Degradation of Hydrazine and Monomethylhydrazine for Fuel Waste Streams using Alpha-ketoglutaric Acid

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DEGRADATION OF HYDRAZINE AND MONOMETHYLHYDRAZINE IN FUEL WASTE STREAMS USING ALPHA-KETOGLUTARIC ACID

by

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ABSTRACT

Alpha-ketoglutaric acid (AKGA) is an organic acid important for the metabolism of essential amino acids as well as for the transfer of cellular energy. It is a precursor of glutamic acid which is produced by the human body during the Krebs Cycle. AKGA has a specific industrial interest as it can be taken as a dietary supplement and is also widely used as a building block in chemical synthesis.

Collectively termed as hydrazine (HZs), hydrazine (HZ) and monomethylhydrazine (MMH) are hypergolic fuels that do not need an ignition source to burn. Because of the particular HZs’ characteristics the National Aeronautics and Space Administration (NASA) at Kennedy Space Center (KSC) and the US Air Force at Cape Canaveral Air Force Station (CCAFS) consistently use HZ and MMH as hypergolic propellants. These propellants are highly reactive and toxic, and have carcinogenic properties. The handling, transport, and disposal of HZ waste are strictly regulated under the Resource Conservation and Recovery Act (RCRA) to protect human health and the environment. Significant quantities of wastewater containing residuals of HZ and MMH are generated at KSC and CCAFS that are subsequently disposed off-site as hazardous waste. This hazardous waste is shipped for disposal over public highways, which presents a potential threat to the public and the environment in the event of an accidental discharge in transit. NASA became aware of research done using AKGA to neutralize HZ waste. This research indicated that AKGA transformed HZ in an irreversible reaction potentially leading to the disposal of the hypergols via the wastewater treatment facility located at CCAFS eliminating the need to transport most of the HZ waste off-site.

New Mexico Highlands University (NMHU) has researched this transformation of HZ by reaction with AKGA to form stabilized pyridazine derivatives. NMHU’s research suggests that the treatment of HZ and MMH using AKGA is an irreversible reaction; once the reaction takes place, HZ and/or MMH cannot re-form from the byproducts obtained. However, further knowledge relating to the
ultimate end products of the reaction, and their effects on human health and the environment, must still be addressed. The known byproduct of the AKGA/HZ neutralization reaction is 6-oxo-1,4,5,6-tetrahydropyridazine-3-carboxylic acid (PCA), and the byproduct of the AKGA/MMH reaction is 1-methyl-6-oxo-4,5-dihydro-pyridazine-3-carboxylic acid (mPCA).

This research addressed several primary areas of interest to further the potential use of AKGA for HZ and MMH neutralization: 1) isolation of the end-product of the MMH-AKGA degradation process, 1-methyl-6-oxo-4,5-dihydro-pyridazine-3-carboxylic acid (mPCA), and determination of several physical properties of this substance, 2) evaluation of the kinetics of the reaction of AKGA with HZ or MMH, 3) verification of the chemical mechanism for the reaction of the individual hypergols with AKGA, 4) determination of whether the addition of a silicone-based antifoaming agent (AF), citric acid (CA) and/or isopropyl alcohol (IPA) to the AKGA and HZ or MMH solution interferes with the degradation reaction, 4) application of laboratory bench scale experiments in field samples, and 5) determination of the reaction enthalpy of these reactions.
DEDICATION

All the efforts of these years of work are especially dedicated to my little Valeria.

Daughter, thanks for your unconditional love, for always being there with a smile, a kiss, and a hug when I needed it the most. Thanks for teaching me to be a better person, and mostly a better mom.

This was not an easy journey but you helped me achieving this important step in our lives. Always remember, who perseveres conquers; never give up your dreams.

You are the reason for everything I do!

I love you with all my heart.
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<th>Full Form</th>
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</thead>
<tbody>
<tr>
<td>ACGIH</td>
<td>American Conference of Governmental Industrial Hygienists</td>
</tr>
<tr>
<td>AFS</td>
<td>Air Force Station</td>
</tr>
<tr>
<td>AKGA</td>
<td>Alpha-ketoglutaric acid</td>
</tr>
<tr>
<td>ATSDR</td>
<td>Agency for Toxic Substances and Disease Registry</td>
</tr>
<tr>
<td>BSTFA</td>
<td>N,O-bis(trimethylsilyl)trifluoroacetamide</td>
</tr>
<tr>
<td>CA</td>
<td>Citric Acid</td>
</tr>
<tr>
<td>CalEPA</td>
<td>California Environmental Protection Agency</td>
</tr>
<tr>
<td>CCAFS</td>
<td>Cape Canaveral Air Force Station</td>
</tr>
<tr>
<td>DOT</td>
<td>Department of Transportation</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>FDEP</td>
<td>Florida Department of Environmental Protection</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatograph</td>
</tr>
<tr>
<td>Hazmat</td>
<td>Hazardous Materials</td>
</tr>
<tr>
<td>HWWTS</td>
<td>Hydrazine Waste Water Treatment System</td>
</tr>
<tr>
<td>HZ</td>
<td>Hydrazine</td>
</tr>
<tr>
<td>IARC</td>
<td>Institutional Agency for Research on Cancer</td>
</tr>
<tr>
<td>IDLH</td>
<td>Immediately Dangerous to Life and Health</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropyl Alcohol</td>
</tr>
<tr>
<td>KSC</td>
<td>Kennedy Space Center</td>
</tr>
<tr>
<td>L</td>
<td>Liter</td>
</tr>
<tr>
<td>μg/g</td>
<td>micrograms per gram</td>
</tr>
<tr>
<td>μg/mL</td>
<td>micrograms per milliliter</td>
</tr>
<tr>
<td>mg/m³</td>
<td>milligrams per cubic meter</td>
</tr>
<tr>
<td>mg/L</td>
<td>milligrams per liter</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>MLSS</td>
<td>Mixed liquor suspended solids</td>
</tr>
<tr>
<td>MMH</td>
<td>Monomethylhydrazine</td>
</tr>
<tr>
<td>mPCA</td>
<td>1-methyl-6-oxo-4,5-dihydro-pyridazine-3-carboxylic acid</td>
</tr>
<tr>
<td>MRL</td>
<td>Minimal Risk Level</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometer</td>
</tr>
<tr>
<td>m/z</td>
<td>mass to charge ratio</td>
</tr>
<tr>
<td>NASA</td>
<td>National Aeronautics and Space Administration</td>
</tr>
<tr>
<td>NIOSH</td>
<td>National Institute of Safety and Health</td>
</tr>
<tr>
<td>NMHU</td>
<td>New Mexico Highlands University</td>
</tr>
<tr>
<td>NPD</td>
<td>Nitrogen Phosphorus Detector</td>
</tr>
<tr>
<td>OSHA</td>
<td>Occupational Safety and Health Administration</td>
</tr>
<tr>
<td>PCA</td>
<td>6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid</td>
</tr>
<tr>
<td>PEL</td>
<td>Permissible Exposure Limit</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>RCRA</td>
<td>Resource Conservation and Recovery Act</td>
</tr>
<tr>
<td>RCS</td>
<td>Reaction Control System</td>
</tr>
<tr>
<td>REL</td>
<td>Recommended Exposure Limit</td>
</tr>
<tr>
<td>%RSD</td>
<td>Relative Standard Deviation</td>
</tr>
<tr>
<td>SPM</td>
<td>Suspended Particulate Matter</td>
</tr>
<tr>
<td>STEL</td>
<td>Short Term Exposure Limit</td>
</tr>
<tr>
<td>TLV</td>
<td>Threshold Limitation Value</td>
</tr>
<tr>
<td>TMCS</td>
<td>Trimethylchlorosilane</td>
</tr>
<tr>
<td>TRI</td>
<td>Toxics Release Inventory</td>
</tr>
<tr>
<td>TVD</td>
<td>Toxic Vapor Detector (Interscan® Series 4000 Portable Gas Analyzer)</td>
</tr>
<tr>
<td>TWA</td>
<td>Time Weighted Average</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-Visible Spectrophotometer</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>% (w/w)</td>
<td>Percent by weight</td>
</tr>
<tr>
<td>% (v/v)</td>
<td>Percent by volume</td>
</tr>
<tr>
<td>WWTU</td>
<td>Waste Water Treatment Unit</td>
</tr>
</tbody>
</table>
HYPOTHESIS

The reaction of HZ or MMH with AKGA can be implemented for field-scale use in industrial applications economically and safely with no byproducts found to be toxic to waste water treatment plant standards.
EXPERIMENTAL METHODS

Background information and materials acquisition are self-explanatory and were accomplished during an assigned time. Materials acquisition included purchasing a nitrogen-phosphorus detector (NPD) for one of our gas chromatographs (GC), purchase of different columns for the gas chromatographs, and obtaining certain materials through NASA or URS including HZ and MMH solutions from NASA and dosimeter badges (hyergol vapor detection) through URS. KSC and Wiltech were also visited during this time to observe handling and safety protocols used at those locations to put into practice at UCF laboratories. Method development was explored by first reviewing procedures commonly used for HZ/MMH and PCA/mPCA analysis. HZ and MMH analysis was done using the GC-NPD procedures used at Wiltech with modified and improved methods. PCA and mPCA analysis was investigated using gas chromatograph-mass spectrometer (GC-MS), high performance liquid chromatography (HPLC) with ultraviolet light (UV) detector and an ultraviolet-visible light (UV-VIS) spectrometer (Agilent 8453 UV-Visible Spectrophotometer equipped with deuterium (UV) and tungsten (visible) lamps). As a confirmatory test for PCA and mPCA products, NMR was used with carbon 13 labeled material obtained from New Mexico Highlands University. This NMR with labeled carbon 13 was also used for biodegradation analysis. For the proposed mechanism, unsymmetrical dimethyl hydrazine (UDMH) was used and analyzed with liquid chromatography-mass spectrometry (LC-MS) as well as verifications with GC-NPD.

