was hydrogen gas at 2.0 mL/min. The GC/MS separation conditions were: Column type: DB-5; 30 m; 0.25 mm i.d.; 0.25 μm film thickness; splitless injection; carrier gas: He; flow 1.0 mL/min; injector temperature: 280 °C; oven temperature program: the temperature of the column was set at 80 °C and held at this temperature for 2 min, then heated to 300 °C at rate of 15 °C/min; quadrupole temperature: 300 °C.

3. Results and discussion

3.1. Destruction of mirex using different metals

The structures of mirex and its derivatives are shown in Fig. 1. The retention times (r.t.) for these compounds are as follows; mirex (1) (r.t. 14.99 min.), 10 monohydro mirex (2) (r.t. 13.75 min.), 5,10 dihydro mirex (3) (r.t. 13.23; 13.16 min), 10,10 dihydro mirex (4) (r.t. 12.87 min.), 2,8 dihydro mirex (5) (r.t. 2.65 min) and 8 monohydro mirex (6) (r.t. 13.45 min). Using *n*-butyl amine and mirex, reactions were conducted with five different metals (Ca, Mg, Zn, Al and Cu) at 100 °C for 1 h. *n*-Butyl amine was selected for these reactions because it was easy to handle (liquid form). The main goal of these reactions was to select the metal that would best enhance the complete destruc-

tion of mirex. The samples were not analyzed by GC/MS. No internal standard was used in analyzing the reactions, so quantitative calculations were not possible. The conclusion drawn from these reactions was only based on qualitative analysis. The chromatograms were scanned to see if mirex with r.t. 14.99 min was still present (not completely destroyed) or was not present (completely destroyed). Traces of mirex were still present in the cases of all metals except for copper where complete destruction of mirex was achieved. Zero-valent metals have been observed to dehalogenate some chlorinated organic compounds in aqueous solutions [11]. In the literature found, iron was the metal of choice for most testing because it is inexpensive and environmentally innocuous. Other metals like zinc, aluminum, copper, palladium and tin, particularly zinc and tin can degrade chlorinated compounds much more rapidly than iron [12]. The set of reactions conducted in this section have qualitatively shown that copper was the most efficient zero-valent metal in completely degrading mirex. The role of copper as a zero-valent metal in the dehalogenation of mirex will be further discussed in Section 3.2. It is worth mentioning that mirex did not degrade in the absence of a zero-valent metal (peak area of mirex remaining in the absence of a metal is very large compared to that of mirex remaining when metals were used).

3.2. Dehalogenation of mirex using different amines

A reaction using mirex, 0.092 mmol and copper, 0.156 mmol, was conducted with each one of the amine solvents (listed in Section 2.1) at 100 °C for 1 h. These reactions were conducted in order to study the relative dehalogenating abilities of the amines. As seen in Table 2, the main products of these reactions were mono- and dihydro-mirex derivatives. The identification of these products was confirmed by comparing the retention times of

Table 2
Dehalogenation of mirex using amines

Amine used	Mirex remaining (%)	Mirex derivative produced (%)
<i>n</i> -Butyl amine (l)	Not detected	10 Monohydro mirex (2) 2.7% 5,10 Dihydro mirex (3) 25.1%
Ethyl amine (g)	Not detected	5,10 Dihydro mirex (3) 35.7%
Diethyl amine (l)	Not detected	10 Monohydro mirex (2) 51.4% 5,10 Dihydro mirex (3) 35.2% 10,10 Dihydro mirex (4) 7.6%
Dimethyl amine (g)	Not detected	8 Monohydro mirex (6) 2.9% 5,10 Dihydro mirex (3) 29.1%
Triethyl amine (l)	78.6	None
Trimethyl amine (g)	83.5	None
Ammonia (g)	93.6	None

