Development Of Reductive Metal Systems For The Degradation Of Energetic Compounds (tatp, Tnt, And Rdx)

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DEVELOPMENT OF REDUCTIVE METAL SYSTEMS FOR
THE DEGRADATION OF ENERGETIC COMPOUNDS (TATP,
TNT, AND RDX)

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry in the College of Sciences at the University of Central Florida Orlando, Florida

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ABSTRACT

Triacetone triperoxide (TATP), a cyclic peroxide explosive, is frequently used by terrorists and amateur chemists due to the ease of synthesis and the availability of reagents. TATP is extremely sensitive to shock, heat, and friction thus a safe and rapid method for treating TATP is needed. The major objective of this dissertation was to develop in situ methodologies that could safely degrade TATP in various field situations. Initial studies focused on using zero-valent metals and mechanically alloyed metals to decompose TATP samples in both aqueous and organic solutions. The metal systems tested included zero-valent iron, magnesium, and magnesium bimetal, Mg/Pd. The TATP degradation reaction with the different reactive metal systems followed pseudo-first order reaction kinetics with respect to TATP concentration, and the half-lives for TATP degradation with the different reactive metal systems were calculated to test their effectiveness. The major degradation product for the TATP decomposition was determined as acetone, and carbon material balance was calculated to determine each reactive system’s efficiency. The mechanism of TATP degradation using these reactive metal/bimetal particles was also explored, including reaction pathway, intermediates, and activation energies.

In addition to investigating the use of zero-valent metals to degrade TATP, studies were also conducted on the use of certain metal and semimetal ionic species. Antimony (III) ions were found to have the greatest effect of TATP concentration. Various spectroscopic analyses were completed to try to characterize the reaction
between the Sb$^{3+}$ and TATP. The Sb$^{3+}$ was theorized to instantaneously cleave the ring structure of the TATP molecule forming a Sb$^{3+}$ complex thus Sb$^{3+}$ systems could be used to successfully treat TATP.

In order to treat TATP in the field, the metal and bimetal reactive particles were combined with an application technology, liquid membrane systems to form emulsified zero-valent metal (EZVM) systems. EZVM systems containing the reactive metal/bimetal particles were made from an organic outer layer (corn oil), water, and a nonionic surfactant (SPAN 80). The EZVM systems were observed to absorb and dissolve the TATP into the emulsion droplets where TATP degradation then occurred. EZVM systems would be ideal for degrading dry TATP residues that might be found on a carpet, door entrance, steel, concrete, plastics, etc. The other neat metal systems could also be used to degrade aqueous slurries of TATP on different surfaces if an efficient delivery system was used.

Other studies focused on the use of microscale mechanically alloyed bimetals, particularly Mg/Pd, Fe/Pd, and Fe/Ni, as alternative remediation methods for the catalytic reduction of environmental contaminants: 2, 4, 6-trinitrotoluene (TNT), and 1, 3, 5-trimethylene-2, 4, 6-trinitramine (RDX) which have been found to contaminate soil and ground/surface water near industrial production sites. All the bimetals tested were shown to reduce TNT and RDX contamination in water samples with varying reactivities under ambient reaction conditions. These metal systems could be combined with EZVM or paste treatment systems (bimetal treatment systems, BTS) for the in situ treatment of these environmental contaminants.
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CHAPTER ONE: MOTIVATION FOR DISSERTATION

The initial motivation for this dissertation was for the development of an in-situ treatment for the degradation of triacetone triperoxide (TATP). Initial work was supported through funding from Unconventional Concepts, Inc, and development of this methodology for the degradation of TATP was based on previous methodologies that were successful in treating other types of contaminants, including trichloroethene (TCE), polychlorinated biphenyls (PCBs), and heavy metal contamination $^{1-5}$.

The primary methodology focused on the use of emulsified reactive agents, particularly emulsified zero-valent metals (EZVM), to degrade the TATP. Initially the main focus was on the use of emulsified nanoscale zero-valent iron (Fe), however, other reactive species in the emulsion system were also tested. These other metal systems included the use of mechanically alloyed bimetal systems, metal and semimetal ions, and other zero-valent metals. These systems have also been used to treat a wide range of contaminants including energetic materials as well as halogenated contaminants $^{4,6,7}$.

Initial studies focused on neat metal vial studies which determine the ability of the reactive metal particles to degrade TATP in a solvent (aqueous or organic). One of the major goals of the neat metal studies was to determine the effectiveness of each system. This goal was accomplished by ascertaining the reaction order and calculating the kinetic rate constants and half-lives of the TATP degradation reaction. Another key objective of this dissertation research was to determine the reaction mechanism of the degradation of the TATP with these reactive metal particle systems. After completing the neat metal
vial studies, the reactive metal particles were also tested in combination with EZVM to remove TATP from an aqueous suspension.

After completing initial studies with these systems for TATP degradation, other energetic compounds were also tested. These compounds included environmental contaminants, nitroaromatic and nitro explosives, particularly 2,4,6-trinitrotoluene (TNT) and 1,3,5-trimethylene-2,4,6-trinitramine (RDX). Mechanically alloyed bimetal systems, including Mg/Pd, Fe/Pd, and Fe/Ni, were all explored for their effectiveness in reducing TNT and RDX concentration in aqueous solutions under ambient reaction conditions. These systems could be combined with remediation technologies such as bimetal treatment systems (BTS) or emulsified systems to treat environmental contamination. The ability of these types of systems would be useful for treating contaminated areas such as surfaces, soil, and ground/surface water.
CHAPTER TWO: INTRODUCTION

Triacetone Triperoxide (TATP)

Triacetone triperoxide (TATP, Figure 2.1) is nine-membered cyclic organic peroxide that has been used for its explosive properties by terrorist organizations as well as clandestine chemist due to the ease of synthesis and availability of the reagents needed for synthesis. Homemade TATP recipes are prevalent throughout the internet, and the reagents needed for preparation can be found at any hardware supply store. The popularity of TATP has been increasing, and TATP residues has been found in various situations including targets of terrorists, drug crimes, and in clandestine laboratories.

TATP was first synthesized by Wolffenstein in 1895 and is prepared using a mixture of acetone and hydrogen peroxide. Milas and Golubovic later introduced an acid catalyzed synthetic reaction that is currently used in many literature articles to prepare TATP. TATP was determined to be the major product of the synthesis, while diacetone diperoxide (DADP, Figure 2.2) is a minor product. The reaction sequence for the synthesis is shown in Figure 2.3.
Figure 2.1: Molecular Structure of TATP

Figure 2.2: Molecular structure of DADP
TATP and DADP both have been shown to exhibit explosive properties with TATP having an expansion of 250 cm$^3$ compared to 300 cm$^3$ of TNT in the Trauzl test for explosive power and a detonation velocity of 3060 m/s$^{13,14}$. Dubnikova et al. also reports the explosive nature of TATP proceeds through an entropy driven reaction where one molecule of TATP yields 4 molecules of product, one molecule of ozone and three molecules of acetone (detailed in Equation 1)$^{15}$.

$$C_6H_{18}O_6 \rightarrow 3 C_3H_6O + O_3$$  \hspace{1cm} (1)$$

Although TATP does have explosive characteristics, the compound does not have any industrial or military purposes due to a variety of undesirable properties. TATP is
extremely sensitive to shock, heat and friction which makes transporting and handling difficult. TATP is also extremely volatile, with TATP losing 66% of its mass within weeks of its synthesis. TATP has been reported in literature to have a vapor pressure of approximately 7 Pa in ambient condition which is high relative to other common explosives. The melting point of TATP was determined to be 98°C while the DADP melting point is 132°C as reported in literature. Denekamp et al. also determined that TATP has two stable conformations at room temperature with an energy difference of 26.3 kcal/mol, both which can be analyzed using GC/MS.

The detection of TATP include analytical methods such as gas chromagraphic (GC) techniques in combination with detectors such as mass spectrometer (MS), flame ionization detector (FID), and electron capture detector (ECD), liquid chromatography (LC) with post column irradiation followed by UV and fluorescence detection, LC-MS, and infrared spectroscopy.

Degradation of TATP

The instability of TATP makes the clean-up of contaminated areas and confiscated bulk materials a challenging problem resulting in the need for a safe and rapid in situ degradation and clean-up method. Figure 2.4 shows an example of a TATP reaction mixture that could be encountered in the field. Currently detonation is used to treat TATP in the field, but not all TATP residues can be safely detonated. Other methods for field degradation need to be developed.
Limited methods for the treatment of TATP have been reported in literature. Many of these methods require harsh reaction conditions including low pH and high temperatures. TATP has been shown to thermally degrade in the temperature ranges of 130-160°C to the major product of acetone. The product distribution varies with a strong dependence on the phase of TATP (condensed or vapor phase) and the solvent. The pathway of thermal decomposition was determined to be through a radical mechanism initiated by the homolytic cleavage of the peroxide linkage. The activation energy reported for the thermal decomposition was 151 kJ/mol which is in agreement with the bond dissociation energy of a peroxide bond (154.8 kJ/mol). The major products formed from the degradation of TATP include acetone and CO₂ while other side products include methyl acetate, molecular oxygen, ozone, and radical side products.²⁰
Other degradation methods reported in literature involved the chemical destruction of TATP using metals and metal ions. One of the initial methods for the chemical degradation of the TATP involved refluxing TATP in toluene with SnCl\textsubscript{2} for 30 min at 65 °C. Similar reaction conditions at room temperature saw no decrease in TATP concentration. The risk of detonation of TATP was determined within this study to be greatly reduced after being dissolved in toluene with no detonation initiated in solutions containing 28% TATP \textsuperscript{21}.

One patented method describes the destruction of acetone peroxide by exposure to copper at a low pH and elevated temperature \textsuperscript{22}. Oxley et al. explored the degradation of TATP with mixtures of different metal salts and metals, and determined that copper and zinc mixed with their corresponding metal salt (copper chloride and zinc sulfate) were able to degrade TATP within hours \textsuperscript{6}. In addition to testing mixtures of different metals and metal salts, this group also determined that TATP was destroyed in the presence of strong acids, particularly sulfuric acid, however using this method was only useful for smaller quantities of TATP. Quantities of TATP larger than 1 g detonated with the addition of just 1 mL of concentrated sulfuric acid \textsuperscript{6}.