HZ, MMH, and (UDMH) solutions were obtained from NASA and dosimeter badges (hyergol vapor detection) through URS. The solutions obtained were aqueous solutions at a 30% w/w of each of the reagents. All other chemicals and solvents used were reagent grade and used without further purification unless specified. mPCA was obtained from Enamine Chemical Suppliers, PCA was obtained from Alfa-Aesar (Shore Road, Heysham, Lancs), and AKGA was obtained from Fisher Scientific (Waltham, Massachusetts). Triple distilled water with 18 ΩM resistivity (Barnstead B-Pure) was used for
all aqueous solutions. Labeled PCA, mPCA, and AKGA were obtained from NMHU where it is
synthesized.

HZ and MMH analysis was done using the GC-NPD procedures used at NASA with modified
methods to produced better analytical sensitivity on our instrument. The disappearance of the reactants
HZ and MMH was studied via GC-NPD. A Perkin Elmer Autosystem XL equipped with a nitrogen
phosphorus detector (NPD) was used. Both the detector and injector temperatures were set to 250º C.
The oven temperature was isothermal set to 75 ºC and the helium carrier flow was set constant and to 2
mL/min. The injection run was set split-less to obtain a better analyte signal. Separation occurred on a
Restek Stabilwax silica capillary column with Crossbond polyethylene glycol stationary phase (60 m
length x 0.25 mm ID, 0.25 um df). The sample volume was 1 µL. The gas flows on the nitrogen
phosphorus detector equipped with a Rubidium bead were optimized for nitrogen with a hydrogen flow of
2 mL/min and an air flow of 100 mL/min.

The kinetics of the formation of the products during the reaction of the hypergols and AKGA
was detected using a UV-Visible spectrophotometer at a specific wavelength determined with PCA and
mPCA standards. An Agilent 8453 UV-Visble Spectroscopy System was used with a minimum ratio of
spectral band width (SBW) of 3.0. A quartz cuvette with a 10 mm path length and 4mm path width
dimensions was also used to contain the analyte. The analysis of the products was verified through high
performance liquid chromatography (HPLC) as a qualitative method. A Perlkin-Elmer series 200
HPLC (Santa Clara, California) consisting of a series 200 binary pump, a series 200 UV-VIS detector
with deuterium lamp set at a maximum absorption of 272 or 260 nm (depending on the analyte), a
series 200 autosampler, and a series 200 vacuum degasser was used. The analytical column in place
was a Zorbax SB-C18 with 3.5 µm, 4.6 x 150 mm dimensions; the mobile phase was CH₃CN:H₂O =
70:30 with a 0.1 cm³/min flow rate.
For NMR analysis a Varian VN-NMR 500 MHz (Palo Alto, California) with an 11.74T Oxford magnet was used. The $^{13}$C spectra were observed at 125.7 MHz with a 4.6 µs pulse (45 degrees), a one second acquisition time, and one second recycle delay. For mPCA and AKGA samples 256 scans were required and 512 scans were necessary for PCA samples as the dilution is greater. NMR tubes from Wilmad were used with a 5 mm diameter. D$_2$O was used as locking solvent from Cambridge Isotope Labs.
CHAPTER 1: INTRODUCTION

1.1 Chemical Structure and Physical Properties of HZ, MMH, and AKGA

1.1.1 HZs

HZ, $N_2H_4$ (Figure 1 left) is an industrial chemical that can be found as a colorless, oily liquid or as white crystals. It can be manufactured from the reaction of ammonia or dimethylamine with hydrogen peroxide or sodium hypochlorite. It is mainly used as an intermediate in the production of agricultural chemicals, in the production of spandex fibers, plastic foams, and antioxidants. It is also used as an oxygen scavenger in boiler water treatment, as a scavenger for gases, and as an intermediate in polymerization catalysis. HZ is a highly reactive and flammable fuel that does not need an ignition source to create combustion. It can be mixed with strong oxidizers such as hydrogen peroxide, fluorine, or chromic acid among others to create such ignition. For this specific characteristic, it is widely used in rocket and spacecraft fuel systems (Nakui H, 2007; Agency, 2007).

MMH, $CH_3(N_2H_3)$ (Figure 1 right), has the same hypergolic characteristics as HZ. It is a colorless liquid with ammonia like odor. It can be prepared from primary amines or substituted ureas and treatment with nitrous acid, reduction and hydrolysis; it can be also produced from the Raschig process by reaction of chloramine with methylamine. MMH is primarily used as a high-energy fuel propellant in the rocket and spacecraft industry and as fuel for thrusters. Table 1 lists some of the most important physical properties for both of these HZs (Agency, EPA, 2007)
Figure 1: HZ and MMH chemical structures respectively

Table 1: Physical properties for HZ and MMH

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>HZ</th>
<th>MMH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (g/mole)</td>
<td>32.1</td>
<td>46.1</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>65.0</td>
<td>87.8</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1.4</td>
<td>-21</td>
</tr>
<tr>
<td>Density (g/mL)</td>
<td>1.011 at 25 °C</td>
<td>0.875 at 20 °C</td>
</tr>
<tr>
<td>Vapor pressure (mm Hg)</td>
<td>5 at 25 °C</td>
<td>37.5 at 20 °C</td>
</tr>
<tr>
<td>Flash point (°F)</td>
<td>-4</td>
<td>70</td>
</tr>
<tr>
<td>Solubility</td>
<td>Water soluble</td>
<td>Water soluble</td>
</tr>
</tbody>
</table>

1.1.2 AKGA

AKGA is one of the two ketones produced by glutaric acid (Figure 2). It is an essential dicarboxylic acid that plays an important role in the Krebs or CA cycle for the proper metabolism of essential amino acids and helps in the transfer of energy. It is a substance found naturally in human organisms and has a particular industrial interest as it can be used as building block for chemical synthesis, as dietary supplement, and as a wound healing material. AKGA can be manufactured from succinic acid and oxalic acid diethyl esters, from cyanohydrines, or by hydrolysis of acyl cyanides. Also, it has been found that some bacteria and yeasts have the ability to produce AKGA (Chernyavskaya OG, 2000; Sttotmeister U, 2005; Huang HJ, 2006). Even though research about AKGA is very limited, it may have some beneficiary health effects such as the reduction of ammonia formed in the brain, muscle, and kidneys, improved kidney function of patients with heart conditions, balance the body’s nitrogen
chemistry preventing excess nitrogen in body tissue and fluids, and enhance athletic performance as it stabilizes blood sugar levels during exercise. It may also help to treat and prevent bacterial infections, cataracts, and yeast infections. Table 2 lists some of the physical properties of AKGA (Laboratories, 2008; Chernyavskaya OG, 2000)

![Figure 2: AKGA Chemical structure](image)

**Table 2: Physical properties for AKGA**

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>AKGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (g/mole)</td>
<td>146.1</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>323</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>115</td>
</tr>
<tr>
<td>Density (g/mL)</td>
<td>1.499 at 25 °C</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>177</td>
</tr>
<tr>
<td>Solubility</td>
<td>Water soluble</td>
</tr>
</tbody>
</table>

### 1.2 History of HZ and Current Applications

It took over 50 years for HZ to reach its potential in industrial applications. HZ’s value as a rocket fuel was discovered during World War II by the Germans. Based on this discovery, several facilities were installed and implemented for the production of HZ, going from a few tons to about 150 tons per month. Most of this German production was obtained in the hydrate form as anhydrous HZ was more difficult to obtain. Germans already dominated the field of HZ production and immediately after
World War II the use of HZ as rocket propellants was sponsored by governmental agencies; therefore, the private sector cooperated in investigations that were more focused toward the nonmilitary use of HZ. Since the applications for the use of HZ and its derivatives were growing, the price was expected to drop but the large production of HZ failed, making its price considerably higher. The two major producers were Mathieson Chemical Corp. and Fairmount Chemical Co. who started the first large plant in the United States in 1953 located at Lake Charles, La. To foster greater development of HZ another company was created, Matholin Corp., who assumed the responsibility for HZ production, sales, and research (Troyan, 1953).

Since then, HZ has been extensively utilized in industry because of its versatility. HZ and HZ derivatives are used in the agricultural industry in the production of pesticides and herbicides. It is also consistently used as an oxygen scavenger in boilers to prevent corrosion, as a blowing agent, and as a gas scavenger. HZ derivatives are commonly used in the polymer industry as building blocks in the polymer synthesis and as pharmaceutical intermediates. The reducing properties of HZ also make it suitable for metallurgical applications and ceramic elaboration (Schmidt, 2001; Program, 2011; Labor, 2009). Although HZ has several industrial uses, one the most important is as a rocket and spacecraft fuel. Various forms of HZ are used extensively as a propellant in rockets and thrusters. As monopropellants, HZs cannot compete with hydrocarbon fuels in terms of heating value, handling safety, or availability. However, these highly reactive and flammable fuels are strong reducing agents that react hypergolically in the presence of strong oxidizers such as chromic acid, fluorine, hydrogen peroxide, or sodium chlorite. The result is spontaneous combustion. In comparison to HZs as monopropellants, hypergolic bipropellant combinations are advantageous in that they produce combustion in the absence of external ignition sources. For this reason, hypergols are used widely in rocket engines that require frequent restarting, such as those responsible for attitude control. Hypergolicity can minimize the tendency toward destructive resonant instabilities in liquid rocket engines. And, from a launch facilitation perspective, hypergols can be stored at room temperature without boil-off losses or refrigeration as is required by cryogenic
propellants. Another advantage presented by HZ bipropellant combinations is that a loaded, bipropellant rocket can be stored in a state of instant readiness for years. Moreover, they are relatively lightweight, which is beneficial in terms of payload minimization (Schmidt, Hydrazine and its Derivatives: Preparation, Properties, Applications, 2001).