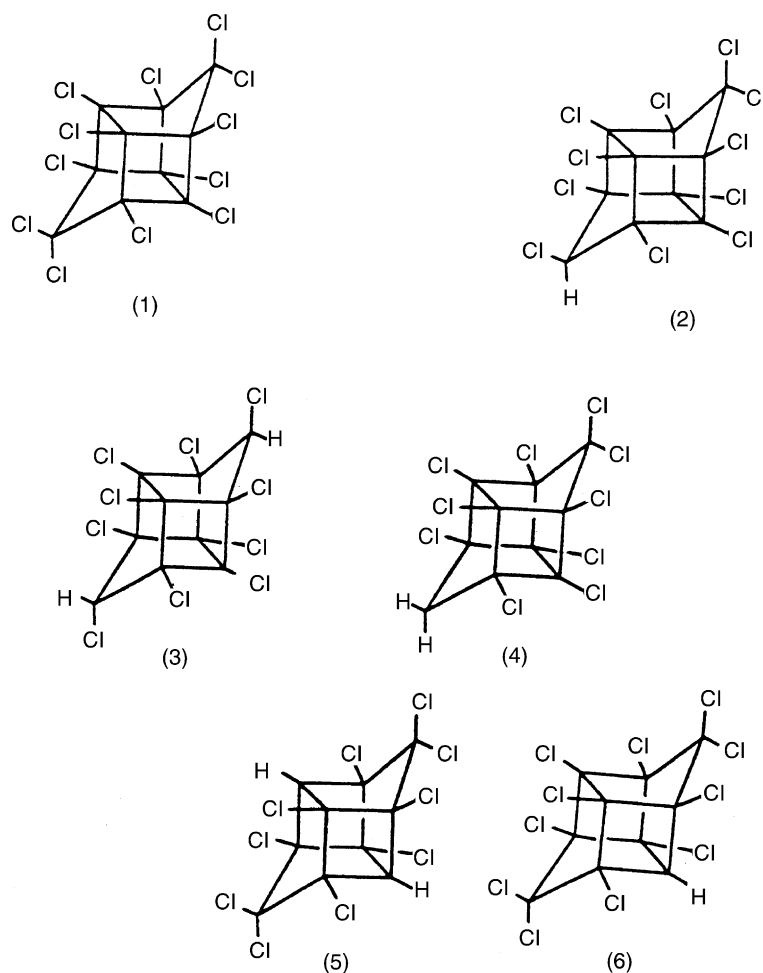


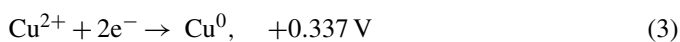
Fig. 1. Structures of mirex and its derivatives. Mirex (1), 10 monohydro mirex (2), 5,10 dihydro mirex (3), 10,10 dihydro mirex (4), 2,8 dihydro mirex (5) and 8 mono-hydro mirex (6).

authentic derivatives. Fig. 2a is a chromatogram of the reaction between mirex and copper in the presence of diethyl amine at 100 °C for 1 h. The following retention times were observed; 10 monohydro mirex 13.75 min, 5,10 dihydro mirex 13.23 min; 13.16 min and 10,10 dihydro mirex 12.87 min with tetradecane (internal standard) at 6.69 min. The chromatogram indicated clearly the complete degradation of mirex (no peak at 14.99 min) and the formation of mirex derivatives. This reaction was also analyzed by GC-MS. The identity of compounds (2–4) was confirmed by matching their spectra with the spectra of standards. Fig. 2b shows the MS spectra of 10 monohydro mirex derivative $C_{10}Cl_{11}H$ giving cyclopentadiene isotope pattern consistent with $C_5Cl_5^+$ (molecular ion) at m/z 237.6; in addition, the isotopic abundance ratio of the cluster indicated the presence of five Cl atoms. Similarly, both Fig. 2c and d showed the presence of 5,10 dihydro mirex $C_{10}Cl_{10}H_2$ and 10,10 dihydro mirex $C_{10}Cl_{10}H_2$ with cyclopentadiene isotope patterns appearing at m/z 237.5 ($C_5Cl_5^+$ molecular ion) and at m/z = 203.7 ($C_5Cl_4H_2^+$ molecular ion), respectively. From the data illustrated in Table 2, it is shown that primary and secondary amines have a relatively good ability to degrade mirex; because in cases where they were used, mirex disappeared completely. However, in the case of tertiary amines and ammonia the relative dehalogenating

ability dropped remarkably with only 8–20% of mirex disappearing. Although the dehalogenating ability of primary amines and dimethyl amine was high, a lot of material in form of lumps were produced and were not soluble in methylene chloride; thus they were not identified. In the case of diethyl amine, doing a mass balance accounting for mirex was possible since 94% of the degraded mirex was accounted for. Thus, diethyl amine gave the best dehalogenation and mass balance.

3.3. Mechanism of the dehalogenation reaction

Mirex was dehalogenated by copper metal in the presence of diethyl amine, acting as an appropriate proton donor. The redox couple formed by zero oxidation state metallic copper, Cu^0 , and dissolved, Cu^{2+} , has a standard reduction potential of +0.337 V [13]



The estimated standard reduction potential for aliphatic alkyl halides (methanes, ethanes and ethylenes) is greater than +0.5 V at pH 7 [14]. Since mirex is a chlorinated aliphatic compound,