Although these methods were found to decrease TATP concentrations, many of these degradation methods would be unsuitable for field applications due to the need for elevated temperature ranges and severe reaction conditions and chemicals. The need for an \textit{in situ} treatment method led to the investigation of other degradation methods, especially those using zero-valent metals Fe, Mg, and bimetal systems. The following chapters discuss the methods and results for testing different reactive metal systems, zero-valent and mechanically alloyed bimetals for the degradation of TATP.
Reductive Metal Systems

Zero Valent Metals

Iron

Zero-valent iron (ZVI) has been used extensively in literature to degrade and reduce a wide range of compounds. ZVI systems have been shown to be successful in the hydrodehalogenation of halogenated organics such as methylene chloride, perchloroethene (PCE), trichloroethene (TCE), chlorophenols, and polychlorinated biphenyls (PCBs) \(^5, 23-27\). These chlorinated compounds are reduced by ZVI to less chlorinated intermediates/products and to the corresponding reduced aliphatic/aromatic products. Research has also explored the use of ZVI in anaerobic environments for the treatment of nitroaromatics such as TNT and nitrobenzene to reduce to the corresponding aminoaromatics via nitrosoaromatic intermediates \(^28-31\). In addition to treating organic compounds, ZVI has been used to reduce heavy metal contamination, particularly lead and hexavalent chromium \(^32-34\). ZVI mediated reactions are highly affected by reaction conditions, such as pH, dissolved oxygen concentrations, and temperature. Undesirable reaction conditions cause corrosion of the ZVI surface which can limit its reduction capabilities. ZVI reactions are typically surface area dependent thus a wide range of ZVI particle sizes have been explored from turnings, microscale, and nanoscale ZVI particles \(^35\).
Magnesium

Some of properties of ZVI, particularly its highly corrosive properties, can limit its field use thus other research has focused on the use of magnesium systems. Mg is thermodynamically favored over ZVI. Magnesium (-2.37 V vs. SHE) has a higher standard reduction potential over ZVI (-0.44 V vs. SHE). As stated previously, ZVI is highly corrosive while Mg has a self-limiting oxide layer which is favorable in oxidative environments 36.

Mg has been utilized considerably in organic synthetic reactions typically in the form of Grignard type reagents 37. Grignard reagents are formed from the addition of Mg to aryl or alkyl halides followed by the insertion of the Mg into the halide carbon bond. This reagent has been used for oxidation and reduction reactions, alkylation or arylation reduction and coupling reactions, to list a few 38. Mg has also been used for the hydrodehalogenation of chlorobenzenes through a mechanical mixing process 39. In addition to using Mg alone, Mg has been also been explored in the use of bimetallic systems which are discussed within the next section.

Bimetal Systems

Bimetallic systems have been explored in a wide variety of applications to improve degradation rates of compounds of interest over the zero-valent metal alone. Bimetal systems consist of a zero valent “base” metal combined with a catalyst or
“enhancer/promoter” metal. The catalysts chosen for the production of bimetals are typically hydrogenation/reduction catalysts, such as Pd, Ni, Pt, or Cu, depending on the target reaction.

Bimetallic systems can be produced through various methods while the most common production method in literature is electrodeposition. Another method for producing bimetals is through a mechanical alloying or “ball-milling process” in which the two metals, the “base” metal and the catalyst are forcibly alloyed and melded together. Aitken et al. describes the optimization of a mechanically alloying process used to produce Mg/Pd for the degradation of PCBs. Bimetallic systems produced using either of these methods have been effective in degrading/reducing a wide range of compounds.

Zhang et al. has explored the use of bimetallic particles, Pd/Fe, Pd/Zn, Pt/Fe, and Ni/Fe for the degradation of chlorinated compounds, and surface area normalized rate constants were observed within these studies to be 100 times higher than those obtained from ZVI alone. DeVor et al. successfully used mechanically alloyed Mg/Pd to treat PCBs congeners both in alcohol and aqueous solutions. This same mechanically alloyed system has also been able to debrominate polybrominated diphenyl ethers (PBDEs). Mg/Pd systems have also been used for the complete dechlorination of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT). Various Fe/Cu loading systems have been explored for the treatment of TCE, and Wei et al. explored the use of nanoscale Fe/Pd for the catalytic hydrodechlorination of 2,4-dichlorophenol.
CHAPTER THREE: MATERIALS AND METHODS FOR THE TATP DEGRADATION STUDIES

Materials

Metals

The metals used in the experimental studies included nanoscale iron obtained from Toda America Inc. (Schaumburg, IL); microscale iron (1-3 µm diameter) obtained from BASF (Iselin, NJ); microscale magnesium (2-4 µm diameter) from Hart Metals, INC (Tamaqua, PA); and 1% palladium on carbon from Engelhard (Iselin, NJ).

Chemicals

Acetone, toluene, methanol (Optima® grade), concentrated hydrochloric acid, glacial acetic acid, and the 30% hydrogen peroxide solution were all purchased from Fisher Scientific (Pittsburgh, PA). Absolute ethanol was obtained from Pharmco-AAPER (Brockfield, CT). TATP standard solutions in acetonitrile used for concentration calibration (0.1 mg/mL) were obtained from AccuStandard (New Haven, CT). Antimony trichloride (99.9+) and Quercetin Dihydrate (98%) were purchased through Alfa Aesar (Ward Hill, MA).
Methods

Mg/Pd Preparation

The optimal ball-milling process used was developed in-house \(^{42}\). Each bimetal was prepared by ball-milling 78 g of ZVM and 7 g of the catalyst for 30 minutes using a Series 5400 Red Devil Paint Shaker (Figure 3.1). The final metal and catalyst loading for the prepared Mg/Pd were 91.8% Mg, 0.08% Pd, and 8.12% C. An SEM image of the prepared Mg/Pd is found in Figure 3.2.

Figure 3.1: Series 5400 Red Devil Paint Shaker and canisters used for the preparation of the mechanically alloyed bimetal (Mg/Pd)
Appropriate safety precautions were required in preparing the TATP in the laboratory. One-hundred microliters of both acetone and 30% hydrogen peroxide were added to a microcentrifuge tube on ice. Ten microliters of hydrochloric acid was added to the reaction, and the reaction was allowed to sit on ice for a total of 15 minutes. The reaction mixture was then washed with 1 mL of a 1% sodium bicarbonate solution to remove any residual acid, centrifuged, and decanted. The wash step was repeated until the wash reached a pH 7. The TATP crystals were then transferred into an appropriate
solvent. Literature has reported other products of this TATP synthesis and has shown as much as 30% impurity from hydroperoxy-terminated oligomeric peroxides \(^\text{48}\), thus the TATP concentration of the solution was determined through a toluene extraction and analysis using gas chromatography/mass spectrometry (GC/MS) \(^\text{49}\).

**TATP Kinetic Studies**

Depending on the kinetic vial studies, TATP solutions were exposed to 0.25 g of Mg, Mg/Pd, or Mg/C in clear 20 mL borosilicate reaction vials, and all experiments were performed in duplicate. Depending on the kinetic study, the different acids were added immediately after the addition of the TATP solution. Any unreacted TATP was extracted using toluene, and the reaction mixture was filtered using a nylon Puradisc® syringe filter (2 μm pore size) to remove the reacted metal. Water was added to the extracted solution to separate the organic layer, and the sample was shaken for 2 min then centrifuged at 1200 rpm for 4 min. The organic layer was then removed for analysis using GC/FID or MS.

**EZVM Preparation**

EZVM was prepared using active metal (Mg/Pd particles), corn oil, surfactant, and water as described in the literature \(^\text{2, 50}\). The EZVM was emulsified in a high speed blender. One hundred-milliliters of water was added to 20 g of the prepared Mg/Pd
coated with 20 g of glycerin and mixed. While mixing, 80 mL of corn oil mixed with 7 g of surfactant (SPAN 80) was added slowly into the water-metal mixture to create the EZVM. A microscopic image of an EZVM droplets formed are shown in Figure 3.3.

Figure 3.3: Microscopic image of the EZVM droplet

TATP Analysis

Gas Chromatography

The methods used for analysis of TATP and acetone are modified from literature 51. TATP concentrations were determined using GC/MS. Acetone concentrations were determined through analysis with GC paired with a flame ionization detector (FID). The summary of the analytical methods are found in Table 3.1. If headspace concentration
was determined, a 7 μm polydimethylsiloxane (PDMS) solid phase microextraction (SPME) fiber and sampling apparatus was used. One minute adsorption and one minute desorption within the GC injection port was used for analysis. Figure 3.4 pictures the SPME fiber sampling the headspace above a TATP solution.

Table 3.1: GC/MS and GC/FID methods for the analysis of TATP and acetone

<table>
<thead>
<tr>
<th></th>
<th>TATP (GC/MS)</th>
<th>Acetone (GC/FID)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Injector Temperature</strong></td>
<td>110° C (1.0 µL)</td>
<td>170° C (2:1 split) (2.0 µL)</td>
</tr>
<tr>
<td><strong>Detector Temperature</strong></td>
<td>Ion Source: 150° C</td>
<td>250 ° C</td>
</tr>
<tr>
<td><strong>Column</strong></td>
<td>Rtx-5 (30 m, 0.25 mm id, 0.25 µm if)</td>
<td>Stabilwax (30 m, 0.53 mm id, 1 µm if)</td>
</tr>
<tr>
<td><strong>Carrier (He)</strong></td>
<td>1.2 mL/min</td>
<td>5.2 mL/min</td>
</tr>
<tr>
<td><strong>Oven Program</strong></td>
<td>Initial Temp: 50° C (1 min)</td>
<td>Initial Temp: 50° C (1 min)</td>
</tr>
<tr>
<td></td>
<td>Ramp: 10° C/min</td>
<td>Ramp: 10° C/min</td>
</tr>
<tr>
<td></td>
<td>Final Temp: 150° C (1 min)</td>
<td>Final Temp: 150° C (1 min)</td>
</tr>
<tr>
<td><strong>Total Analysis Time</strong></td>
<td>11.0 min</td>
<td>11.0 min</td>
</tr>
</tbody>
</table>
Figure 3.4: SPME sampling of TATP headspace

Ultra-Violet/Visible (UV/Vis) Spectroscopy

An Agilent UV-Vis Spectrometer was used for analysis of the Sb$^{3+}$ complexes in both the UV and Vis Regions. A 1 mL quartz cuvette (path length 1 cm) was used in all analyses. HPLC grade acetonitrile (AcCN) was used to prepare all solutions for UV/Vis analysis. The scanning region ranged from wavelengths of 190-800 nm.
Hydrogen Gas Volume Measurements

The experimental setup for hydrogen gas volume measurements is found in Figure 3.5. The appropriate solutions were added to 0.25 g of metal using a gas tight syringe after the appropriate volume of air was removed to maintain atmospheric pressure. The change in gas volume was measured using a gas tight syringe at appropriate reaction time intervals. The hydrogen volumes were measured using different reaction conditions including Mg/Pd alone with H$_2$O, Mg/Pd with a TATP in H$_2$O solution, Mg/Pd in 90/10 H$_2$O/methanol, and Mg/Pd with PCB-151 (2,2’,3,5,5’,6-hexachlorobiphenyl) in 90/10 H$_2$O/methanol. All samples were repeated in duplicate.
Figure 3.5: Hydrogen gas volume measurements
CHAPTER FOUR: INITIAL METAL STUDIES FOR THE DEGRADATION OF TATP USING MICROSCALE AND NANOSCALE IRON

Introduction

Microscale and nanoscale zero-valent iron (ZVI) has been used to successfully degrade a wide range of compounds including nitro based energetic compounds and halogenated aliphatics, and halogenated aromatics thus the use of ZVI was promising for the degradation of TATP.