1.3 Hazards of HZ and Its Exposure Limits

Human and animal occupational data from several agencies state that HZs are considered highly toxic and have a potential to be carcinogenic. Some of the agencies that have listed HZ as a possible carcinogen to humans are the International Agency for Research on Cancer (IARC), the United States Environmental Protection Agency (USEPA), the Department of Health and Human Services, and the World Health Organization among others (Labor, 2009). The exposure to HZ can affect the body in many different ways that go from direct immediate contact to long term contact. The sources of potential exposure include individuals that are exposed in the workplace on a daily basis or in the vicinity of aerospace or industrial facilities, accidental discharge during transportation, storage, and improper disbursement into air, water, or soil. Also small traces of HZ have been found in tobacco smoke. The symptoms of acute toxicity to high levels of HZ include irritation of the eyes including temporary blindness, irritation of nose and throat, dizziness combined with headaches and nausea, seizures, and even coma in humans. It can also damage the liver, kidneys, and the central nervous system. When there is direct contact with the skin, HZ is very corrosive and can cause chemical burns and severe irritation. Chronic or long term exposure to HZ has been tested in animals by inhalation causing damage to the respiratory system, lungs, liver, spleen, and thyroid. Reproductive or developmental effects have not been studied yet in humans but some tests done in rats resulted in fetotoxicity with an increased rate of fetal and neonatal mortality (Labor, 2009; Agency, 2007).

To protect workers exposed to HZ as well as the public and the environments, state and federal government agencies have established different exposure limits for HZ and MMH. The California
Environmental Protection Agency (CalEPA) calculated a chronic inhalation reference exposure level of 0.0002 mg/m³ and the Agency for Toxic Substances and Disease Registry (ATSDR) has a calculated intermediate inhalation minimal risk level (MRL) of 0.005 mg/m³ or 0.004 ppm based on animal studies (Environmental Protection Agency Web site, 2007). An independent agency called the American Conference of Governmental Industry of Hygienist (ACGIH) recommended a threshold limit value (TLV) of 0.01 mg/m³ or 0.01 ppm for HZ for a person exposed to an eight hour shift per day or a 40 hour shift per week, which is a time weighted average (TWA) for continuous exposure. The Occupational Safety and Health Administration (OSHA) has set a permissible exposure limit (PEL) of 1.3 mg/m³ or 1.0 ppm for HZ and 0.35 mg/m³ or 0.2 ppm for MMH for an employee exposed to HZ vapors in an eight hour workday. The exposure to HZ vapors are not only via inhalation but through skin and eyes. The National Institute for Occupational Safety and Health (NIOSH) set more careful exposure limits for HZ with a recommended exposure limit (REL) of 0.04 mg/m³ or 0.03 ppm. This concentration is the lowest detected by NIOSH methods which is considered a ceiling exposure in a 120 min period of time. The NIOSH also set an immediately dangerous to life or health (IDLH) concentration of 50 ppm for HZ and 20 ppm for MMH for a 15 minute short term exposure limit (STEL) (OSHA Web site). Table 3 shows a summary of the different exposure limits set by these agencies for HZ and MMH (Labor, 2009).
Table 3: Exposure limits for HZ and MMH issued by government agencies

<table>
<thead>
<tr>
<th>Agency</th>
<th>Exposure Duration</th>
<th>HZ (mg/m³)</th>
<th>HZ (ppm)</th>
<th>MMH (mg/m³)</th>
<th>MMH (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATSDR MRL</td>
<td>TWA (8 hrs/day)</td>
<td>0.005</td>
<td>0.004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACGIH TLV</td>
<td>TWA (8 hrs/day; 40hrs/week)</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>OSHA PEL</td>
<td>TWA (8 hrs/day; 40hrs/week)</td>
<td>1.0</td>
<td>1.3</td>
<td>0.2</td>
<td>0.35</td>
</tr>
<tr>
<td>NIOSH REL</td>
<td>120 min</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>0.08</td>
</tr>
<tr>
<td>NIOSH STEL</td>
<td>15 min (IDLH)</td>
<td></td>
<td>50</td>
<td></td>
<td>20</td>
</tr>
</tbody>
</table>

1.4 Environmental Release

Besides the environmental contamination produced by agricultural, pharmaceutical, and aerospace industries, HZ can also occur naturally as a product of nitrogen fixation by algae and tobacco smoke. There is no known natural source of MMH production. The main source of contamination for HZs results from the inadvertent release in the environment and accumulation of it in wastewater. The Toxics Release Inventory (TRI) by EPA (1988) reported HZ releases of 30,000 pounds from manufacture, in 1995 the same agency reported a considerably reduced amount of HZ released from manufactured of about 17,000 pounds (Agency, EPA, 2007).

Release of HZ into the environment is caused by different factors. The majority of HZ that is released into the air come from its use in the aerospace and rocket industry as well as its use in boiler water treatment. Emission into the air is also expected from production and from tobacco smoking. Release of HZ into the water and soil occurs during production, processing, and use, as well as spills and leakages from industries and improper use or disposal of the chemical.
1.5 Environmental Fate

The unintentional release or improper disposal of HZ into the environment from industrial and propellant uses ends in large accumulation of the chemical in different environmental compartments. The potential hazards of this chemical and the results from different animal studies have led to the concern about its fate in water, air, sediment, and soil.

1.5.1 Air

HZs are chemicals with low vapor pressures; consequently, volatilization is not expected to be an important removal process. Under laboratory conditions, reported evaporation rates from aqueous solutions were 0.49 mg/cm² minute (Services, 2012). HZs are able to rapidly degrade with ozone, hydroxyl radicals, and nitrogen dioxide present in the air.

When HZ reacts with ozone, the reported half-life for HZ ranged from less than 10 min with large amounts of ozone to 2 hours under normal conditions. This half-life was calculated based on the second order reaction rate constant when HZ reacts in the presence of excess ozone to yield hydrogen peroxide. The rate constant is $3 \times 10^{-17}$ cm³ molecule⁻¹ sec⁻¹. Other reported results indicate a rate constant of $2.5 \times 10^{-16}$ cm³ molecule⁻¹ sec⁻¹ for HZ which results in an estimated half-life of less than 1 min. When HZ reacts with hydroxyl radicals in the atmosphere it yields nitrogen gas and ammonia; its half-life ranges from 1 hour in polluted conditions to 3 to 6 hours in more normal conditions with a rate constant of $6.1 \times 10^{11}$ cm³ molecule⁻¹ sec⁻¹. HZ can also go through autoxidation when present in the atmosphere. Experimental half-lives in dark reaction chambers ranged from 1.8 to 5 hours with a higher presence of humidity (Choudhary G, 1997; Pitts JN, 1980; Services, 2012).

1.5.2 Water

HZ or MMH released to water may volatilize into air or sorb onto soil. The degradation speed of HZ in water depends on the water conditions such pH, oxygen content, alkalinity, temperature, hardness and the presence of metals or organic matter. Oxidation and biodegradation are the major mechanisms of
removal. In the presence of dissolved oxygen the degradation is catalyzed by metal ions. Also the reaction is enhanced at high pH, it proceeds faster under alkaline conditions. When HZ degrades in water it produces nitrogen gas, although it may produce ammonia if metal ions are present (Choudhary G, 1997; Services, 2012).

If there are low concentrations of HZ in ambient waters, biodegradation with bacteria is an effective pathway but if concentrations are too high it can kill the available microorganisms. Other studies demonstrate that HZ and MMH are toxic to bacteria populations. Kane and Williamson reported that HZs reduced bacterial metabolism by 50% with concentrations that ranged from 14.6 to 145 mg/L. Therefore, bacterial biodegradation is not useful when these toxic chemicals are spilled into the aquatic environment (Kane DA, 1983).

1.5.3 Soil and Sediment

HZ degrades more rapidly in soil than water. It undergoes complex interactions with soils including physical sorption and irreversible chemisorption. As in water, oxidation and biodegradation are the two major processes in HZ degradation. Different types of soils have been tested and HZ adsorption into soil seems to be highly dependent on pH, as it appears to be adsorbed by different mechanisms under acidic and alkaline conditions (Services, 2012).

