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The complete dechlorination of DDT by magnesium/palladium bimetallic particles

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Abstract

The complete dechlorination of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) by a magnesium/palladium bimetallic system has been accomplished. The reaction takes place under ambient temperature and pressure and mild reaction conditions requiring only 0.25 g of magnesium and 0.3% palladium (wt/wt) to drive the dechlorination of 100 μg DDT (50 ppm in 2 ml). The process is both rapid and complete requiring less than 10 min to attain total dechlorination within the detection limit (~10 pg for DDT) of electron capture detection gas chromatography (GC-ECD). The major product formed, as deduced from mass spectrometry (GC–MS) is the hydrocarbon skeleton, 1,1-diphenylethane. This technology may allow for the development of an economic and environmentally benign method of DDT remediation. © 2001 Published by Elsevier Science Ltd.

Keywords: Pesticide; Zero-valent; Hydrodehalogenation; Diphenylethane

1. Introduction

Over the past two decades there has been a strong movement to discontinue the use of numerous pesticides, and the search for remediation methods addressing existing pesticide accumulation has been pursued with fervor (Hitchman et al., 1995; Renner, 1998). DDT use in USA began in 1939 and continued extensively until its ban in 1972. Today, due to its effectiveness and low cost, it remains the chemical of choice for combating mosquitoes in Malaria infested areas of the world. DDT has proven to be especially recalcitrant because of its chemical stability and poor soil mobility. Currently, there is no single method that can satisfactorily address the remediation of DDT. One approach that holds promise, however, is dechlorination. It is generally accepted that by removing the chlorine from DDT, the hydrocarbon backbone that results is far less toxic. In contrast with the present method of disposal, chemical dechlorination may prove to be a low energy alternative to high temperature incineration.

Recent literature has not indicated that rapid and complete dechlorination of DDT has been achieved. Furthermore, many methods involve complicated procedures such as anaerobic conditions, high energy input, or several hours or even days to reach completion (Sherman et al., 1971; Otero and Rodenas, 1986; Hall et al., 1996; Sayles et al., 1997; Wei, 1999). The method described in this communication is rapid, simple, and complete under room temperature and pressure conditions and thus represents a promising step towards an ideal mechanism for DDT destruction.

The method is based on the reduction potential of magnesium metal coupled with the catalytic activity of small amounts of palladium. This system reduces the

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chlorinated organic compound to its hydrocarbon skeleton

$$\text{R–Cl} + \text{H}^+ + 2\text{e}^- \rightarrow \text{R–H} + \text{Cl}^-, \quad E^0 = 0.5\text{–}1.5\ \text{V S.H.E.} \tag{1}$$

This reductive process has been studied in a similar system consisting of iron and palladium and has been demonstrated by Grittini et al. (1995) to effectively dechlorinate polychlorinated biphenyls (PCBs), and by Muftikian et al. (1995) to dechlorinate trichloroethene (TCE) and other chlorinated organic compounds. Like iron, magnesium ions are environmentally benign, but magnesium was chosen for this work for several reasons. It has a greater thermodynamic driving force, which is illustrated by a comparison of reduction potential:

$$\text{Mg}(0) \rightarrow \text{Mg}^{2+} + 2\text{e}^-, \quad E^0 = -2.2\ \text{V vs S.H.E.} \tag{2}$$

$$\text{Fe}(0) \rightarrow \text{Fe}^{2+} + 2\text{e}^-, \quad E^0 = -0.44\ \text{V vs S.H.E.} \tag{3}$$

However, the key advantage palladized magnesium holds over iron, and palladized iron, is that dechlorination by Mg/Pd takes place in the presence of oxygen and does not require any surface pretreatment. In all instances of successful dechlorination by zero-valent or palladized iron, reactions require anaerobic conditions and careful surface pretreatment with acid (Grittini et al., 1995; Muftikian et al., 1995; Sayles et al., 1997; Doyle et al., 1998; Fennelly and Roberts, 1998). Such advantage of Mg(0) over Fe(0) may be due the relative solubility of its hydroxide ($\text{pK}_{\text{sp}}\ \text{Mg(OH)}_2 = 11.15$) vs that of iron's ($\text{pK}_{\text{sp}}\ \text{Fe(OH)}_2 = 15.1$). The increased hydroxide solubility may decrease the tendency towards passivation thus increasing metal reactivity.

Uncatalyzed zero-valent iron alone has been demonstrated to dechlorinate DDT, however, palladized magnesium is vastly superior with regard to reaction time requiring 10 min compared to several hours or days for the former (Sayles et al., 1997). On a semipreparative scale, both iron and magnesium are relatively inexpensive and comparable in cost. Furthermore, field-scale handling of magnesium will prove more economical since aerobic degradation of Mg/Pd is not an issue as it is with Fe(0) or Fe/Pd.