Typical reaction conditions include the use of a protic solvent (alcohol or H$_2$O), and the oxidation of ZVI through corrosion provides the possibility of electron transfer to reduce the compound of interest. The redox potential of ZVI is -0.44 V vs. SHE (standard hydrogen electrode), and the typical chemical reactions involved in the reduction of halogenated organics (which has been studied extensively) by ZVI are described in Equation 2:

$$\text{Fe}^0 \rightarrow \text{Fe}^{2+} + 2 \, \text{e}^-$$

$$\text{RX} + 2 \, \text{e}^- + \text{H}^+ \rightarrow \text{RH} + \text{X}^- \,
\text{(2)}$$

Surface area and surface chemistry of ZVI as well as pH of reaction solutions plays an important role in the effectiveness of the ZVI particles for reduction reaction.
This chapter discusses the initial experimental studies exploring the use of ZVI for the degradation of TATP. Both microscale and nanoscale ZVI were tested. These studies exposed aqueous solutions of TATP prepared in the laboratory as described in Chapter Three to different particle sizes of ZVI to determine their effectiveness in treating TATP.

Results and Discussion

TATP concentrations for the vial studies for both the microscale and nanoscale ZVI were monitored using GC/FID analysis described in Chapter Three after headspace sampling using a SPME fiber.

Microscale Iron Studies

The kinetic data for the degradation of TATP using microscale Fe is found in Figure 4.1. The last time point was obtained after 24 hours of exposure to the microscale ZVI. Figure 4.2, Figure 4.3, and Figure 4.4 plot the kinetic degradation data for 0, 1st, and 2nd order reaction, respectively. Based on the correlation coefficients (R²) obtained from those plots, the overall reaction order for the degradation of TATP using the microscale Fe was determined to be either pseudo-1st order or pseudo-2nd order with respect to TATP.
In order to compare the degradation rates to other systems, the rate constant was calculated by determining the slope of the best fit linear regression line from the 1\textsuperscript{st} order kinetic plot (Figure 4.3). The rate constant for the degradation of TATP using microscale ZVI was determined to be 0.003 min\textsuperscript{-1}. The 1\textsuperscript{st} order half life for this reaction is calculated as 231 min.

Figure 4.1: Degradation data for the degradation of TATP using microscale ZVI particles. Final time point was taken after approximately 24 hours to test for any remaining TATP.
Figure 4.2: 0\textsuperscript{th} order kinetic plot for the degradation of TATP using microscale ZVI

Figure 4.3: 1\textsuperscript{st} order kinetic plot for the degradation of TATP using microscale ZVI
The kinetic data for the degradation of TATP in an aqueous solution using nanoscale Fe is found in Figure 4.5. Since the TATP concentration was determined through headspace sampling, initial concentrations were taken at 66 minutes to allow for equilibration of the headspace. Figure 4.6, Figure 4.7, and Figure 4.8 show the kinetic degradation data plotted for 0, 1st, and 2nd order reaction orders, respectively. Based on the correlation coefficients obtained from linear regression methods for each of the reaction order plots, the degradation of TATP using nanoscale ZVI was determined to be pseudo-1st order with respect to TATP. This observation is in agreement with those
The rate constant was calculated in a similar manner as the microscale ZVI rate constant using the slope of the best fit linear regression line for the 1st order kinetic plot found in Figure 4.7. The rate constant was calculated as 0.013 min⁻¹, and the 1st order half life is 53 min. The more rapid degradation rate observed from the nanoscale ZVI vs. the microscale ZVI was expected. The increased rate of reaction was due to the increase surface area of the nanoscale ZVI particles over the microscale ZVI particles, and this effect has been observed in other reaction studies ⁵⁴.
Figure 4.5: Degradation of TATP using nanoscale ZVI
Figure 4.6: 0\textsuperscript{th} order kinetic plot for the degradation of TATP using nanoscale ZVI

\[ y = -0.0075x + 1.4691 \]
\[ R^2 = 0.9808 \]

Figure 4.7: 1\textsuperscript{st} order kinetic plot for the degradation of TATP using nanoscale ZVI

\[ y = -0.013x + 0.857 \]
\[ R^2 = 0.995 \]
Conclusion

Microscale and nanoscale ZVI particles were determined to be effective in the degradation of aqueous solutions of TATP. Both micro and nanoscale ZVI particles exhibited pseudo-1\textsuperscript{st} order reaction rate laws with respect to TATP which is agreement with other degradation studies with ZVI. Due to the nature of the reduction reactions involving ZVI, surface area and surface chemistry can greatly affect the degradation rates. The degradation rate varied greatly with the surface area of the ZVI used. The nanoscale ZVI half-life was calculated to be 4 times shorter than that of the microscale ZVI, 53 min vs. 213 min. The higher reactivity of the nanoscale ZVI was expected, and has been observed with other systems\textsuperscript{54}. 

Figure 4.8: 2\textsuperscript{nd} order kinetic plot for the degradation of TATP using nanoscale ZVI
In order to try to produce more rapid TATP degradation rates, other zero-valent systems, particularly Mg systems which has a higher reduction potential than that of ZVI (-2.37 V vs. SHE for Mg compared to -0.44 V vs. SHE for ZVI). The next three chapters discuss the use of Mg systems including mechanically alloyed bimetal systems (Mg/Pd) and activated Mg systems.
CHAPTER FIVE: DEGRADATION OF TATP USING MECHANICALLY ALLOYED MG/PD

Introduction

Mechanically alloyed Mg/Pd particles have been explored as a reductive catalytic system that can degrade TATP to produce non-explosive byproducts. This physical process for producing bimetallic particles was developed as an alternative to electrodeless deposition of Pd onto a base metal (Fe or Mg). Mg/Pd has been shown to successfully degrade organic halogens, such as polychlorinated biphenyls and trichloroethylene \(^4\), \(^7\), \(^55\) thus Mg/Pd appears promising for the degradation of TATP \(^56\).

Combining Mg/Pd particles with technologies such as emulsified zero valent metal (EZVM) could provide a promising \textit{in situ} method for the treatment TATP contaminated areas. EZVM consists of metal particles contained in an aqueous inner membrane encased by an outer oil membrane (Figure 5.1). The outer oil membrane of the EZVM has been observed to absorb TATP crystals \(^56\), which can then be degraded by Mg/Pd particles that are contained within the inner aqueous layer. Application of the EZVM technology has been shown to successfully treat trichloroethylene contamination \(^2\), thus EZVM technology using Mg/Pd particles presents a promising technique for the treatment of both wet and dry TATP contamination.
Results and Discussion

Kinetic Vial Studies

The data obtained from the multiple kinetic experiments using the various metal particles tested are found in Figure 5.2 and Figure 5.4. The degradation of TATP and the production of acetone were compared to data obtained from experiments that had no metal particles present in which no TATP degradation or acetone production was observed.
Figure 5.2: Degradation of TATP with micro-scale magnesium particles
Figure 5.3: Degradation of TATP with 10% Pd on activated carbon
Figure 5.4: Degradation of TATP with Mg/Pd particles

Mg and Pd/C particles (Figure 5.2 and Figure 5.3, respectively) were tested over a 4.5 hour period, and a slight decrease in TATP concentration was observed in addition to a slight increase in acetone concentration. The amount of Pd/C in the kinetic experiment found in Figure 5.3 had approximately 10 times the amount of Pd found in the mechanically alloyed Mg/Pd.

Initial testing of the Mg/Pd particle system was performed over a 4.5 hour period similar to that of the Pd/C and Mg particle testing, however approximately 90% of the initial TATP concentration was degraded within the first 30 minutes reaction time. Subsequent kinetic testing was executed within the first 30 minutes to provide additional data of the degradation of TATP with Mg/Pd particles (Figure 5.4).
Determination of Reaction Order

The overall reaction order for the degradation of TATP in water was determined by fitting the TATP concentration data into the 0th, 1st, and 2nd order kinetic plots (Figure 5.5, Figure 5.6, and Figure 5.7, respectively). This data was obtained through SPME headspace sampling of the TATP concentration described in Chapter Three. Based on the 0th, 1st, and 2nd order kinetic plots, the degradation of TATP using the Mg/Pd was determined to be pseudo-1st order. The term “pseudo” was used because the metal particles and the solvent were considered in excess, and rate dependence of these active substances was not determined. Because the degradation data appear to follow a pseudo first-order rate law (Equation 4), this equation was used to calculate rate constants:

\[
\frac{d[TATP]}{dt} = -k_{TATP}[TATP]
\]  

(4)

The data obtained from these kinetic studies agrees with data obtained from degradation of other compounds with comparable metal systems \(^4,7,55\).
Figure 5.5: 0\textsuperscript{th} order kinetic plot for the degradation of TATP using Mg/Pd particles

\[ y = -0.011x + 0.941 \]

\[ R^2 = 0.855 \]
Figure 5.6: 1st order kinetic plot for the degradation of TATP using Mg/Pd particles

\[ y = -0.028x + 0.230 \]
\[ R^2 = 0.980 \]
Figure 5.7: 2nd order kinetic plot for the degradation of TATP using Mg/Pd particles

Calculation of Rate Constants

The rate constants were obtained from fitting the data to the first-order kinetic integrated rate equation (Equation 5):

\[
\frac{[TATP]}{[TATP]_0} = e^{-k_{TATP}}
\]  

(5)
The rate constants ($k_{\text{TATP}}$) obtained from the first-order kinetic fitting are found in Table 5.1. The rate constants are normalized to the metal concentration ($\rho_m$). The half-life data for the degradation of TATP with the metal are also compared in Table 5.1.

Table 5.1: Normalized rate constants and half-lives for the degradation of TATP.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Metal Concentration ($\rho_m$)</th>
<th>Normalized Rate Constant (L g$^{-1}$ min$^{-1}$)</th>
<th>Half life (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>5.0x10$^1$</td>
<td>8.0x10$^{-6}$</td>
<td>1.7x10$^3$</td>
</tr>
<tr>
<td>Pd/C</td>
<td>5.0x10$^0$</td>
<td>1.6x10$^{-4}$</td>
<td>8.7x10$^2$</td>
</tr>
<tr>
<td>Mg/Pd</td>
<td>5.0x10$^1$</td>
<td>1.2x10$^{-3}$</td>
<td>1.1x10$^1$</td>
</tr>
</tbody>
</table>

Metal Loading

The effect of metal loading on the TATP degradation rate was also tested. Figure 5.8 shows the degradation rate dependence on the Mg/Pd particle loading. One-quarter gram Mg/Pd loading was determined to be in excess thus this loading was used for all the kinetic studies.
Figure 5.8: The effect of metal loading on the degradation of TATP

Product Determination

Acetone was observed as the major product from the degradation of TATP with the Mg/Pd particles. The molar ratio of acetone produced to TATP degraded for the overall reaction was calculated from the kinetic data as 2.76 to 1. A material balance of carbon was also completed for the degradation of the TATP using Mg/Pd, Figure 5.9. The total C recovery was calculated as 94 ± 5% from the TATP degradation reaction with Mg/Pd.
Figure 5.9: Carbon material balance for the degradation of TATP with Mg/Pd particles.