1.6 Remediation Techniques

The wide use of HZ in manufacturing and its use as a propellant in the aerospace industry generate large amounts of waste for disposal. The toxicity and potential carcinogenic properties have led many researchers to investigate different techniques for its degradation and transformation into less or non-toxic compounds in order to comply with the governmental agencies requirements. Several methods for HZ treatment have been evaluated including oxidation, biodegradation, reduction, and incineration. All of these techniques have associated drawbacks and liabilities which make them unsuitable for industrial uses.
Resource Conservation and Recovery Act (RCRA) established federal regulations that require strict control of hazardous waste from the point of generation to ultimate disposal (cradle to grave); these regulations can be found at 40 Code of Federal Regulations (CFR) 260 - 270. HZ and MMH are specifically identified as listed hazardous waste in 40 CFR 261.33. The hazardous waste code for HZ is U133 (reactive, toxic waste) and for MMH is P068 (acute hazardous waste). Waste management requirements under RCRA allow on-site accumulation of HZ hazardous waste on KSC and CCAFS for no more than 90-days; then waste must be transported off-site for disposal. If the regulatory required treatment standard were to be achieved within those 90-days at KSC and CCAFS, the waste could be considered non-hazardous thus limiting the requirements related to management of the HZ waste and the cost for disposal. The land disposal restriction (LDR) treatment standards for both HZ and MMH are technology-based and include Chemical Oxidation (CHOXD), Chemical Reduction (CHRED), Carbon Adsorption (CARBN), Biodegradation (BIODG) or Combustion (CMBST); a description of these technology-based standards is found at 40 CFR 268.42 Table 1. (Agency, EPA Hazardous Waste Codes, 2007). Hazardous wastes which have been pre-treated to meet LDR standards may be discharged to a Federally Owned Treatment Works such as the CCAFS wastewater treatment plant pursuant to the Federal Facilities Compliance Act. (Agency, EPA, 2007)

In the present time, based on the hazards associated with handling and flammability of HZ and MMH, NASA practices a neutralization technique which consists of the addition of a 14% w/w aqueous solution of CA to lower the vapor pressure and therefore minimize the off-gassing of its vapors. Also, the same 14% w/w CA solution is used with small amounts of IPA and an anti-foaming agent ‘scrubber soap’ to entrap and neutralize HZ vapors. Under these characteristics the waste can be held on site for up to 90 days until it is sent off-site for incineration; this disposal technique costs NASA approximately $120K per year at KSC alone. The neutralization process is not a destruction process for these toxic hypergols and the reaction is reversible and pH dependent. After the waste gets shipped out and incinerated off-site, it promotes the formation of nitrogen oxide (NOx) gases which are regulated greenhouse gases leading to
an air pollution problem. It also has a disadvantage as it has to be transported and an accidental release may happen putting the public and the environment in danger (Oropeza, 2011; Schmidt, 2001).

Biodegradation studies have been widely investigated to observe the effect of bacteria in the transformation of HZs. In 1976 Slonim and Gisclard analyzed the effect of bacteria on HZ by taking different sources of water with different bacterial content, from water with much organic debris to rainstorm water and treated water. They observed that within the first couple of hours the most polluted water caused the greatest breakdown of HZ, to about one third of the initial concentration. Temperature, hardness, and dissolved oxygen levels played an important role on the rate of breakdown as well. The cleanest water with no organic matter did not show significant HZ degradation until the second day, and reached only 35% degradation by the fourth day. Only treated city water exhibited the original amount of HZ after 96 hours (Gisclard JB, 1976; Judeikis H, 1991). The use of the biocatalyst diazoluminomelanin, a synthetic melanin, and a humic substance isolated from bacteria has been used as well as a free radical generator to react with HZ molecules in an in-situ environment. These engineered bacteria were patented back in 1997 and have shown some positive results (Hurley, 1997). More recent bioremediation studies have been proposed but even at low HZ levels, the use of conventional treatment processes have shown to have a serious toxic effect on microorganisms (Nwankwoala A, 2001; Kane DA, 1983; LaRue T, 1979).

Most of oxidation techniques are effective in the degradation for waste streams containing only HZ. Oxidation with chlorine at pH 4 was found to be effective at degrading HZ without unwanted by-product formation. But when applied to MMH it was found to produce environmental contaminants with significant amounts of chloromethane, and small amounts of nitrogen compounds including nitrogen trichloride, N,N-dichloromethylamine, N-chloromethylamine, dochloromethane, and chloroform (Schmidt, Hydrazine and its Derivatives: Preparation, Properties, Applications, 2001). Schmidt also tried oxidation with chlorine at pH of 5 with the aid of UV illumination, which showed effectiveness in
degrading water streams with all types of HZ contamination. The process required UV light input and sodium thiosulfate to treat excess amounts of chlorine.

Oxidation of HZ with hypochlorite was effective. However, when used with MMH, it produces the carcinogens N-nitroso, alkylchlorides, and other mutagenic by-products. Hypochlorite salts (NaOCl and Ca(OCl)₂) are economical and readily available (Schmidt, Hydrazine and its Derivatives: Preparation, Properties, Applications, 2001). Oxidation has also been done with hydrogen peroxide with only water and nitrogen as by-products. The reaction is very slow in the absence of a catalyst or UV-light which enhances radical formation (Zhong Y, 1989). Ozonation is effective in HZ destruction with nitrogen, oxygen, and water as by-products. When applied to MMH, it requires an extended treatment time as it produces as an intermediate, the carcinogen N-nitrosodimethylamine (NDMA). Table 4 shows a summary of the different reactions of HZ going thorough oxidation (Castegnaro M, 1986).

**Table 4: HZ treatment by different oxidants**

<table>
<thead>
<tr>
<th>Oxidation Type</th>
<th>Chemical Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation with sodium hypochlorite</td>
<td>( N_2H_4 + 2NaOCl \rightarrow 2NaCl + 2H_2O + N_2 )</td>
</tr>
<tr>
<td>Oxidation with calcium hypochlorite</td>
<td>( N_2H_4 + Ca(OCl)_2 \rightarrow CaCl_2 + 2H_2O + N_2 )</td>
</tr>
<tr>
<td>Oxidation with hydrogen peroxide</td>
<td>( N_2H_4 + H_2O_2 \rightarrow 2H_2O + N_2 + H_2 )</td>
</tr>
<tr>
<td>Oxidation with ozone</td>
<td>( N_2H_4 + 2O_2 \rightarrow N_2 + 2O_2 + 2H_2O )</td>
</tr>
</tbody>
</table>

Another type of HZ destruction or transformation is by reductive pathways. These reductions are mostly done in the presence of catalysts to speed up the reaction and improve effectiveness. Even though the approaches have been found to have a potential to destroy HZ-laden waste, a large scale process for industrial use is impractical and hard to achieve useful reaction rates. The studies evaluated the application of nickel-based reductions. One of the studies used Raney nickel in the presence and absence of exogenous hydrogen. It was found that the addition of hydrogen was necessary to achieve better reduction rates, which is not practical in the field. The other study used aluminum-nickel alloy added to
alkaline solution to generate hydrogen and spongy nickel. This is also not useful in the field because of the alkalinity needed to achieve degradation rates (Lunn G, 1983).

1.7 Suggested Remediation Technique

In 2006 Helveston et al. in New Mexico Highlands University (NMHU) patented a reaction for the transformation of HZ and MMH into other organic compounds. This treatment technique is an exothermic, irreversible conversion of HZs into stable organic, less toxic compounds. The reaction consists of the use of AKGA for remediation of these toxic hypergolic fuels in contaminated equipment and surfaces. HZ reacts with AKGA to produce 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid (PCA) (Figure 3) and MMH reacts with AKGA to yield 1-methyl-6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid (mPCA) (Figure 4) (Helvenston MC, 2006). The patent specifically states the use of AKGA for remediating HZs but it also mentions treatment of other dicarbonyl compounds such dialdehydes, diketons, aldehyde-ketones, aldehyde-acids, aldehyde esters, keto-acids, and keto-esters (Helvenston MC, 2006; Dibbern, 2008).

![Reaction of HZ and AKGA to produce PCA](image)

**Figure 3: Reaction of HZ and AKGA to produce PCA**
The patent claims that the conversion of aqueous HZ and MMH with AKGA is rapid and can be quantitative. To validate the statement Helvenston et al cited Gene Kaupp and Jens Schmeyer who claim with their research that the solid state HZ-hydroquinone complex reacts with AKGA to produce 98% PCA when ball milled in a 2:1 ratio. Moreover, in 1945 Evans and Wiselogle reported PCA preparation from aqueous HZ and AKGA with a 50% yield. In 1965 Kline and Cox also reported preparation of PCA and mPCA with 88% and 56% respectively for conversion to DL-glutamine by hydrogenation of the pyridazine by-products catalyzed by palladium or carbon (Helvenston MC, 2006).

This HZ remediation technology is of interest to NASA if it can provide a cost-effective treatment to improve safety for workers and diminish potential environmental impact. Some studies relating the use of AKGA were already done with promising results. However, a complete investigation of the by-products had to be obtained including its toxicity, kinetics, by-products analysis, and determination of the effects of possible interferences that could stop or delay the reaction.

1.8 Research Objectives

The objective of this dissertation is to address the applicability of implementing this new alternative of HZ neutralization technology and its full application in NASA facilities. This project will address several primary areas of interest to further the potential use of AKGA for HZ and MMH.
neutralization: isolation of the end-product of the MMH-AKGA degradation process mPCA as no specific physical properties are known, evaluation of the kinetics of the reaction of AKGA with HZ or MMH and reactant optimization, as well as proposing a chemical mechanism for the reaction, the determination of whether the addition of a silicone-based AF, CA and/or IPA to the AKGA and HZ or MMH solution interferes with the degradation reaction, and determination of the reaction enthalpy of these reactions.
CHAPTER 2: MPCA ISOLATION AND CHARACTERIZATION

2.1 Introduction

Physical properties of a substance are characteristics that can be observed or measured with different instruments without changing the substance into another one. Knowing the physical properties of different chemical substances is important as it will allows for the identification of that compound as well as for the prediction of specific behaviors under varying conditions (i.e. solubility).

Physical properties for PCA are well known, however physical properties for mPCA have not been previously studied. PCA’s molecular weight is 142 g/mole, melting point is between 196-198 °C, and its density is 1.65 ± 0.1 g/cm³ at 20 °C. It is slightly soluble in water and it is stable under normal temperature and pressure. Toxicological properties of these products have not been studied, though it is believed that the materials are non-hazardous.

This dissertation chapter focuses in the determination and characterization of the physical properties for mPCA in order to obtain a better understanding of its behavior.