In a previous investigation, Cheng et al. (1997) proposed a detailed mechanism to explain the role of the palladium in the hydrodehalogenation process. It is based on the ability of palladium to intercalate hydrogen, which in turn acts as a powerful reducing agent at the palladium/zero-valent metal interface, where chlorinated organic compounds are likely adsorbed. This model includes the presence of protons in solution and therefore requires aqueous or mixed organic/aqueous solvents. In mixed solvents, the addition of small amounts of a weak acid increases proton availability for hydrogenation.

2. Experimental

2.1. Dechlorination solutions

Dechlorination solutions began with the addition of 100 μg DDT (isomer mix, purchased from Chem Service, Westchester, PA) to a 5 ml vial containing 0.25 g of 20 mesh magnesium metal (Aldrich, Milwaukee, WI) and 2.5 mg of K_2PdCl_6 (Alfa, Ward Hill, MA) (0.27% wt/wt Pd/Mg). The magnesium was washed with acetone prior to use in order to remove any adsorbed organic compounds, then stored in an airtight container. This mix was then diluted to 2 ml such that the final solution was 50 ppm DDT in 50/50 percent (v/v) acetone/water. Finally, 1 drop of glacial acetic acid was added. The vial was then shaken vigorously for several seconds and vented to allow for the escape of hydrogen gas. Deposition of the palladium onto the magnesium ensued spontaneously after addition of the aqueous component. After 10 min, the dechlorination products were extracted into 1 ml of hexane and immediately analysed by GC-FID, GC-ECD and GC–MS.

2.2. Sample analysis

FID analyses were performed on a Hewlett Packard 5890 gas chromatograph equipped with an Alltech EC-5 capillary column of 0.320 mm ID, 0.25 μm film thickness and 30 m length. ECD analyses were performed on a separate Hewlett Packard 5890 gas chromatograph equipped with a Alltech AT-5 capillary column also of 0.320 mm ID, 0.25 μm film thickness and 30 m length. Injection was made in splitless mode with a 30 s purge delay for both instruments. Carrier gas and make-up gas were helium for FID, and nitrogen for ECD at flow rates of 3.0 and 30 ml/min (carrier/make-up) for both. The following temperature program was used for the chromatograms in Figs. 1(a)–2(b): the initial temperature of 100°C was held for 3 min, then ramped at 10°C/min up to the final temperature of 275°C for 9.5 min. Mass spectrometry was performed on a Hewlett Packard 6890 gas chromatograph equipped with a JOEL JMS-AX505HA mass spectrometer and a 30 m HP-5 capillary column (320 μm ID, 0.25 μm film). The helium carrier gas flow rate was set at 3.0 ml/min. The injection port was utilized in splitless mode with a 45 s purge delay and maintained at 270°C. The temperature program ramped from 125–275°C at a rate of 5°C/min and was held for 5 min at the initial and final temperatures. 70 eV electron impact ionization was used with a source temperature of 200°C.

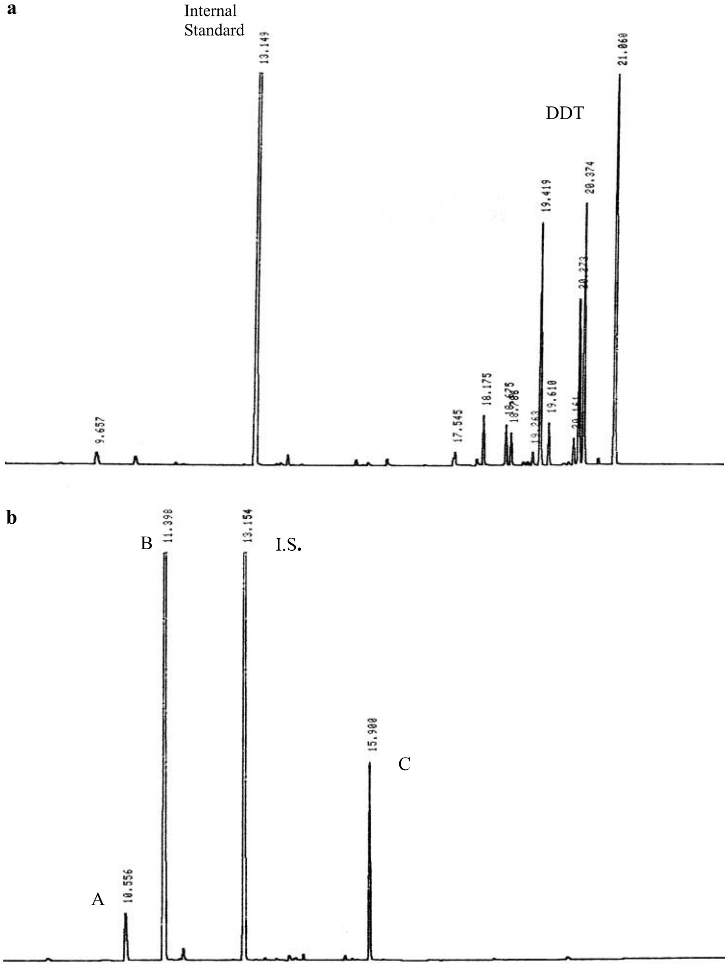

Fig. 1. (a) GC-FID of 330 ng DDT with 160 ng internal standard (area 48,750). 4-chlorobiphenyl (BZ#3) was used as the internal standard for all chromatograms; (b) GC-FID of 330 ng DDT after dechlorination by the Mg/Pd bimetallic system with 160 ng I.S. (area 48,372). Peaks A–C were identified by GC–MS as diphenyl methane (A); 1,1-diphenylethane (B); and tetraphenylbutane (C, speculative).