The suggested reaction pathway for the degradation of TATP with Mg/Pd particles is shown in Figure 5.10. Mg is oxidized in the presence of a protic solvent (water or methanol) to form molecular hydrogen. Molecular hydrogen is adsorbed onto the Pd surface, and the hydrogen is available to react with the TATP molecule to form a hydrated acetone intermediate. The loss of water then forms the ending product acetone.
Figure 5.10: Reaction Pathway for the degradation of TATP with Mg/Pd particles.
**EZVM Studies**

Initial studies were performed to test the potential of EZVM to remove TATP from an aqueous solution. TATP concentration was monitored by sampling with SPME the headspace above the EZVM as shown in Chapter Three. The data from this study is found in Figure 5.11. Approximately 90% of the initial TATP is removed from the aqueous solution after 24 hours. This initial testing of EZVM for the removal of TATP is promising for the clean-up of aqueous TATP samples. EZVM was also observed to absorb dry TATP crystals thus EZVM could also be applied to dry crystals (Figure 5.12).

![Graph showing the removal of TATP from using EZVM](image)

Figure 5.11: Graph showing the removal of TATP from using EZVM
Figure 5.12: Time elapsed micrographs (20x magnification) of TATP crystal being absorbed into EZVM

Conclusion

Mechanically alloyed Mg/Pd has been shown to successfully degrade TATP. The normalized rate constant obtained from the reaction of TATP with Mg/Pd is approximately one and three orders of magnitude greater than that of Pd/C and Mg degradation rates, respectively. The reaction of TATP with Pd/C in the absence of molecular hydrogen may suggest a different mechanism than that seen with the mechanically alloyed Mg/Pd which must be further investigated.
The major product of the reaction of TATP with the mechanically alloyed Mg/Pd was determined to be acetone. A material balance for carbon accounted for 94 ± 5% of the carbons in TATP being degraded to form acetone.

Initial testing was completed to determine if Mg/Pd used in combination with remediation technologies such as EZVM would be effective in removing TATP from aqueous media. EZVM removed 90% of the TATP concentration within 24 hours thus combining Mg/Pd with EZVM appears promising for the *in situ* treatment of TATP.

In order to understand this reaction further, additional studies were completed to elucidate the reaction mechanism. Chapter Six explores the mechanism of the TATP degradation reaction through a series of experiments.
CHAPTER SIX: DETERMINATION OF TATP DEGRADATION MECHANISM USING MG/PD

Introduction

Chapter Five discussed the effectiveness of mechanically alloyed Mg/Pd for the degradation of TATP in aqueous solutions. This chapter addresses a study that documented that mechanically alloyed Mg/Pd particles were able to degrade TATP in aqueous solutions with a half-life of 10.8 min. As discussed in Chapter Five, the degradation reaction proceeded with a pseudo-1st order overall reaction order dependent on TATP concentration when the Mg/Pd particles and the active solvent (H₂O) were in excess. These observations were in agreement with other literature studies using similar types of systems ⁴, ⁷, ⁵⁵. The reaction pathway introduced in Chapter Five (Figure 5.10) was the initial basis for the elucidation of the TATP degradation mechanism using Mg/Pd particles.

Two possible degradation pathways were considered in determining the reaction mechanism, and these two pathways are detailed in the flow chart in Figure 6.1. The two main pathways proceed through the radical mechanism or through the direct metal reduction mechanism. Both of these mechanisms have been suggested through various studies in literature under different reaction conditions. Both of these mechanisms will be explored further to try to determine the reaction mechanism of the TATP degradation reaction with Mg/Pd as discussed in Chapter Five.
The radical pathway suggested in literature occurs through the homolytic cleavage of the peroxide bond producing products such as intermediate cyclic rearrangement products, DADP and dioxirane. Typical molar ratios of TATP decomposition exhibit approximately 2 moles of acetone produced to every 1 mole of TATP degraded at higher temperatures, and higher ratios in the presence of protic solvents. Protic solvents can stabilize the radical intermediates produced from the decomposition reaction; however these types of radical mechanisms typically do not occur in protic solvents. Cyclic rearrangement intermediates (DADP and dioxirane) and radical products (methyl acetate) were also not observed during the Mg/Pd facilitated TATP degradation studies. The product ratio (2.76:1 acetone:TATP) observed from studies presented in Chapter Five was higher than that seen with radical decomposition mechanism which suggest the degradation path proceeds through an alternate mechanistic pathway.
Figure 6.1: Flow chart of the possible reaction mechanisms of the degradation of TATP using Mg/Pd
The second possible pathway would be the direct reduction of TATP using reactive metal species. This pathway could occur through two different ways. The first pathway proceeds through an oxidation-reduction reaction. The oxidation of Mg in the presence of a protic solvent provides electrons that can be transferred from the Mg to the TATP. If this was the reaction pathway, the degradation of TATP should occur with just the presence of Mg, but as seen in Chapter Five, no degradation occurs with the Mg alone. The addition of the Pd was necessary for degradation to occur thus the reaction pathway must utilize the Pd catalyst.

Hydrogenation mechanisms involving the catalyst Pd have been studied extensively \(^{57, 58}\). Figure 6.2 depicts the reduction mechanism of the hydrogenation reaction by a Pd catalyst. Molecular hydrogen is absorbed into the bulk of the Pd and dissociatively adsorbed onto the surface of the Pd. The adsorbed hydrogen species can participate in hydrogenation or hydrodehalogenation reactions where it can hydrogenate other adsorbed species such as unsaturated hydrocarbons or halogenated compounds \(^{58}\).
Previous studies using Mg/Pd for the degradation of PCBs determined that the reduction mechanism proceeds through this similar type of mechanism. Devor et al. deduced that hydrogen produced from the oxidation of the zero-valent Mg in the presence of a protic solvent (Equation 6), such as water, is adsorbed onto the Pd surface.

\[
\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \quad (6)
\]

There were three possible hydrogen reactive species responsible for the hydrodehalogenation of adsorbed PCBs: hydride, hydride radical, and atomic hydrogen. Since the TATP reaction was thought to proceed through a similar mechanism,
however the actual hydrogen species was yet to be determined. The reaction pathway suggested in Chapter Five was updated as seen in Figure 6.3.

![Figure 6.3: TATP degradation pathway using Mg/Pd particles in H₂O. The H* species are responsible for the reduction of TATP.](image)

Results and Discussion

In order to understand the degradation reaction further, a series of experiments were designed to determine the degradation mechanism. The experimental setups for these studies were discussed in detail in Chapter Three.

*Activation Energy Calculation*

The first study determined the activation energy of the degradation reaction. The 1st order reaction rate constants of the TATP degradation reaction were determined at different temperatures (Figure 6.4) by plotting the degradation data into 1st order kinetic plot. The rate constants were calculated by determining the slope of the best fit line by
fitting the data using linear regression software. In order to compute the activation energy of the reaction the Arrhenius equation was used, and the 1st order rate constants were plotted against reciprocal temperature. Figure 6.5 shows the Arrhenius plot of the 1st order kinetic rate constants obtained at different temperatures vs. reciprocal temperature. Using the Arrhenius equation (Equation 7), the activation energy was calculated from the slope of the best fit linear regression analysis.

$$\ln k_{T\text{ATP}} = -\frac{E_a}{R} \left( \frac{1}{T} \right) + \ln A$$ \hspace{1cm} (7)

The activation energy was calculated as 21.0 ± 1.22 (mean ±standard deviation) kJ/mol.
Figure 6.4: The TATP degradation data using Mg/Pd at different temperatures
Figure 6.5: Arrhenius plot of the degradation of TATP using Mg/Pd

\[ y = -2520x + 6.30 \]

\[ R^2 = 0.970 \]
Based on the low activation energy and the entropy driven degradation pathway, the degradation reaction was determined to be favored both thermodynamically and kinetically. The bond dissociation energy for the homolytic cleavage of the peroxide bond was reported as 154.8 kJ/mol, and the activation energy for the thermal decomposition of TATP reported by Oxley et al. was calculated to be 151 kJ/mol\(^{20}\). Comparing the activation energy calculated in the degradation of TATP using Mg/Pd, it was presumed that this reaction rate limiting step does not proceed through the homolytic cleavage of the peroxide bond. This conclusion supports the metal reduction pathway proposed earlier within this chapter. Further studies detailed in the following sections were conducted to elucidate the reactive specie(s) involved in the degradation mechanism.
Determination of Hydrogen Reactive Species

As introduced earlier within this chapter, a possible reaction pathway was suggested in Figure 6.3. In order to understand the reaction steps further, the mechanism of H₂ production using Mg in H₂O was explored. This reaction has been investigated by other research groups, and Taub et al. determined the mechanism of dihydrogen production using Mg in H₂O. The reaction mechanism introduced from Taub et al. is detailed in Equation 8:

\[
\begin{align*}
\text{Mg} & \rightarrow \text{Mg}^{2+} + 2e_{s(p)}^- \\
e_p^- & \rightarrow e_s^- \\
e_s^- + H^+ & \rightarrow H^+ \\
2H_2O + 2e_s^- & \rightarrow H_2 + 2OH^- \\
H^+ + H^+ & \rightarrow H_2
\end{align*}
\]

Based on the mechanism suggested by Taub et al. various reactive species are produced and involved in the production of molecular hydrogen from the oxidation of Mg in H₂O. These species can react with other compounds introduced into the reaction as shown by Taub et al. Any of these species could be responsible for the degradation of TATP including solvated electrons (e_s), atomic hydrogen (H^·), and molecular hydrogen (H₂).

In order to determine the identity of the hydrogen reaction species responsible for the degradation of TATP, a series of studies comparing the hydrogen production under
different reaction conditions were performed. These studies measured the volume of H$_2$ gas produced during different reaction conditions. If any of the species involved in the mechanism of molecular hydrogen production (Equation 8) reacts with TATP or if the TATP degradation reaction consumes molecular hydrogen, a decrease in the volume of molecular hydrogen should be observed as observed during the experiments completed by Taub et al. 59. Figure 6.6 shows the molecular hydrogen volume measurements obtained during those experiments. The amount of H$_2$ produced was measured during different reaction conditions including Mg/Pd in water, Mg/Pd in water with TATP, Mg/Pd in 90/10 H$_2$O/methanol, and Mg/Pd in 90/10 H$_2$O/methanol with PCB-151 (2,2',3,5,5',6-hexachlorobiphenyl). As seen from the data in Figure 6.6, the amount of H$_2$ produced from the TATP sample vs. the Mg/Pd alone was consistent. This result indicates that the TATP did not consume H$_2$ nor does it react with solvated electrons or atomic hydrogen to prevent the production of molecular H$_2$ according to the mechanism described in Equation 8. This result suggests that molecular H$_2$ produced from the oxidation of Mg in H$_2$O is not involved directly in the reduction of TATP. In addition to this finding, the TATP reaction with Mg/Pd was also verified to not produce gaseous products. If TATP degradation with Mg/Pd produced gaseous products this should be indicated by an increase of gas production volume which was not observed. As a comparison, the PCB reaction with Mg/Pd did show a decrease in H$_2$ production which agrees with the mechanistic pathways reported previously $^3$. 