2.2 Experimental Procedure

For the mPCA separation procedure an aqueous solution of 30% w/w diluted MMH was prepared at a 1% v/v in ultra-pure water. The total reaction volume was 100 mL and was prepared by taking a 0.19 M (8740 ppm) MMH aqueous solution into a beaker. This was prepared by adding 3.33 mL of the 30% diluted MMH solution into 50 mL of ultra-pure water and 0.64 M (93440 ppm) AKGA solution into another 50 mL of ultra-pure water. Reagents were mixed and the reaction was allowed to proceed for over 24 hours. The reaction was then put under a soft nitrogen gas stream and gentle heat, allowing the aqueous part to evaporate until the solid mPCA was obtained. Then it was washed and recrystallized.
mPCA reagent grade from Enamine Laboratories was obtained for solubility, flammability, and melting point procedures. Solubility was done by taking small amounts of mPCA, 0.5 g at a time, into 1 mL of ultra-pure water and observing how it readily dissolved until a saturation point was obtained. The vial was placed on top of a stirring plate with a stirring bar in order to facilitate dissolution. A flammability procedure was done by taking a small amount of mPCA that was placed in line over a ceramic tile to prevent heat transfer. Open flame was applied to the end of the mPCA line. For determining the melting point, a very small amount of mPCA was contained in a capillary glass tube and placed inside the melting point instrument. Observations were done as the reagent showed changes in its physical appearance.

2.3 Results and Discussion

Because mPCA is currently not a commercial product, there has been little research focusing on the physical properties of this substance. However, in the reaction of AKGA with MMH, mPCA is the only product seen besides water. The focus of this task was to verify that mPCA can be removed from an aqueous system and to identify some of the more common physical properties associated with it.

2.3.1 Separation

An aqueous mPCA solution can be easily evaporated under gentle heat and a soft nitrogen stream to yield the solid mPCA. The mPCA can then be carefully washed in acetone and recrystallized. When heating the solution to allow the aqueous part to evaporate, care must be taken to prevent overheating as the mPCA can decompose and identification of the decomposition by-products was not carried out under this project.

2.3.2 Solubility

mPCA was found to be readily soluble in ultra-pure water at room temperature (23 °C) at a level of 0.25 g/mL. Stirring was done for a period of 3 hours and solubility increased to 0.40 g/mL. For comparison, PCA was determined to have a solubility of only 0.0004 g/mL after almost one week of stirring. mPCA is at least 1000 times more soluble than PCA.
2.3.3 Flammability

mPCA does not readily ignite based on common methods for determining ignitability. mPCA is not flammable based on EPA Method 1030 (EPA, 1996), Ignitability of Solids, section 7. Figure 5 shows that upon exposure of mPCA to a flame of greater than 1000°C (per EPA Method 1030) it does not ignite or begin to burn. After a few seconds, it does begin to melt but even the melting stops when the open flame is removed.

![Figure 5 (a-b): Ignitability and flammability test for mPCA before exposure to flame, ignitiability and flammability test for mPCA after three exposures to open flame respectively](image)

2.3.4 Vapor Pressure

mPCA does not produce a measureable vapor pressure as it is a non-volatile solid at room temperature and as such does not have a measureable vapor pressure.

2.3.5 Melting Point

The melting point for mPCA was determined to be in the range of 162-164°C after five replicate tests (average 160.4 ± 0.4 °C). Figure 6 shows photographs of the process as the melting temperature was approached. The pictures are shown in order, the first one shows solid powdered mPCA, the third one shows it completely melted, in the next one it starts to boil until it reaches its decomposition in the last picture. Boiling occurred at 164.2 ± 0.7 °C and continued until 240.0 ± 0.8 °C when the compound began to decompose. Decomposition temperature of mPCA was measured to be 240.0 ± 0.8 °C.
Figure 6: Photographs of mPCA characterization as it approaches melting (162-164 °C), boiling (164.2 °C), and decomposition (240 °C) points
CHAPTER 3: ANALYTICAL ANALYSIS OF HZ AND PCA, LABORATORY STUDY OF KINETICS OF HZ WITH AKGA, AND TREATMENT RATIO OPTIMIZATION FOR FUEL WASTE STREAMS

3.1 Introduction

In 2006 Helveston et al. in New Mexico Highlands University (NMHU) patented a reaction for the transformation of HZ through its reaction with AKGA to produce 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid (PCA). This treatment technique is an exothermic, irreversible conversion into a stable and non-toxic compound (Helvenston MC, 2006). The patent specifically states the use of AKGA for remediating HZs but it also mentions treatment of other dicarbonyl compounds such as dialdehydes, diketons, aldehyde-ketones, aldehyde-acids, aldehyde esters, keto-acids, and keto-esters.

This HZ remediation technology is of interest to NASA if it can provide a cost-effective treatment to improved safety for workers and diminished potential environmental impact. Some studies relating the use of AKGA were already done with promising results (Helvenston MC, 2006; Oropeza, 2011). However, a complete investigation of the by-products was needed including its toxicity and kinetics. This chapter focuses on the analytical study of HZ and its product PCA as well as in the kinetics of the reaction with AKGA. An optimization of the AKGA:HZ ratio was also assessed for feasible industrial uses.

The rate of reaction of HZ and AKGA was measured by analyzing for the reaction product, PCA using the UV-VIS method described previously. The reaction of HZ with AKGA is fast and precipitation of the only slightly soluble PCA limits the time that the experiment can be followed via this method, as no solids can be present for a neat UV-VIS spectrum. However, based on the concentration of PCA in solution before precipitation occurs, the reaction is up to 98% complete at this point depending on the AKGA amount. Early experiments were carried out with a high ratio of AKGA:HZ, as high as 15:1, and
HZ salts were used instead of solutions of HZ. Under these conditions the reaction could be modeled as a pseudo-first order reaction with the AKGA concentration essentially unchanged.

3.2 Experimental Procedure

For HZ analysis via GC-NPD a standard solution of HZ reactant and its product were prepared. HZ standard solution was prepared in reagent grade acetone at concentrations that vary from $0.80 \times 10^{-5}$ to $0.80 \times 10^{-4}$ M (0.26 – 2.6 ppm). First, a standard solution of 0.0050 M of HZ was prepared followed by serial dilution until all concentrations were obtained. Once the HZ solution was prepared a calibration curve was run via NPD in order to obtain lower and higher limits of detection as well as elution time for the hypergol. After the calibration curve was constructed the reaction of HZ/AKGA was run to see how the hypergol concentration decreased as time progressed. For the reaction, a 0.32 M solution of the 30% w/w aqueous solution was prepared by adding 3.3 mL into a 50 mL volumetric flask filled to the mark with water. A 0.32 M AKGA solution was prepared in this case by adding 16 mL of a 2.0 M AKGA solution previously prepared to another 50 mL volumetric flask filled to the mark with water. The two solutions were mixed on a beaker and allowed to react. Chromatograms were taken at times 0, 12, 60, and 90 minutes. In order to be able to see these hypergol within the NPD limits of detection several dilutions in acetone had to be done, generally between 500 and 100 fold. This method was also used to verify the time of completion of the reaction after the kinetics work was studied.

UV-Visible spectrophotometer analysis was used for kinetics studies of the byproduct formation. First, standard reagent grade PCA was taken to construct calibration curves and an aqueous solution was prepared with ultra-pure water as background. Solutions that vary from $0.70 \times 10^{-5}$ to $0.00030$ M (1.0 - 43 ppm) were obtained by serial dilution from a 0.00035 M standard PCA solution. This solution was prepared by adding 0.025 g of reagent grade PCA to 500 mL of water. The mixture had to be sonicated for over an hour to ensure dilution of the slightly soluble PCA. Since preliminary
results for product detection was successful, the same procedure was repeated when using PCA in aqueous AKGA solution as background as a AKGA would be part of the reaction at all times. The pH of the water would be acidified and that could have an effect on the absorption. The concentration of AKGA used was 0.0038 M and the concentration of PCA varied from $0.40 \times 10^{-5}$ to $0.00030$ M (0.57 – 43 ppm). Then the same reaction that was prepared for the NPD analysis was used for the UV-Vis one but in this opportunity different AKGA:HZ concentration ratios were used. Spectra of the PCA formation was recorded at times 0, 4, 8, and 12 min. Different trials were performed under different concentrations and different reactant solutions until optimization of the reaction was found. **Table 5** shows a summary of the different HZ and AKGA concentrations used.

To study the rate of kinetics in dilute solution, 0.00043 M (56 ppm) HZ salt (HZ sulfate) solution was prepared in acidified water, pH = 4.0, as well as a 0.0054 M (784 ppm) AKGA solution in the same solvent. A 10 mL aliquot of the AKGA solution was transferred to a beaker with a stirring bar on a stirring plate. Then, a 10 mL aliquot of the HZ solution was added and samples were then analyzed using UV-Vis for a period of 3 hours. Then, another approach was taken by using samples of aqueous HZ stock solution obtained from NASA-KSA. A sample of this solution was diluted from 30% w/w to 0.00025 M, also a 0.0038 M solution of AKGA was prepared (still a 15:1 AKGA:HZ ratio) in a total volume of 700 mL, the reactants were mixed and allowed to react. Samples of the reaction were analyzed every hour via UV-Vis until the reaction ceased.