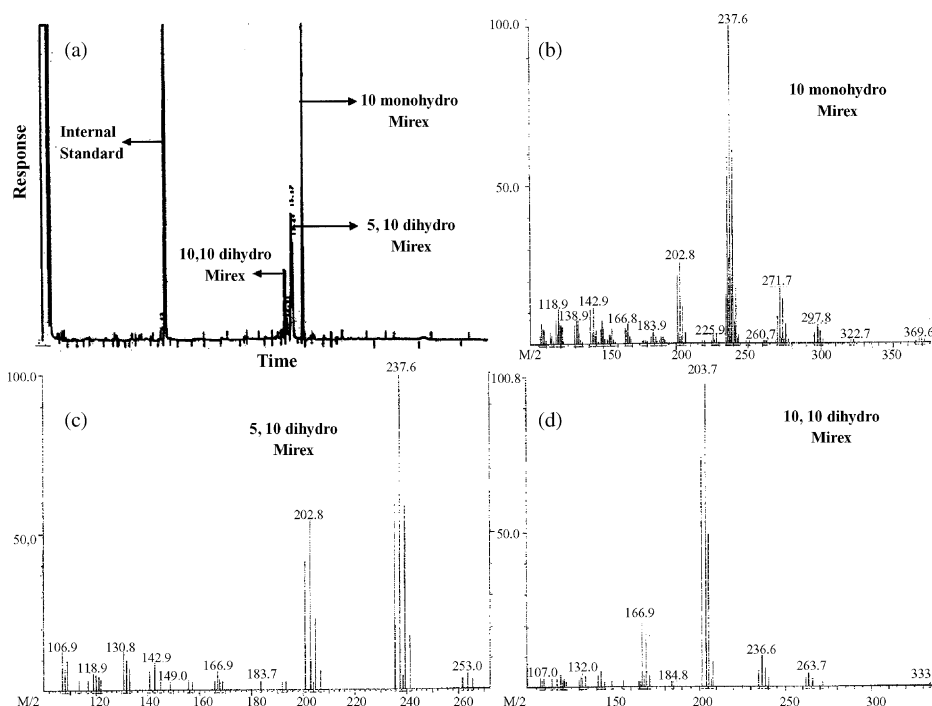
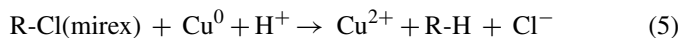


Fig. 2. (a) Dehalogenation reaction of diethyl amine with mirex at 100 °C for 1 h with copper. (b–d) GC/MS spectra for 10 monohydro mirex; 5,10 dihydro mirex; 10,10 dihydro mirex, respectively.

its standard reduction potential is definitely greater than +0.5 V



Thus, the net reaction (Eq. (5)) of Eqs. (3) and (4) is thermodynamically very favorable (ΔG° is negative in this case; spontaneous reaction) under most conditions



The need for proton donors such as primary and secondary amines is very essential for the production of hydrogenated mirex (R-H). This is clearly illustrated in Table 2 where neither monohydro mirex nor dihydro mirex derivatives were produced in the case of trimethyl amine and triethyl amine since neither is a hydrogen/proton donor.

When ammonia was used, the relative dehalogenation ability dropped drastically. This is due to the strong hydrogen bonding interaction between nitrogen and hydrogen, which makes it difficult for ammonia to be a proton donor; as a result, hydrogenated mirex products were absent. As methyl and ethyl groups replace the hydrogens in ammonia, the partial charge on nitrogen will decrease and the hydrogen bond between nitrogen and hydrogen will weaken. In case of ammonia, the partial charge on nitrogen is -1.05 , and this value decreases in the case of dimethyl amine (-1.00) and diethyl amine (-0.85) [15]. Also, the deprotonation reaction in the case of dimethyl amine ($\Delta H^\circ = 1658 + 3.8$ kJ/mol) is thermodynamically favored in comparison to the deprotonation reaction in case of ammonia ($\Delta H^\circ = 1688 + 3.3$ kJ/mol) [16]; thus making dimethyl amine a better proton donor than ammonia (Table 2).

4. Conclusion

Although many dehalogenation reactions of mirex have been studied by previous investigators, this study was an attempt to implement a zero-valent metal/amine system in dehalogenating mirex. This system, which combined both copper and diethyl amine at high temperature worked in degrading mirex completely and 94% of the remediated mirex was accounted for. Mirex is an aliphatic chlorinated compound; as a consequence, currently this system is being tested with aromatic and olefinic chlorinated compounds and the preliminary results are promising. This dehalogenating system might be tested in the future to remediate soils contaminated with chlorinated compounds by mechano-chemical dehalogenation. This could be achieved by combining the contaminated soil with both the zero-valent metal and the amine solvent in a ball mill where an intense mixing of these components will take place at the desired temperature for the desired time. However, this proposed application should show to be cost effective and environmentally friendly (no gas emissions; no release of contaminants) before its implementation in full-scale remediation of contaminated soils.

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