58
Figure 6.6: \( \Delta V_{H_2} \) volume measurements for the different reaction conditions
Based on the observations from the hydrogen volume experiments, it was assumed that the hydrogen source responsible for the reduction of TATP must be introduced directly from the solvent molecules rather than from the molecular \( \text{H}_2 \) production. This reaction mechanism has been suggested previously with similar types of metal systems \(^{60, 61}\) where the solvent molecules are bound to the zero-valent metal, in this instance, Mg. The activated Mg bound water molecules can transfer hydrogen to an acceptor molecule, TATP, which is adsorbed onto the surface of the Pd. Figure 6.7 illustrates this possible mechanism. The products of this mechanistic pathway are in agreement with those seen in the results observed in the TATP degradation studies presented in Chapter Five.
Figure 6.7: Direct hydrogen transfer from the activated H$_2$O bound to the Mg to the TATP molecule adsorbed onto the Pd surface
Another possible scheme is depicted in Figure 6.8, in which both the H$_2$O and the TATP are adsorbed onto the surface of the Pd. The adsorbed H$_2$O transfers hydrogen to the adsorbed TATP producing similar products to the pathway proposed in Figure 6.7. In other bimetal systems, the zero-valent metal can provide a source of electrons that can be transferred from the bulk of the zero-valent metal to the catalyst surface$^3,25$. This scheme, as drawn, does not require the presence of the Mg, however as determined in Chapter Five, both the Mg and the Pd are necessary for TATP degradation to occur. If the Mg somehow was involved in the reaction mechanism by providing an electron source or activating the adsorbed water for hydrogen transfer, this scheme shown in Figure 6.8 could be a possible reaction mechanism for the degradation of TATP.
Figure 6.8: Direct hydrogen transfer from H₂O to the TATP, both adsorbed onto the surface of the Pd
Conclusion

A mechanism for the degradation of TATP using mechanically alloyed Mg/Pd has been explored. A series of experiments were performed to try to determine the possible reaction mechanism. The activation energy of the degradation of TATP using Mg/Pd was calculated using the Arrhenius equation to be 21.0 kJ/mol. This low activation energy suggests that the rate limiting step for the degradation of TATP using Mg/Pd does not proceed through the homolytic cleavage of the peroxide bond. The bond dissociation energy of the homolytic cleavage of a peroxide bond is reported as 154.8 kJ/mol, thus it is unlikely that the degradation occurs through a direct homolytic peroxide cleavage. The low activation energy and the entropy driven reaction suggest that the decomposition of TATP with Mg/Pd is favored both thermodynamically and kinetically.

As seen in Chapter Five, decomposition of TATP occurred only with the presence of both the Mg and the Pd catalyst thus the mechanism had to involve both these systems. Previous mechanistic studies with Mg/Pd and PCBs suggest the possible hydrogen reactive species (hydrogen radicals, hydride-like radicals, and hydride) produced from the dissociative adsorption of molecular hydrogen \(^3\). These species were thought to be responsible for reduction on the Pd surface, however it was determined through a series of experiments, that molecular hydrogen (and the species responsible for its production: solvated electrons and atomic hydrogen) was not directly involved in the TATP degradation mechanism. Previous mechanisms using similar type systems that did not involve the production of molecular hydrogen, suggest the possibility of a direct hydrogen transfer for Mg bound H\(_2\)O molecules to TATP adsorbed on the Pd surface \(^60\).
Another mechanism was suggested which included the direct hydrogen transfer from \( \text{H}_2\text{O} \) to TATP both which are adsorbed on the Pd surface. However it was determined if this mechanism was responsible for the reduction of TATP, the Mg must be involved because no degradation was observed with Pd alone.

Two possible degradation reaction mechanisms for the decomposition of TATP using Mg/Pd in \( \text{H}_2\text{O} \) to acetone product were suggested. Understanding the degradation mechanism for this system will assist the application of this system for field use. Also, by understanding the mechanisms involved in using the Mg/Pd, Mg/Pd could be applied to treat other compounds.
CHAPTER SEVEN: ACTIVATION OF ZERO-VALENT MAGNESIUM USING ACETIC ACID FOR THE DEGRADATION OF TATP IN ETHANOL

Introduction

As discussed in Chapters Five and Six, degradation of TATP was extremely successful using mechanically alloyed Mg/Pd in aqueous reaction mixture, therefore the use of similar systems using Mg for the degradation of TATP in ethanol (EtOH), was promising. Mg has also been used as a reducing agent for peroxides in the presence of an iodine catalyst in methanol 62, and the use of Mg is used extensively in synthetic reactions 37. Mg has also been used in degradation reactions combined with catalysts for degradation reactions for different compounds including TATP 4, 51, 63. By substituting H2O with EtOH, the solubility of TATP in the reaction solutions would drastically increase making EtOH a more suitable solvent for TATP reactions. This chapter explores the activation of Mg as well as the optimization of the Mg system for the degradation of TATP in EtOH which could be used as a treatment and clean-up method for TATP.
Results and Discussion

Kinetic Studies

Mg and Mechanically Alloyed Mg/Pd

Initial degradation studies were performed with zero-valent Mg in EtOH, and as seen in Figure 7.1, Mg in EtOH (with no acid) did not readily degrade TATP during the 4.5 hour reaction time period. Due the inactivity of Mg in the degradation of TATP in EtOH, attempts were made to activate the Mg particles in EtOH. Mg/Pd had been used to degrade TATP in a water/methanol solvent \(^{51}\), thus the mechanically alloyed Mg/Pd was also tested in EtOH solvent. Similar to the Mg system, TATP degradation was not achieved using the mechanically alloyed Mg/Pd in EtOH during the 4.5 hours reaction time period (Figure 7.2).
Figure 7.1: Degradation study of TATP with Mg particles in EtOH
Activation of Mg using Acids

Acid activation was also explored for the degradation of TATP in EtOH using Mg. Acid has been used to activate Mg for Grignard reagents by removing the passive oxide/hydroxide layer of the Mg particles thereby exposing the surface of the active Mg\textsuperscript{37}. Different acid types and structures (structures found in Figure 7.3) were tested including a strong mineral acid (HCl), organic carboxylic acids (acetic acid, formic acid, propionic acid, benzoic acid), as well as a vinylogous acid (ascorbic acid). The final concentrations of the acids used to activate the Mg are found in Table 7.1. The concentrations for each of the acids were calculated from the equilibrium concentration.
of hydronium ions from the particular acid in water (the true hydronium ion concentration in EtOH was assumed to be lower than in water, however those exact concentrations were not calculated). The TATP degradation results for the different acids tested are found in . The short chain carboxylic acids had the greatest effect on the degradation of TATP even over those acids with lower pKₐ values with acetic acid being the most effective in improving the degradation rate of TATP. Computational studies have shown Mg²⁺ to complex with carboxylate anions ⁶⁴, ⁶⁵, which may explain the effectiveness of the smaller carboxylic acids to enhance the Mg for the reduction of TATP even compared to strong acids. Because of this effect, the carboxylic acid was thought to have two separate and significant purposes: (i) removal of the passive oxide/hydroxide layer exposing the zero-valent Mg and (ii) complexation of the carboxylate anion complexes with the oxidized Mg possibly enhancing the electron transfer or hydrogen transfer between the Mg and the TATP molecule ⁶⁴, ⁶⁵.
Figure 7.3: Molecular structures of tested acids.

Table 7.1: The concentrations of acid used in the reaction solutions.

<table>
<thead>
<tr>
<th>Acid</th>
<th>$\text{pK}_a$</th>
<th>[Acid] (M)</th>
<th>Final [H+] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Acid</td>
<td>4.75</td>
<td>0.161</td>
<td>0.0017</td>
</tr>
<tr>
<td>Ascorbic Acid</td>
<td>4.10</td>
<td>0.037</td>
<td>0.0017</td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td>4.19</td>
<td>0.044</td>
<td>0.0017</td>
</tr>
<tr>
<td>Formic Acid</td>
<td>3.75</td>
<td>0.013</td>
<td>0.0015</td>
</tr>
<tr>
<td>Hydrochloric Acid</td>
<td>-8.00</td>
<td>0.002</td>
<td>0.0017</td>
</tr>
<tr>
<td>Propionic Acid</td>
<td>4.87</td>
<td>0.134</td>
<td>0.0013</td>
</tr>
</tbody>
</table>
Figure 7.4: The TATP degradation rate comparison of different acids for the activation of Mg
The kinetic data for the three carboxylic acids found to activate the Mg in the
degradation of TATP are compared in Figure 7.5. Acetone has been determined to be the
major product of the degradation of TATP with Mg/Pd, thus degradation of TATP was
confirmed by analyzing for the production of acetone. Rate constant determination and
reaction order for the different carboxylic acids are discussed later.

Figure 7.5: TATP degradation rate comparison for the activation of Mg in EtOH with the
addition of the acetic acid, formic acid, and propionic acid.
Since TATP has been shown in literature to degrade readily in concentrated acids and acid vapors, the effect of the acid on the TATP in the absence of Mg was tested to confirm that the presence of the Mg-carboxylic acid-EtOH system was in fact responsible for the degradation of TATP, and the TATP was not degraded in the presence of only the acid. The addition of acid (concentrations reported in Table 7.1) to TATP solutions in EtOH showed no reduction in TATP concentration, as well as, no production of acetone in the absence of the Mg.