**Table 5**: HZ and AKGA concentrations for the different reactions in dilute and more concentrated solutions

<table>
<thead>
<tr>
<th></th>
<th>Reactions with Dilute Solutions</th>
<th>Reactions with Concentrated Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HZ Sulfate/AKGA</td>
<td>Aqueous HZ/AKGA</td>
</tr>
<tr>
<td>[HZ] (M)</td>
<td>0.00056</td>
<td>0.00025</td>
</tr>
<tr>
<td>[AKGA] (M)</td>
<td>0.0054</td>
<td>0.0038</td>
</tr>
</tbody>
</table>
To study kinetics at a more concentrated level, 1% v/v HZ concentration solutions were used by diluting portions from the 30% w/w previously obtained sample. A 0.32 M HZ solution was prepared by adding 3.3 mL of the 30% w/w diluted solution to a 50 mL volumetric flask filled to the mark with water. Several concentrations of AKGA were prepared from a 2.0 M stock solution based on the ratio to be tested, 0.64, 0.48, and 0.35 M of AKGA solutions were obtained for the 2:1, 1.5:1, and 1.1:1 AKGA:HZ ratios respectively. The AKGA solution was added to a beaker with a stirring bar on a stirring plate already containing the hypergol and allowed to react. Time was measured as the reaction was monitored via UV-Vis and spectra at 0, 4, 8, and 12 minutes were obtained.

As another verification method for the formation of PCA from the reaction of HZ and AKGA, $^{13}$C NMR analysis was performed. A Varian VN-NMR 500 MHz (Palo Alto, California) with an 11.74T Oxford magnet was used. The $^{13}$C spectra were observed at 125.7 MHz with a 4.6 µs pulse (45 degrees), a one second acquisition time, and one second recycle delay. A concentrated standard solution was first prepared with the $^{13}$C labeled PCA and analyzed. Then, a sample of the 30% w/w solution was taken and the concentration in molarity calculated in order to prepare a 1.1:1 AKGA:HZ ratio solution. Since the concentration of this sample was 9.4 M, a 10.3 M AKGA solution was prepared for the reaction sample. For the 0.50 M PCA standard sample, 570 mg of alternating labeled PCA were used in 8.0 mL of ultra-pure water. As PCA is slightly soluble in water, the sample was sonicated for 2 hours and then centrifuged. The 0.50 M AKGA standard was prepared by adding 150 mg of alternating labeled AKGA in 2.0 mL of ultra-pure water. Then, the previously made concentrated reactants were mixed and allowed to react for NMR analysis. The amount of scans required for AKGA samples were 256 while for PCA 512 scans were necessary as the dilution was greater. Five nm diameter NMR tubes from Wilmad were used as well as D$_2$O as locking solvent from Cambridge Isotope Labs. Specific $^{13}$C labeled material was obtained from New Mexico Highlands University with different labeling characteristics.
3.3 Results and Discussion

3.3.1 HZ Analysis via GC-NPD

Various modifications were performed to the method already used at NASA for fast and better reactant analysis using UCF instruments. Several trials were first done in order to obtain accurate retention time for HZ until the method for analysis allowed clear separation of the peaks and consistent results. Figure 7 shows a sample of the retention time for HZ and Figure 8 shows a sample of the retention time for a mixture of HZ and MMH. The retention time at which HZ elutes is about 5.1 min. Once this retention time was observed, a calibration curve (Figure 9) was run via NPD in order to obtain lower and higher limits of detection of HZ. After the calibration curve was constructed, the reaction of HZ/AKGA was run to see how the hypergol concentration decreased as time progressed. In order to be able to see these hypergols within the NPD limits of detection, dilutions in acetone had to be done. This method was also used to verify the time of completion of the reactions after the kinetics work was completed.
Figure 7: Sample chromatogram of a 0.00070 M HZ standard solution. Elution time for HZ 5.1 was 6 minutes.
Figure 8: Sample chromatogram of a 0.0007 M HZ/MMH standard solution mixture. Elution time for HZ was 5.1 minutes and for MMH was 5.5 minutes.

Figure 9: Sample calibration curve for HZ via GC-NPD
GC-NPD sensitivity makes the analysis challenging but with daily calibration curves the analysis was successfully achieved. The reaction was monitored independently and as a mixture until no HZs were observed with the NPD. **Figure 10** shows a chromatogram of a reaction of HZ with AKGA as time progresses at a 1:1 AKGA:HZ ratio. The dilution utilized in this reaction was 150 fold through all the reaction and an extra run with a 100 fold was done for the last run at 180 minutes (minimum dilution that can be used for column analysis purposes) to ensure no HZ was present. The reaction had to be carried at a lower AKGA ratio amount in order to easily observe the decrease in the HZ peak throughout time. At higher AKGA ratios the reaction happens so quickly that initial time sample measurements are difficult to observe. **Table 6** shows a summary of the mole balance between HZ reacted vs. PCA formed in triplicate runs at a specific 1:1 AKGA:HZ ratio; the mole balance was 0.0297 ± 0.00008 moles vs. 0.032 moles or 92.5 ± 0.3% conversion, which confirms that there are no other by-products formed, besides water, from the starting material.
Figure 10: HZ disappearance in reaction with AKGA at a 1:1 AKGA:HZ ratio via GC-NPD. Elution time for HZ was 5.06 minutes.

Table 6: HZ and PCA mole balance after the reaction of HZ and AKGA at a 1:1 AKGA:HZ ratio

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Hz moles</th>
<th>PCA moles</th>
<th>Hz moles</th>
<th>PCA moles</th>
<th>Hz moles</th>
<th>PCA moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0320</td>
<td>0</td>
<td>0.0320</td>
<td>0</td>
<td>0.0320</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>0.00740</td>
<td>0.0226</td>
<td>0.00689</td>
<td>0.0226</td>
<td>0.00738</td>
<td>0.0226</td>
</tr>
<tr>
<td>60</td>
<td>0.00105</td>
<td>0.0286</td>
<td>0.000891</td>
<td>0.0286</td>
<td>0.00101</td>
<td>0.0286</td>
</tr>
</tbody>
</table>

HZ/PCA mole balance

The chromatogram shows the reaction progress at various time points.
3.3.2 PCA Analysis via UV-Vis

GC-MS analysis was attempted first with PCA. A specialized GC column for acid analysis was purchased and efforts were made to analyze the compounds directly. This was not successful at least partly due to the high boiling point/decomposition temperature of the compound of interest and maximum temperatures allowed by the columns. The next effort was to use trimethylchlorosilane (TMCS) in combination with N,O-bis(trimethylsilyl)trifluoroacetemide (BSTFA) to produce a derivative that could be observed using the GC-MS (Fluka Chemie AG, 1995) as the products itself were not clearly and consistently detected by the instrument. This type of reaction produces a product that is less polar, more volatile, has increased thermal stability and therefore should produce better results for GC analysis. A standard procedure for silylation was followed (Sigma Aldrich, 1995). The primary negative issue with this method was sensitivity to humidity and the resulting inconsistencies in the analysis. The reaction must be run in nonaqueous solvent (pyridine was used for our experiments). The silylation compound itself is highly sensitive to moisture and thus extreme efforts were made to keep it in a dry environment. Even in laboratory controlled conditions, this proved to be difficult and the analysis (and quantification) of PCA was not consistent using this method due to the silylation reagent being affected so quickly by any moisture in the environment. It was decided to pursue other methods for analysis of the two products of the reactions.

Next, HPLC analysis was explored. While this provides for a fast analysis, it does not effectively separate PCA and mPCA with a clean baseline, both necessary components for accurate quantitation. PCA analysis was accomplished in only five minutes and without sample preparation but adequate separation of the two peaks (PCA eluted at 1.6 min) proved difficult and could not be accomplished in the time period allotted for this work. PCA was run separately on this instrument and the lowest level used in these experiments was $0.10 \times 10^{-5}$ M or approximately 1.4 ppm for PCA. The solvent system used on the instrument was 70% acetonitrile and 30% water. Further optimization of this method could yield another method for rapid detection of both products.
A method for using UV-Vis proved to be fast, accurate, and with detection limits of $0.40 \times 10^5$ M (0.57 ppm) for PCA. There is no sample preparation necessary for this method and the sample can be pulled directly from the reaction vessel, poured into the cuvette and measured within two minutes. PCA has a maximum peak wavelength of 260 nm. This method also provided linear calibration within the range needed for our experiments. AKGA can also be quantified using this method as it has a UV absorption at 320 nm. Based on the fast analysis, limit of detection, and reproducibility, the UV-Vis method was chosen for further analysis of PCA.

Quantitation had previously been based on calibration curves with water as the background. The background was changed to a 0.0038 M aqueous solution of AKGA as this will be the system used in all of the reactions for the rest of the investigation. While the wavelength of absorbance measurements did not change, the linear equation used to quantify PCA did change. Figure 11 and 12, shows the UV-Vis calibration for PCA with AKGA as background.

![Standard PCA Absorption at Different Concentrations](image)

**Figure 11:** UV-Vis spectrum of PCA at different concentrations with AKGA aqueous solution as background
3.3.3 PCA Formation from HZ Salt – Dilute Concentration

The aliquot that was taken from the 0.00043 M (56 ppm) HZ salt (HZ sulfate) solution was in acidified water was analyzed in the UV-Vis at 0 min. The sample was analyzed again every three min for a period of approximately three and a half hours, where no increase in absorbance was observed anymore. Figure 13 shows the PCA formation throughout these three and one half hours at different chosen times (every 36 min).
Figure 13: UV-Vis spectrum of PCA formation from HZ Salt solution and AKGA at pH of 4.0

The absorbance of the last sample analyzed at 216 min at 260 nm wavelength was 2.2 au. With this absorbance and the calibration curve previously obtained for PCA, the concentration of total PCA formed was found to be 0.0002 M (29 ppm) which yields a 52% conversion from HZ salt.