3. Results and discussion

Figs. 1(a)–2(b) illustrate the efficiency of this system. A 100 μg sample (2 ml at 50 ppm) of DDT is completely dechlorinated by the Mg/Pd bimetalic within the detection limit of GC-ECD (~10 pg). The ECD chromatogram in Fig. 2(b) clearly shows not only the complete destruction of DDT but also the absence of any partially dechlorinated by-products. Multiple samples were analysed with similar results. A control solution consisting of the magnesium metal alone proved to be ineffective – no decrease in DDT nor appearance of product was observed over several hours. A detailed mass balance was not possible without the existence of dechlorination product standards. The dechlorination products are, however, easily detected by GC-FID (Fig. 1(b)), and identified by mass spectrometry. All three of the major products detected display base peaks at *m/z* 167 of the electron impact mass spectra. These correspond to diphenylmethane, which for peak A (Fig. 1(b)) is also the molecular ion. Comparison of the peak A mass spectrum with that of diphenylmethane from the NIST database bears a near identical resemblance. The presence of the molecular ion at *m/z* 182 in the peak B mass spectrum led to its identification as diphenylethane, the hydrocarbon backbone of DDT. This is the major product of DDT dechlorination. It is speculated that peak C is tetraphenylbutane due in part to strong similarities between its mass spectrum and that of diphenylmethane, and also to the longer chromatographic retention time. Although a corresponding molecular ion peak at *m/z* 362, the molecular weight of tetra-

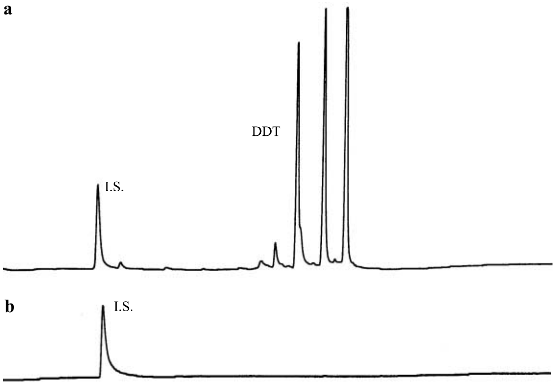

Fig. 2. (a) GC-ECD of 3.3 ng DDT with 1.6 ng I.S. (t_R 9.6 min, area 79,489) in hexanes; (b) GC-ECD of 3.3 ng DDT after dechlorination by the Mg/Pd bimetallic system with 1.6 ng I.S. (t_R 9.6 min, area 74,619) in hexanes.

phenylbutane, does not exist, it is reasonable that tetraphenylbutane would not survive the electron impact ionization.

After the 10-min dechlorination period, most of the magnesium metal still remains. Visual observations indicate that magnesium metal completely corroded to $Mg(OH)_2$ within 48 h. This would be undesirable for application in reactive barriers, which require a much longer lifetime. A kinetic study may eventually find it feasible to use larger surface area particles and higher pH conditions that extend the lifetime of the Mg/Pd bimetallic. On other hand, because of the rapid kinetics of dechlorination the demonstrated Mg/Pd system is much more ideally suited to the batch destruction of DDT/DDE. Such situations arise from the surfactant-based clean-up of polluted soils (Abdul and Gibson, 1991; Evdokimov and von Wandruszka, 1998).

Based on the results published by Doyle et al. (1998) that the dechlorination of PCBs produce biphenyl in 100% yield, diphenylethane was the expected outcome. However, significant amounts of tetraphenylbutane and diphenylmethane were produced as well. Reductive dechlorination of aliphatic chlorine most likely proceeds by a radical mechanism, which may lead to the coupling and/or cleavage of dechlorinated hydrocarbon products. This was observed by Grittini et al. (1995) with the Fe/Pd bimetallic reduction of trichloroethylene. In the case of DDT this led to the coupling of two diphenylethane molecules at either of the two aliphatic carbon atoms forming the tetraphenylbutane dimer. These observations may be rationalized on the basis of the stabilization of radical intermediates by aromatic systems.

The Pd/Mg bimetallic system examined in this paper dechlorinates DDT quickly and completely down to a hydrocarbon backbone. This is the first such demonstrated case in which dechlorination does not yield toxic intermediates, i.e. DDD (1,1-dichloro–2,2′-bis-(p-chlorophenyl)ethane), and DDE (2,2′-bis(p-chlorophenyl)–1,1′-dichloroethylene) under such mild conditions. Furthermore, the process is able to complete the dechlorination reaction under room temperature and pressure conditions without attention to aerobic contamination. The Pd/Mg bimetallic system may form the basis of an economical alternative to present methods of DDT destruction.

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