The addition of water to the reaction vial was also tested. The TATP degradation results of the water tests are found in Figure 7.6. Higher molar ratios of water to Mg inhibited the degradation reaction, however smaller ratios of water to Mg enhanced the degradation reaction of TATP using Mg-acetic acid-EtOH system. The presence of higher molar ratios of water was thought to consume greater quantities of the Mg or passivate the Mg surface; therefore the Mg was not readily available for the TATP degradation reaction. It was necessary for the Mg to be in excess to have the capability to degrade TATP within the EtOH-acetic acid system.
Figure 7.6: Testing the affect of water on the degradation of TATP using the Mg-acetic-EtOH system.
The effect on the addition of C to the Mg particles through a ball-milling process was also explored. The addition of the C to the Mg particles adds a highly adsorptive material that has the ability to adsorb the TATP molecules within closer proximity to the Mg surface permitting for reduction of the TATP by the Mg. Initial testing of the Mg/C with the addition of acetic acid was performed over a 4.5 hour period similar to that of the Mg/Pd and Mg particle testing, however approximately 99% of the initial TATP concentration was degraded within the first 30 min of the reaction time. Additional kinetic testing was performed within the first 30 min to provide additional data of the degradation of TATP with Mg/C particles (Figure 7.7). The Mg/C combined with the acetic acid and EtOH was very successful in degrading TATP.
Figure 7.7: Degradation of TATP with Mg/C-acetic acid-EtOH (a) and 1\textsuperscript{st} order rate plot (b).
Since mechanically alloyed Mg/Pd has proved successful in degrading TATP in aqueous solution \(^{51}\), Mg/Pd was also tested for its ability to degrade TATP in EtOH. Acetic acid addition was also tested with the mechanically alloyed Mg/Pd system in EtOH. As observed with the Mg/C and the Mg systems, Mg/Pd was also activated by the acetic acid to degrade TATP in EtOH (Figure 7.8). The degradation data for the three tested metal systems are compared in Figure 7.9. As seen in Figure 7.9, the Mg/Pd system was more effective in degrading the TATP after the addition of the acetic acid than the Mg alone which is thought to be due to the presence of C that is ball-milled with the Pd. The hydrogenation catalyst does not appear to enhance the reaction given that the rate of degradation with Mg/Pd was not observed to be greater than that seen with Mg/C.
Figure 7.8: Degradation of TATP with Mg-acetic acid-EtOH (a) and 1st order rate plot (b).
Figure 7.9: Comparison of the degradation rates of three different Mg systems using acetic acid
Calculation of Rate Law and Rate Constants

The kinetic data for the degradation of TATP with Mg, Mg/Pd, and the Mg/C activated by acid exhibited pseudo-first order rate constants as seen in Figure 7.8 and Figure 7.9. The overall rate law for the pseudo-first order reaction is found in Equation 9.

\[
\frac{dTATP}{dt} = -k_{TATP}[TATP]
\]  \hspace{1cm} (9)

In order to calculate the rate constant \(k_{TATP}\), the data was fit to \(\ln[TATP]\) vs. time plot characteristic of first order reactions, and \(k_{TATP}\) corresponded to the slope of the best-fit line obtained through linear regression analysis. The comparison of the rate constants for the different systems tested are found in Table 7.2 and Table 7.3. The half-lives for the disappearance of TATP using Mg, Mg/C, and Mg/Pd activated with acetic acid were calculated as 210 min, 2.24 min, and 69.3 min, respectively. The amount of TATP degraded was corrected for adsorption (determined through the metal studies with no acid) and the ratio of TATP to acetone produced was determined (Table 7.3). The conversion efficiency of the three systems is shown in Figure 7.10. The ratio of acetone to TATP degraded varied depending on the metal system used; however these varying ratios may be due the extent of completion of the degradation reaction. The Mg/C
system was determined to have the highest ratio of acetone to TATP (2.94:1) and 100% TATP degradation efficiency was also observed.

Table 7.2: Kinetic data for the degradation of TATP using different carboxylic acids.

<table>
<thead>
<tr>
<th>Acid</th>
<th>$k_{TATP}$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propionic Acid</td>
<td>0.0010</td>
</tr>
<tr>
<td>Formic Acid</td>
<td>0.0015</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>0.0033</td>
</tr>
</tbody>
</table>

Table 7.3: Kinetic data for the degradation of TATP using different acified Mg systems activated by acetic acid.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$k_{TATP}$ (min$^{-1}$)</th>
<th>Acetone: TATP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.0033</td>
<td>1.72</td>
</tr>
<tr>
<td>Mg/C</td>
<td>0.31</td>
<td>2.94</td>
</tr>
<tr>
<td>Mg/Pd</td>
<td>0.01</td>
<td>2.44</td>
</tr>
</tbody>
</table>
Figure 7.10: Carbon balance of the TATP degradation using the three different Mg systems activated by 1% acetic acid in EtOH. The total carbons (C) were calculated based on the initial TATP concentrations. The recovered C were those C corresponding to the acetone produced. The unrecovered was determined by taking the recovered C and subtracting from the total C.
Conclusion

The addition of carboxylic acids successfully activated Mg in EtOH for the degradation of TATP. The activation seen by the carboxylic acid was hypothesized to have two distinct purposes for the degradation of TATP using the Mg systems. One purpose is that the carboxylic acid removes the outer passive oxide/hydroxide layer exposing the zero-valent surface of the Mg. If this were the only purpose in activating the Mg systems for degradation of TATP, any acid should show a similar effect which was not observed during the testing of different acids which leads to the second purpose, the possibility that the carboxylic acids have significant involvement in the degradation mechanism. The Mg$^{2+}$-carboxylate complex formed in solution may enhance electron or hydrogen transfer required between the Mg and the TATP $^{64, 65}$. The observed activation from only the carboxylic acids, especially acetic acid, even over stronger acids was unexpected; however, the mechanism of activation will be the focus of future research. In addition to determining the mechanism of activation, future research will also test this system on other target compounds which are not susceptible to degradation with Mg in EtOH.

Of all acids studied, the addition of 1% acetic acid was determined to be most successful in activation of the Mg-EtOH systems. The half-lives observed from the Mg, Mg/C, and Mg/Pd systems for the disappearance of TATP are 210 min, 2.24 min, and 69.3 min, respectively. Acetone was observed as the major product of these degradation studies which is in agreement with the results obtained from other degradation studies $^{20, 51}$. The increased solubility of TATP in EtOH, in addition to the successful use of Mg-
acetic acid-EtOH systems for the chemical destruction of TATP is a promising degradation and *in situ* treatment method for TATP.
CHAPTER EIGHT: SPECTROSCOPIC ANALYSIS OF THE CHEMICAL DESTRUCTION OF TATP USING ANTIMONY (III) CHLORIDE

Introduction

Literature has reported the possible ability of TATP to complex to metal ions using both Hartree-Fock calculations (HF) and density functional theory calculations (DFT) \(^{68}\). Some metals ions were determined to theoretically bind to the intact ring structure of the TATP molecule while other ions were proposed to have large binding energies to the peroxide oxygen which could theoretically cause cleavage of the ring structure of the TATP molecule. These HF and DFT calculations determined that ions Sc\(^{3+}\), Ti\(^{4+}\), and Sb\(^{3+}\) energetically favored ring opening (162, 241, 898 kcal/mol respectively over the closed ring TATP-In\(^{3+}\) structure) when complexing with the TATP molecule \(^{68}\). The theoretical capability of these ions to open the TATP is favorable to degrading or decomposing TATP and, was accordingly explored further.

Preliminary tests using these different metal ions, Sb\(^{3+}\) in the form of Antimony (III) chloride was found to be the most successful in decreasing TATP concentrations in acetonitrile solutions. In order to explore the complexation of TATP with the Sb\(^{3+}\) ion further, spectroscopic methods were used to analyze the Sb\(^{3+}\)-TATP complex. Sb\(^{3+}\) has been shown in literature to complex with a wide range of different compounds including benzene, flavanoids, steroids, and vitamins \(^{69, 70}\). The detection of these types of compounds employed the use of UV-Vis and IR spectroscopy, therefore similar methods were used and reported in this chapter.
Results and Discussion

GC Analysis

The effect of SbCl$_3$ on TATP was first determined through GC/FID analysis. The TATP concentration was measured using GC/FID after the addition of SbCl$_3$. The results of the GC/FID analysis are found in Table 8.1. Thirty-seconds after adding the SbCl$_3$, the TATP concentration was reduced by 85.2 %, and the TATP concentration was reduced to below limits of detection (LOD) in 15 min. These rapid degradation results suggest a stochiometric reaction between the TATP and Sb$^{3+}$ which agrees with the computational data presented in literature$^{68}$. The reaction of the TATP and Sb$^{3+}$ appeared to be limited by the solvation of the SbCl$_3$ within the reaction mixture. Different procedures were also tested in an attempt to slow the reaction so that kinetic data could be obtained. The reaction was performed in a dry ice/acetone bath; however reaction rate was still determined to be too rapid to measure. Additional spectroscopic analysis was performed on this reaction in an attempt to confirm and characterize the complexation of the Sb$^{3+}$ and TATP.
Table 8.1: GC-FID analysis of TATP concentration after addition of SbCl₃

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Concentration of TATP (µg/mL)</th>
<th>% TATP Reacted</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>232.3</td>
<td>0</td>
</tr>
<tr>
<td>0.50</td>
<td>34.37</td>
<td>85.2</td>
</tr>
<tr>
<td>15</td>
<td>Below LOD</td>
<td>100</td>
</tr>
</tbody>
</table>

UV Analysis

The reaction between TATP and Sb³⁺ was analyzed using ultraviolet (UV) spectroscopy. TATP has been reported in literature as not being detected by UV spectroscopy unless chemically treated ⁷¹, ⁷². The UV spectrum of SbCl₃ is found in Figure 8.1 (a). The UV spectra were obtained for different molar concentrations of SbCl₃ (0.035, 0.066, 0.090 µmol). Figure 8.1 (b) shows the UV spectra after the addition of the same molar concentration of TATP (0.94 µmol) to the same molar concentrations of SbCl₃ as analyzed previously. As seen from Figure 8.1, the λ_max for the UV spectra of SbCl₃ in AcCN and the Sb³⁺-TATP complex shifted slightly and the peak profiles varied. These observations suggest that the SbCl₃ reacts with the TATP molecule.
Figure 8.1: UV spectra of SbCl$_3$ (a) and with the addition of TATP (b) in AcCN
Literature has reported the use of Sb\(^{3+}\) to detect the presence of quercetin (Q, Figure 8.2) through its complexation reaction with Sb\(^{3+}\). This Q-Sb\(^{3+}\) complex was reported in literature to have a strong adsorbance in the Vis region with a \(\lambda_{\text{max}}\) of 410 nm. The Vis spectra obtained from the Q-Sb\(^{3+}\) complex is shown in Figure 8.3. Different concentrations of Sb\(^{3+}\) were added to 0.0455 mM Q solution to have different molar ratios of Sb\(^{3+}\) to Q. Based on the Vis spectra obtained in these experimental studies (Figure 8.3), the \(\lambda_{\text{max}}\) for Q was determined to be 373 nm, and the \(\lambda_{\text{max}}\) for the Q-Sb\(^{3+}\) complex was 420 nm.

![Molecular structure of Quercetin](image)

Figure 8.2: Molecular structure of Quercetin
Figure 8.3: UV spectra of 0.0455 mM Quercetin solution with the addition of different concentrations of SbCl$_3$.

The effect of adding TATP to the complexed Q-Sb$^{3+}$ was then tested to determine if TATP would react with the Sb$^{3+}$ after it had reacted with Q. Figure 8.4 shows the changes in Q-Sb$^{3+}$ absorbance (420 nm) and the Q absorbance (373 nm) after the addition of different quantities of TATP. As more TATP is added to the Q-Sb$^{3+}$, the complex absorbance at 420 nm decreases and the Q absorbance increases. This result suggests that the TATP reacts with the complexed Sb$^{3+}$ releasing the Q which is indicated by the increase at the Q absorbance $\lambda_{\text{max}}$ at 373 nm and the decrease of the Sb$^{3+}$-Q $\lambda_{\text{max}}$ at 420 nm. Based on these results, the binding between the TATP molecule and Sb$^{3+}$ is stronger.
than that of the Q-Sb$^{3+}$ because the TATP is able to react even with the already bound Sb$^{3+}$.

![Graph showing UV absorbance of the Quercetin-Sb3+ complex after the addition of different amounts of TATP.](image)

Figure 8.4: UV absorbance of the Quercetin-Sb3+ complex after the addition of different amounts of TATP.