Further work was done to determine the effect of pH under these conditions with the HZ salt solution. Kinetics studies were performed at a pH of 2.5 to determine if lower pH would increase the reaction rate. Three different runs were performed for the HZ salt and AKGA, and it was observed that the reaction time does improve with this modification. Figure 14 shows that PCA forms under more acidic conditions. HZ takes approximately three hours to be converted to PCA up to a concentration of 0.00032 M (42 ppm) (75% conversion), at which time it saturates the detector.
3.3.4 PCA Formation from HZ Solution 30% w/w Aqueous HZ

Based on previous work done with the HZ/AKGA system (Oropeza, 2011), it was concluded that the conversion rate and kinetics were not the same for the salts of HZ compared to pure HZ in aqueous solution. Aqueous HZ (30% w/w) was obtained from NASA-KSC laboratories and kinetics experiments continued using that solution as the stock HZ solution instead of the HZ salts. Quantitation was changed to using the 0.0038 M AKGA aqueous solution as the background.

The stock HZ solution was diluted from 30% by weight to 0.00025 M (8.0 ppm) and a 0.0038 M (547.5 ppm) solution of AKGA (still a 15:1 AKGA:HZ ratio). A plot of the absorbance vs. wavelength, Figure 15, was obtained and intensities were used to calculate concentrations. Close to complete conversion to PCA was achieved in four hours and the kinetics was obtained using a pseudo-first order plot of Ln (concentration) vs. time. This was repeated in triplicates and data is reported in Table 7. An average of the three runs of the pseudo-first order formation of PCA is reported in Figure 16. The rate constant calculated for this reaction is 0.0040 min⁻¹ (averaged over three replicates).
Figure 15: UV-Vis spectrum for PCA formation from reaction of 0.00025 M HZ with 0.0038 M AKGA solution

Table 7: Data of the pseudo-first order PCA formation triplicate runs of the reaction of 0.00025 M HZ with 0.00375 M AKGA (15:1 AKGA:HZ ratio)

<table>
<thead>
<tr>
<th></th>
<th>Run 1</th>
<th></th>
<th>Run 2</th>
<th></th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>Ln([PCA])</td>
<td>ppm</td>
<td>Time</td>
<td>Ln([PCA])</td>
<td>ppm</td>
</tr>
<tr>
<td>(min)</td>
<td>(ppm)</td>
<td></td>
<td>(min)</td>
<td>(ppm)</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>1.38</td>
<td></td>
<td>60</td>
<td>1.44</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>1.47</td>
<td></td>
<td>120</td>
<td>1.83</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>2.03</td>
<td></td>
<td>180</td>
<td>2.02</td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>2.14</td>
<td></td>
<td>240</td>
<td>2.12</td>
<td></td>
</tr>
<tr>
<td>Rate constant = 0.00470</td>
<td>Rate constant = 0.00370</td>
<td>Rate constant = 0.00370</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Kinetics were again performed for the formation of PCA but now in a 2:1 ratio of AKGA:HZ instead of the 15:1 ratio previously tested. The same 0.00025 M (8.0 ppm) HZ solution was prepared with a 30% w/w concentration of HZ in water. The total reaction volume prepared was again 700 mL and the HZ and AKGA concentrations were calculated based on the total reaction volume. The reaction was performed with a 0.00050 M (73 ppm) solution of AKGA. The same procedure was followed for a four hour (240 min) period of time. Figure 17 shows the maximum absorption of PCA as the reaction progressed throughout the four hours.
Figure 17: UV-Vis spectrum of PCA formation at a 2:1 AKGA:HZ ratio in dilute solution

The following data, Table 8, shows a comparison of the absorbance of the 2:1 and 15:1 AKGA:HZ ratios as time progressed and the percentage difference of PCA formation at each of the different ratios. Figure 18 also shows an overlay of the two different ratios as a form of comparison.

Table 8: Comparison of the maximum absorbance of PCA formation at 2:1 and 15:1 AKGA:HZ ratios and percent formation difference

<table>
<thead>
<tr>
<th>Reaction time (min)</th>
<th>2:1 ratio</th>
<th>15:1 ratio</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0309</td>
<td>0.0370</td>
<td>16.5</td>
</tr>
<tr>
<td>60</td>
<td>0.186</td>
<td>1.05</td>
<td>82.2</td>
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<tr>
<td>120</td>
<td>0.321</td>
<td>1.66</td>
<td>80.7</td>
</tr>
<tr>
<td>180</td>
<td>0.485</td>
<td>2.04</td>
<td>76.2</td>
</tr>
<tr>
<td>240</td>
<td>0.562</td>
<td>2.27</td>
<td>75.2</td>
</tr>
</tbody>
</table>
Figure 18: UV-Vis spectrum of PCA formation kinetics overlay of the two different ratios, 15:1 and 2:1 AKGA:HZ ratios in dilute solution

With the tabulated absorbance for the 2:1 AKGA:HZ ratio and the calibration curve previously obtained, the concentration and actual yield after the 4 hour period were calculated considering the concentrations used as well as the total 700 mL volume.

Theoretical yield:

\[
(0.000250 \text{ mole/L}) \times (0.700 \text{ L}) \times \frac{1.00 \text{ mole PCA}}{1.00 \text{ mol HZ}} = 0.000175 \text{ mole PCA}
\]

Actual yield:

\[
(0.0000650 \text{ mole/L}) \times (0.700 \text{ L}) = 0.0000455 \text{ mole}
\]

Experimental yield:

\[
(0.0000455 \text{ mole} / 0.000175 \text{ mole}) \times 100\% = 26.0\%
\]

### 3.3.5 PCA Formation at 1% v/v from HZ Solution 30% w/w Aqueous

Following this work, it was decided that working with higher hypergol concentrations would be more pertinent to field tests and actual usage on site. Further kinetics and interference experiments were all based on a 1% by weight concentration of HZ in aqueous solution. Since the goal for this research is to
explore financially feasible alternatives to the current CA-hypergol treatment, lower ratios of AKGA:hypergol were employed. The ratios of 2:1 and lower were examined for the remaining experiments.

When working with high concentrations of one reactant with respect to another, pseudo-first order modeling can be applied because the concentration of the reactant in high excess does not appreciably change in comparison to the reactant being modeled as first order. However, when both reactants are of similar concentrations, one must consider the decline in concentration of both reactants and the kinetics of both reactants. More simply, as the concentration of HZ reduces, the concentration of AKGA also declines so there are fewer molecules available for reaction and this has an effect on the speed of the reaction. Based on the obtained data and the second order formation kinetics equation, both AKGA and HZ have been determined to behave as first order reactants. The most simple second order model takes into account only one reactant; therefore, a more complicated model had to be used to explain this system that takes into account the concentration decline of both reactants as the reaction proceeds. All further data relating to ratios of 2:1, 1.5:1, and 1.1:1 AKGA:hypergol were treated with this model. The equation shown (Equation 1) below is the mathematical model used for experiments involving these lower concentrations:

\[
kt = \frac{1}{[HZ] - [AKGA]} \cdot \ln \left\{ \frac{[AKGA] \cdot ([HZ] - x)}{[HZ] \cdot ([AKGA] - x)} \right\}
\]

This model is used to calculate the kinetics for the 2:1 AKGA:HZ ratio and the results are shown in Figure 19.
Figure 19: Reaction of 1% by volume aqueous HZ solution with a 2:1 ratio of AKGA:HZ using second order formation kinetics equation shown in Eq. 1

Optimization using lower AKGA:HZ ratios is reported in the following section.

3.3.6 AKGA Optimization of Treatment in the reaction of HZ and AKGA

Because AKGA is not a commodity chemical at this time, cost for the compound can be substantial. To obtain the most reasonable commercial cost for use of the chemical, optimization of the reaction to the lowest required ratio of AKGA:HZ for acceptable degradation of the hypergol was necessary. This section provides results for treatment optimization from 2:1 down to 1.1:1 AKGA:HZ molar ratios. A 0.88 L/mole*min\(^{-1}\) rate constant average value was graphically (Figures 20) determined for PCA formation after HZ (0.32 M) reacts with AKGA at 2:1, 1.5:1, and 1.1:1 AKGA:HZ ratios.
Reaction percentage yields were also calculated. The calculations below show the reaction yield at 12 minutes for PCA formation at 2:1, 1.5:1, and 1.1:1 AKGA:HZ ratio respectively.

**PCA formation reaction yield at 12 min for 2:1 AKGA:HZ ratio:**

**Theoretical yield:**

\[(0.320 \text{ mole/L}) \times (0.100 \text{ L}) \times (1.00 \text{ mole PCA / 1.00 mole HZ}) = 0.0320 \text{ mole PCA}\]

**Reaction yield at 12 min:**

\[(0.315 \text{ mole/L}) \times (0.100 \text{ L}) = 0.0315 \text{ mole PCA}\]

**Experimental yield:**

\[(0.0315 \text{ mole} / 0.0320 \text{ mole}) \times (100\%) = 98.4\%\]

**PCA formation reaction yield at 12 min for 1.5:1 AKGA:HZ ratio:**

**Theoretical yield:**

\[(0.320 \text{ mole/L}) \times (0.100 \text{ L}) \times (1.00 \text{ mole PCA / 1.00 mole HZ}) = 0.0320 \text{ mole PCA}\]
Reaction yield at 12 min:

\[(0.295 \text{ mole/L}) \times (0.10 \text{ L}) = 0.0295 \text{ mole PCA}\]

Experimental yield:

\[(0.0295 \text{ mole/0.0320 mole}) \times (100\%) = 92.2\%\]

**PCA formation reaction yield at 12 min for 1.1:1 AKGA:HZ ratio:**

Theoretical yield:

\[(0.320 \text{ mole/L}) \times (0.10 \text{ L}) \times (1.00 \text{ mole PCA / 1.00 mole HZ}) = 0.0320 \text{ mole PCA}\]

Reaction yield at 12 min:

\[(0.268 \text{ mole/L}) \times (0.10 \text{ L}) = 0.0268 \text{ mole PCA}\]

Experimental yield:

\[(0.0268 \text{ mole/0.0320 mole}) \times (100\%) = 83.8\%\]

Knowing the rate constant for PCA appearance, a calculation of the time that HZ would take to be 99.9% converted at the 1.1:1 AKGA:HZ ratio can be obtained. **Equation 2** shows the mathematical time required to achieve 99.9% conversion of HZ to PCA, which is approximately 2 hours and 44 minutes:

\[
\frac{1}{(0.3200 \text{ M} - 0.3520 \text{ M})} \times \ln \left[ \frac{0.3520 \text{ M} \times (0.3200 \text{ M} - 0.3197 \text{ M})}{0.3200 \text{ M} \times (0.3520 \text{ M} - 0.3197 \text{ M})} \right] = (0.8752) \times t
\]

\[t = 163.7 \text{ min}\]

**3.3.7 NMR Analysis Verification for the Formation of PCA after the Reaction of HZ and AKGA**

For this specific part of the project alternating $^{13}$C labeled material was used in order to ensure a better understanding of the NMR spectra. **Figure 23** shows an example of the PCA labeling pattern used which is a combination of 50% of each of the structures shown; a similar labeling pattern for AKGA was used. This alternating pattern produces split peaks from the labeled $^{13}$C but less complicated to understand.
than when the material is fully labeled, therefore determining the identity of the species is simpler.