**Conclusion**

Based on the results observed in the GC/FID, UV, and Vis analyses, the use of SbCl$_3$ for the chemical destruction of TATP appears promising. The addition of SbCl$_3$ to a solution of TATP was able to produce a dramatic decrease in the TATP concentration observed through GC/FID analysis with an 85.2% decrease within 30 sec after the addition of SbCl$_3$. The reaction proceeded quickly, thus no reaction rate was calculated.
Methods were used to attempt to determine the reaction rate, including lowering reaction temperatures, however those methods were unsuccessful.

In order to attempt to confirm the reaction between SbCl₃ and TATP and characterize the complex formed, UV analysis was performed. Peak profiles changes were observed after the addition of different concentrations of SbCl₃ to a TATP solution vs. the UV spectra of SbCl₃. Also, the ability of TATP to react with Sb³⁺ after the Sb³⁺ was complexed with Q was also tested. These results from the UV spectra confirmed the reaction between the SbCl₃ and TATP.

Further work to determine the effectiveness of the SbCl₃ for the field treatment of TATP is essential. Additional studies include the verification of the exact structure of the TATP-Sb³⁺ complex. The determination of the explosive nature of the TATP-Sb³⁺ complex is also necessary for confirming its use in field application.
CHAPTER NINE: KINETIC STUDY FOR THE REDUCTION OF NITRO EXPLOSIVES (TNT AND RDX) IN WATER USING MECHANICALLY ALLOYED BIMETALS

Introduction

Nitroaromatic and nitro explosives, particularly 2,4,6-trinitrotoluene (TNT, Figure 9.1) and 1,3,5-trimethylene-2,4,6-trinitramine (RDX, Figure 9.2) have become a growing environmental concern \(^{73, 74}\). There are a variety of contamination sources that lead to the introduction of these nitroaromatic and nitro explosives into the environment. Disposal of industrial production waste has introduced nitro explosives contamination into soil, groundwater, and surface water in the vicinity of manufacturing areas as well as at dumping sites. Other types of contamination includes incomplete detonation of these explosives resulting in the dispersal of residue onto surrounding structures and soil \(^{75, 76}\). The increasing concern of nitro-based explosives has led to the development remediation technologies to manage contamination of these energetic compounds.

![Molecular structure of TNT](image)

Figure 9.1: Molecular structure of TNT
Figure 9.2: Molecular structure of RDX

Research has focused on a variety of different methods to remediate nitro explosives including microbial \(^77\) and phytoremediation techniques \(^78\). Other remediation techniques have focused on the use of metals and catalysts. This research includes the use of zero-valent iron (ZVI) \(^{28,31,53}\) as well as complexed Fe \(^79\) and Fenton reactions \(^80\), and nickel catalysts \(^81\). The potential to use Fe systems for the degradation of nitro-based energetic compounds can be limited by their reaction environments. Some of these systems require anaerobic conditions and a controlled pH \(^29\) which could make their use limited. Degradation rates using Fe are also affected by surface corrosion. Other research has tried to overcome the complications of using Fe for the degradation of nitro-based compounds by utilizing transition metals including TiO\(_2\) palladium photocatalysis \(^82,83\) and nickel catalysts \(^81\). Using common catalysts, such as Pd and Ni, allows for the successful remediation of these explosives under ambient conditions, temperatures, as well as, as being active in varying pH ranges. In addition these metal catalysts are less vulnerable to surface corrosion unlike in the use of iron. These remediation techniques
also have their limitations. Some require the use of hydrogen gas \textsuperscript{81} which would make them unrealistic for \textit{in situ} treatment of nitro-explosives contamination.

A zero-valent metal that has been used as a substitute for ZVI is magnesium, which has its advantages over the widely used ZVI as a reductive metal since Mg has a greater reduction potential as that compared to ZVI (Equation 10 and 11):

\[
\text{Mg}^{2+} + 2e^{-} \rightarrow \text{Mg}^{0} \quad E^0 = -2.37 \text{V} \tag{10}
\]

\[
\text{Fe}^{2+} + 2e^{-} \rightarrow \text{Fe}^{0} \quad E^0 = -0.44 \text{V} \tag{11}
\]

Magnesium also possesses a self-limiting oxide layer in addition to a higher reduction potential, thus Mg has its advantages over the corrosive ZVI \textsuperscript{36}. Both Mg and Fe have been combined with common hydrogenation catalysts to produce reductive systems that are successful in reducing chlorinated compounds thus these similar systems appear promising in the reduction of nitro-based explosives such as TNT and RDX \textsuperscript{7, 25, 55, 56}. Since Ni catalysts have shown to reduce nitro-based compounds such as TNT, RDX, and HMX, Fe/Ni was also tested \textsuperscript{81}.

The success of these bimetals in reducing nitro-based explosives contamination allows for the future use of these bimetals in combination with remediation technologies including emulsified zero valent metal (EZVM) \textsuperscript{2} and bimetallic treatment systems (BTS). These technologies will provide an \textit{in situ} method for treating TNT and RDX contamination in groundwater, soil, and on buildings and ordnance have proven successful in treating other recalcitrant compounds. The future field deployment of these
technologies to remediate explosive contamination is the ultimate objective in exploring these metals.

Experimental Procedure

Experimental Procedure

Materials

The metals tested included microscale iron (1-3 um diameter) obtained from BASF (Iselin, NJ); microscale magnesium (2-4 um diameter) from Hart Metals, INC (Tamaqua, PA); 1% palladium on carbon from Engelhard (Iselin, NJ); and 75% Nickel on graphite (<75 um) from Alfa Aesar (Ward Hill, MA). RDX and TNT (5000 ug/mL) standard solutions in acetonitrile were obtained from Restek Corporation (Bellefonte, PA). These standard solutions were each diluted in deionized water to final concentrations of 10 ppm RDX and 5 ppm TNT. Toluene (Optima® grade) was obtained from Fisher Scientific (Fair Lawn, NJ).
Methods

Metal Preparation

Mg/Pd, Fe/Ni, and Fe/Pd were manufactured using an optimal ball-milling process. The mass of zero-valent metal (Fe or Mg) and catalyst used for production of the bimetal was 78 and 8 g, respectively. The final catalyst loading for the prepared bimetals are found in Table 9.1.

Table 9.1: Catalyst and metal loadings for the prepared bimetals

<table>
<thead>
<tr>
<th>Bimetal</th>
<th>ZVM (%)</th>
<th>Catalyst (%)</th>
<th>Carbon (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg/Pd</td>
<td>91.8</td>
<td>0.08</td>
<td>8.20</td>
</tr>
<tr>
<td>Fe/Pd</td>
<td>91.8</td>
<td>0.08</td>
<td>8.20</td>
</tr>
<tr>
<td>Fe/Ni</td>
<td>91.8</td>
<td>6.20</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Vial Studies and Sample Extraction

All vial metal studies were performed in duplicate, in ambient temperature and pressure, and under normal aerobic conditions. Vials (12 mL amber vials) were prepared with 0.25 g of the bimetal or metal and 5.0 mL aqueous explosive sample. The vials were continuously shaken using a reciprocating shaker during the reaction time period. At periodic times, the degradation reaction was stopped and the analytes were extracted from the aqueous layer using toluene, shaking (2 minutes) followed by an ultrasonic bath.
(5 min). The toluene layer was filtered and removed from the metal and water using Puradisc™ 25 mm Diameter 0.45 um pore size syringe filters attached to a glass syringe. The organic layer was analyzed to determine the remaining concentration of the energetic compound.

Sample Analysis

Analyte concentration was determined by analysis using a Perkin Elmer AutoSystem gas chromatograph equipped with an electron capture detector (GC-ECD). A Rtx-5 column (30 m, 0.25 mm i.d., 0.25 um df). The ECD makeup gas was ultra high purity nitrogen at 30 mL/min, and helium was used as carrier gas with a constant pressure of 20 psi and 40 psi for the analysis of TNT and RDX, respectively. The injector temperature was held at 180ºC and the detector temperature for analysis was 325ºC. For TNT analysis, the oven was programmed at an initial temperature 50ºC, held 1 minute, ramped at 8ºC/minute until reaching 250ºC and held a the final temperature for 3 minutes. For RDX analysis, the oven was programmed at an initial temperature of 50ºC held for 1 minute, ramped at 20ºC/min. until reaching a final temperature of 300ºC where it is held for 3 minutes. For identification of products, a Thermo Finnagin gas chromatograph equipped with a DSQ mass spectrometer (GC-MS) was also used. The column, oven temperature program, and injector port were the equivalent to the GC-ECD conditions. The transfer line and the source were both held at 200ºC.
Results and Discussion

*TNT Neat Metal Kinetic Studies*

The degradation of TNT with mechanically alloyed Mg/Pd follows a 1st-order rate law (Equation 12). This kinetic data is consistent with other degradation experiments using comparable metals and compounds \(^{28, 79, 81}\). Rate constants \((k_{\text{TNT}})\) calculated from Equation 13 are normalized with the metal concentration \((50 \text{ g L}^{-1})\) and can be found in Table 2.

\[
\frac{d[\text{TNT}]}{dt} = -k_{\text{TNT}}[\text{TNT}] 
\]  
(Equation 12)

\[
\frac{[\text{TNT}]}{[\text{TNT}]_0} = e^{-k_{\text{rot}}t} 
\]  
(Equation 13)
Table 9.2 Normalized pseudo-1st order rate constants (k\textsubscript{TNT}) for the degradation of TNT in water (*ND=No degradation observed)

<table>
<thead>
<tr>
<th>Metal/Bimetal</th>
<th>Normalized Rate Constant (k\textsubscript{TNT}) (L g\textsuperscript{-1} min\textsuperscript{-1})</th>
<th>Coefficient of Determination (R\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>ND*</td>
<td>NA</td>
</tr>
<tr>
<td>Mg/Pd</td>
<td>5.6x10\textsuperscript{-4}</td>
<td>0.96</td>
</tr>
<tr>
<td>Fe/Pd</td>
<td>5.0x10\textsuperscript{-3}</td>
<td>0.99</td>
</tr>
<tr>
<td>Fe/Ni</td>
<td>2.7x10\textsuperscript{-4}</td>
<td>0.84</td>
</tr>
</tbody>
</table>

As observed in Figure 9.3, TNT in water was successfully degraded by Mg/Pd. To identify the byproducts of this degradation a solution of 50% (v/v) methanol/water was used to increase the solubility of TNT in the aqueous layer. Through GC-MS analysis, products identified include 2,4-dinitrotoluene, 4-amino-2,6-dinitrotoluene, and 2-amino-4,6-dinitrotoluene. These byproducts were observed to increase then diminish as Mg/Pd was expected to have degraded these byproducts in addition to TNT (Figure 9.4).
Figure 9.3: Kinetic degradation plots of TNT in water using Mg/Pd in H$_2$O
Figure 9.4: Degradation data of TNT using Mg/Pd particles in 50% (v/v) water/methanol and byproduct production

As seen in Figure 9.7, no degradation was observed in the presence of the microscale iron at ambient conditions, yet the addition of the hydrogenation catalyst activated the iron to degrade TNT in water (Figure 9.6 and Figure 9.7). The degradation of TNT with Fe/Pd occurs rapidly (Figure 9.7); consequently, the rate constant of the degradation of TNT with Fe/Pd was only calculated during the initial drop (first 20 minutes) of TNT concentration.
Figure 9.5: TNT degradation data after the exposure to microscale Fe. Samples are reacted and stored under ambient reaction conditions.
Figure 9.6: TNT degradation data after exposure to Fe/Ni particles
Figure 9.7: TNT degradation data after exposure to Fe/Pd particles
The final byproducts of the degradation of TNT are very important for the use of bimetals in field type applications. Compounds such as 2,4,6-triaminotoluene (TAT) have been recognized as the major product of the reaction of TNT with ZVI under inert environments. TAT, however, is more hazardous than the TNT contamination being remediated. The nature of the tested bimetals may lead them to proceed in a different reductive pathway than that of ZVI which could result in acceptable byproducts. Other work with Ni catalysts had produced byproducts that did not include TAT, which appears promising for future use of these bimetals for field application utilizing the EZVM and BTS delivery technologies. Further work must be accomplished to determine the byproducts of these reactions, which would verify the suitability for field application.

Additional work was completed to test the effectiveness of microscale iron and iron based bimetals to degrade TNT. As seen in Figure 9.7, TNT was not degraded in the presence of the micro-scale iron at ambient conditions, yet the addition of the hydrogenation catalysts activated the iron to degrade TNT in water. The degradation of TNT with Fe/Pd occurred rapidly; consequently, the rate constant of the degradation of TNT with Fe/Pd was only calculated during the initial drop (first 20 minutes) of TNT concentration.
Similar to TNT, RDX degradation with Mg/Pd followed a pseudo-first-order rate law (Equation 14). Rate constants (k\(_{\text{RDX}}\)) calculated from Equation 14 are normalized with the metal concentration (pm=50gL\(^{-1}\)) and can be found in Table 3.

\[
\frac{d[RDX]}{dt} = -k_{\text{RDX}}[RDX] \tag{14}
\]

\[
\frac{[RDX]}{[RDX]_0} = e^{-k_{\text{RDX}}t} \tag{15}
\]

Table 9.3 Normalized pseudo-first-order rate constants (k\(_{\text{RDX}}\)) of RDX degradation in water. (*ND=No degradation observed)

<table>
<thead>
<tr>
<th>Metal/Bimetal</th>
<th>Normalized Rate Constant (k(_{\text{RDX}}) (L g(^{-1}) min(^{-1}))</th>
<th>Coefficient of Determination (R(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>ND*</td>
<td>NA</td>
</tr>
<tr>
<td>Mg/Pd</td>
<td>1.5x10(^{-4})</td>
<td>0.99</td>
</tr>
<tr>
<td>Fe/Pd</td>
<td>4.4x10(^{-5})</td>
<td>0.97</td>
</tr>
<tr>
<td>Fe/Ni</td>
<td>3.2x10(^{-5})</td>
<td>0.90</td>
</tr>
</tbody>
</table>

A lag-period was observed for the first 100 minutes after exposing RDX to Fe/Pd and within the initial 45 minutes or the degradation with Mg/Pd as seen in Figures 10a and 10b. This lag-period could be the result of the adsorption of the hydrogen to the catalyst’s surface, required for the reaction to occur. These lag-periods were ignored
when calculating the pseudo-first order rate constants for the Mg/Pd and Fe/Pd studies. The data from each metal study with RDX was fit to the previous first-order rate constant and the exponential fit had coefficients of determination at or above 0.90. The zero-order kinetics plots of RDX in water show RDX degraded by Mg/Pd (Figure 9.8), Fe/Pd (Figure 9.9), and Fe/Ni (Figure 9.10) as compared to microscale Fe (Figure 9.11). The microscale Fe showed no degradation after 9 days in ambient conditions Byproducts of RDX degradation were not identified in analyzing for RDX via GC-ECD. Further work and additional analytical technique must be implemented to identify the final byproducts of the RDX degradation.

![RDX degradation data using Mg/Pd](image1)

**Figure 9.8:** RDX degradation data using Mg/Pd
Figure 9.9: RDX degradation data using Fe/Pd
Figure 9.10: RDX degradation data using Fe/Ni
Figure 9.11: RDX degradation data using Fe. Samples are reacted and stored under ambient reaction conditions.

Conclusions

All three bimetals, Fe/Pd, Fe/Ni, and Mg/Pd, were shown to degrade the explosives TNT and RDX in contrast to ZVI which showed no degradation at ambient temperatures and anaerobic conditions. These meals show various activities for the two explosives. For RDX degradation, the activity of the metal was observed as Mg/Pd > Fe/Ni > Fe/Pd whereas the metal activity with TNT was observed as Fe/Pd > Mg/Pd > Fe/Ni (Figure 9.12). Further investigation into the differences in activity may indicate an alternative degradation pathway.
The final products of the degradation of these explosives are very important in the bimetal’s capacity for field type applications. Products, such as TAT, have been recognized as the major product of the reaction with TNT and ZVI under inert environments. TAT, however, is more hazardous than the TNT contamination aiming to be degraded. The nature of the tested bimetals may lead them to proceed in a different reductive pathway than that of ZVI, which could produce more reduced byproducts than that of ZVI.

Figure 9.12: Half-lives comparison of the different bimetals for the degradation of TNT and RDX in water
CHAPTER TEN: CONCLUSION

The purpose of these collective studies focused on the development of in situ treatment methods for energetic compounds, with a main focus on the treatment of TATP. Various degradation methods for energetic materials that utilized reductive metal systems have been reported throughout this dissertation. The different metal systems tested consisted of zero-valent metals (Fe and Mg), mechanically alloyed bimetal systems (Mg/Pd), and activated Mg systems. The results of the experiments detailed in the previous chapters have concluded that TATP can safely be degraded utilizing various reactive metal systems discussed throughout this dissertation.

Initial studies testing ZVI showed that nanoscale and microscale ZVI particles degraded TATP in aqueous solutions. The degradation data obtained from these studies exhibited pseudo-1st order reaction orders with respect to TATP concentration. The half-lives for the microscale and nanoscale ZVI was calculated as 53 and 213 min, respectively. The half-lives obtained from these experiments were observed to be slower than those observed with the bimetal and magnesium systems.

In order to produce more rapid degradation results, Mg systems were also tested in the form of bimetal and activated metal systems. Kinetic data was obtained from different studies in order to calculate the reaction rates and rate constants. One of the Mg systems tested combined Mg and a hydrogenation catalyst through a mechanical alloying process. Mechanically alloyed bimetal (Mg/Pd) systems were also successful degrading TATP in aqueous solutions. This reaction was determined to be pseudo-1st order with respect to TATP, and the degradation half-life was determined to be 10.8 min. The major
product of this degradation reaction was acetone, and the molar ratio of acetone produced to TATP degraded was 2.76. A carbon material balance was performed for this system, and 94±5% of the TATP carbons were accounted for in the production of acetone.

In order to understand the degradation reaction further, studies were conducted to elucidate the mechanism of TATP degradation particularly with Mg/Pd particles. The activation energy of the degradation of TATP using Mg/Pd was calculated using the Arrhenius equation as 21.0±1.22 kJ/mol. The low activation energy and the production of approximately 3 moles of acetone to every 1 mole of TATP decomposed, suggesting that the degradation reaction is favored both thermodynamically and kinetically. Mechanistic studies were also completed to determine the TATP degradation reaction.

Activation of Mg systems with different acids was also explored for the degradation of TATP in EtOH. Short chain carboxylic acids were concluded to have the greatest effect on the degradation rate of TATP. Of the three carboxylic acids tested (formic acid, acetic acid, and propionic acid), acetic acid had the most significant influence on the TATP degradation rate. Activation of other Mg systems with acetic acid were tested including Mg ball-milled with C (Mg/C) and Mg/Pd. The half-lives observed from the Mg, Mg/C, and Mg/Pd systems for the disappearance of TATP are 210 min, 2.24 min, and 69.3 min, respectively with the Mg/C system converting 99% of the TATP to acetone within 30 minutes. Acetone was measured as the major product of all these systems tested. The addition of the acid was hypothesized to have two major roles in the degradation mechanism of TATP with Mg in EtOH: (i) removal of the passive oxide/hydroxide layer exposing the zero-valent Mg and (ii) complexation of the
carboxylate anion complexes with the oxidized Mg possibly enhancing the electron transfer or hydrogen transfer between the Mg and the TATP molecule.

Semimetal ions, particularly Sb$^{3+}$, were also explored to determine if addition of compounds containing these types of ions could complex with TATP molecules. Theoretical computational studies reported in literature suggest that ions such Sb$^{3+}$ could produce binding energies that cleave the TATP ring after complexation. Sb$^{3+}$ was determined to be the most effective in reducing TATP concentrations with an 85.2% decrease in TATP concentration 30 seconds after the addition of SbCl$_3$ solid. Complete TATP removal was observed at 15 minutes. A series of UV/Vis spectroscopic analyses were completed to try to confirm the complexation of TATP with Sb$^{3+}$. Additional work needs to be completed to validate the identity of the TATP-Sb$^{3+}$ structure.

In addition to the degradation of TATP, these reactive metal systems, particularly the bimetal systems were also tested for their effectiveness in degrading other energetic compounds, TNT and RDX. These bimetal systems tested included Mg/Pd, Fe/Pd, and Fe/Ni systems. All these systems were successful in the degradation of TNT and RDX, however varying reactivities were observed. For TNT the metal reactivity was observed as Fe/Pd>Mg/Pd>Fe/Ni with half-lives being calculated as 2.77, 24.8, and 51.3 min, respectively. For RDX degradation, the activity of the metal was observed as Mg/Pd>Fe/Ni>Fe/Pd with half-lives much slower than those seen with TNT, 92.4, 315, and 422 min, respectively. These bimetal systems were compared against microscale Fe which saw no degradation of TNT and RDX after 10 days of exposure under ambient reaction conditions. The bimetal systems were able to successfully reduce TNT and
RDX aqueous concentration in ambient reaction conditions which was not observed with other metal systems reported in literature.

This dissertation presented various degradation methods for TATP using different reductive metal systems, including ZVI, Mg, and Mg/Pd reactive particles, for the treatment of both aqueous and organic solutions of TATP. A laboratory scale study was conducted for the effectiveness of using EZVM (containing Mg/Pd) to reduce TATP concentrations in aqueous solutions. In addition to utilizing these reductive metal systems for the treatment of TATP, these systems were also explored to treat other energetic compounds that are environmental contaminants, TNT and RDX. Additional work that needs to be carried out to be able to employ these methodologies in the field includes a variety of field readiness experiments. One includes laboratory scale-up testing to determine the safety/effectiveness for large-scale samples. Optimization of these systems for different matrices would help initiate field applications. Pilot scale studies also need to be completed to test these systems on field type samples.
REFERENCES