3.3.7 NMR Analysis Verification for the Formation of PCA after the Reaction of HZ and AKGA

For this specific part of the project alternating $^{13}$C labeled material was used in order to ensure a better understanding of the NMR spectra. Figure 21 shows an example of the PCA labeling pattern used which is a combination of 50% of each of the structures shown; a similar labeling pattern for AKGA was used. This alternating pattern produces split peaks from the labeled $^{13}$C but less complicated to understand than when the material is fully labeled, therefore determining the identity of the species is simpler.

![PCA molecule with different $^{13}$C label pattern (alternating pattern) for NMR analysis](image)

The first step in this analysis was the preparation of standard labeled PCA and AKGA that were used as standard chromatograms for comparison in order to identify specific peaks for each of the products formed after the reaction of HZ with AKGA. Figure 22 shows the spectrum for standard AKGA solution. For HZ reaction with labeled AKGA, a 1.1:1 AKGA:HZ ratio was chosen based on previous kinetics results. A 9.4 M HZ solution was used with 10.3 M labeled AKGA; the reaction took place immediately due to the high concentration of the reactants. However the reaction was allowed to proceed for 24 hours before the sample was drawn from the reaction mixture to ensure reaction completion. Because a precipitate formed, the sample had to be centrifuged and filtered before it was placed in the NMR tube for analysis. Figure 23 shows the PCA standard spectrum and Figure 24 shows the PCA
spectrum after its formation from HZ and AKGA. After comparing these two spectra it can be observed that the concentration of PCA is lower in the sample from the reaction than in the standard sample, as the PCA is precipitating out of the solution and only a small amount stays in the analyzed solution. Based on this, the peaks at 20, 24, 146, 166, and 172 ppm vary in height, being much taller in the standard sample than in the reaction sample.

Figure 22: NMR spectra for standard AKGA alternating label pattern (0.50 M)
Figure 23: NMR spectra for standard PCA alternating label pattern (0.50 M)

Figure 24: NMR spectra for PCA formed after the reaction of 9.4 M HZ (1% w/w) and 10.3 M AKGA at 1:1 AKGA:HZ ratio
The peak at 20 ppm (1) corresponds to the CH$_2$ next to the C attached with double bond to the N; it produces a doublet as this C next to it, is labeled as well. The peak at 26 ppm (2) corresponds to the C that forms the ketone next to the labeled CH$_2$, producing another doublet; the peak at 146 ppm (3) corresponds to the C attached with double bond to the N and to the carboxylic acid C forming a doublet of doublets as it is besides two labeled C; the peak at 166 ppm (4) corresponds to the carboxylic acid; the peak at 172 ppm (5) corresponds to the carbon amide forming a doublet as it is beside to another labeled CH$_2$. Moreover, the samples contain some residual succinic acid which is used in the synthesis of these materials; the peaks at 30 and 180 ppm correspond to it. The PCA reaction sample also contains some residual methyl-phenol-sulfoxide used in the AKGA preparation showing small peaks at the 124-132 ppm range.
CHAPTER 4: ANALYTICAL ANALYSIS OF MMH, LABORATORY STUDY OF THE KINETICS OF MMH WITH AKGA AND TREATMENT RATIO OPTIMIZATION FOR FUEL WASTE STREAMS

4.1 Introduction

MMH is also of a particular interest for NASA as this hypergol is used as often as HZ as a rocket propellant and in thrusters. This specific fuel has more toxicity restrictions by the EPA as it is included in the P list (P068) which contains all acute hazardous waste as opposed to HZ that is enumerated in the U list (U133) that contains just toxic waste (Agency, EPA Hazardous Waste Codes, 2007). The 2006 patent obtained by Helveston et al. in New Mexico Highlands University (NMHU) also included the transformation of MMH into another organic compound through its reaction with AKGA to produce 1-methyl-6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid (mPCA). This treatment technique, as the one for HZ, is an exothermic, irreversible conversion into a stable and non-toxic compound (Helvenston MC, 2006).

The MMH remediation technology is as important as the HZ remediation to NASA to improve workers safety and reduce the potential for environmental impact. A complete investigation of the by-product (mPCA) formed by the reaction of MMH and AKGA has to be obtained, including its toxicity and kinetics, as well as the behavior of the product formation when both HZs react together with AKGA. This chapter focuses on the analytical study of MMH and its product mPCA, the kinetics of the reaction with AKGA, a comparison of it reaction speed with HZ at the same concentration, and the behavior of product formation when HZ is added to the reaction at the same time. An optimization of the AKGA:MMH ratio was also assessed for feasible industrial uses.

The rate of reaction of MMH and AKGA was measured by analyzing for the reaction product, mPCA using the UV-VIS method described previously. The reaction of MMH with AKGA is slower than
the one for HZ and AKGA but fast enough for field applications when used with at least 1% by volume hypergol, with a reaction yield after 3 and 4 hours. Early experiments were carried out in dilute solution with a high ratio of AKGA:MMH, as high as 15:1, and MMH salts were used instead of solutions of it. Under these conditions the reaction could be modeled as a pseudo-first order reaction with the AKGA concentration essentially unchanged. However the reaction was too slow for industrial consideration.

4.2 Experimental Procedure

For MMH analysis via GC-NPD standard solutions of MMH and its reaction product, mPCA were prepared. MMH standard solution was prepared in reagent grade acetone at concentrations that vary from $0.80 \times 10^{-5}$ to $0.80 \times 10^{-4}$ M (0.37 – 3.7 ppm). First, a standard solution of 0.0050 M of MMH was prepared followed by serial dilution until all concentrations were obtained. Once the MMH solution was prepared, a calibration curve was obtained via GC-NPD analysis. After the calibration curve was constructed the reaction of MMH/AKGA was run to see how the hypergol concentration decreased as time progressed. For the reaction, a 0.19 M solution of the 30% w/w aqueous solution was prepared by adding 3.3 mL into a 50 mL volumetric flask filled to the mark with water. A 0.29 M AKGA solution was prepared in this case by adding 14.5 mL of a 2.0 M AKGA solution previously prepared to another 50 mL volumetric flask filled to the mark with water. The two solutions were mixed on a beaker and allowed to react. Chromatograms were taken at times 0, 30, 60, 90, and 120 minutes and then another run at 20 hours to ensure complete reaction. In order to be able to see the hypergol within the NPD limits of detection, dilutions in acetone had to be done, generally 100 fold. This method was also used to verify the time of completion of the reaction after the kinetics work was studied.

UV-Visible spectrophotometer analysis was used for kinetics studies of the byproduct formation. First, standard reagent grade mPCA was taken to construct calibration curves and aqueous
solutions were prepared with ultra-pure water used as the background. Solutions that vary from 0.70 x $10^{-5}$ to 0.00030 M (1.1 - 47 ppm) were obtained by serial dilution from a 0.00030 M standard mPCA solution. This solution was prepared by adding 0.027 g of reagent grade mPCA to 500 mL of water. Since preliminary results for product detection was successful, the same procedure was repeated when using mPCA in aqueous AKGA solution as background as AKGA would be part of the reaction at all times. The pH of the water would be acidified and that could have an effect in the absorption. The concentration of AKGA used was 0.0038 M and the concentration of mPCA varied from 0.40 x $10^{-5}$ to 0.00030 M (0.62 – 47 ppm). Then, the same reaction that was prepared for the NPD analysis was used for the UV-Vis one but in this case different AKGA:MMH concentration ratios were used. Spectra of the mPCA formation was recorded at times 0, 30, 60, 90, 120, 180, and 240 min. Different trials were performed under different concentrations until optimization of the reaction was found. Table 9 shows a summary of the different MMH and AKGA concentrations used.

For kinetics in dilute solution, 0.00039 M (56 ppm) the MMH salt (MMH sulfate) solution was prepared in acidified water, pH = 4.0, as well as a 0.0054 M (784 ppm) AKGA solution in the same solvent. A 10 mL aliquot of the AKGA solution was transferred to a beaker on a stirring plate. Then, a 10 mL aliquot of the MMH sulfate solution was added and the samples were then analyzed using UV-Vis for a period of 36 hours. Another approach was taken by using samples of the obtained aqueous MMH stock solution from NASA-KSA. A sample of this solution was diluted from 30% w/w to 0.00025 M, also a 0.0038 M solution of AKGA was prepared (15:1 AKGA:MMH ratio) using a volume of 700 mL; the reactants were mixed and allowed to react. Samples of the reaction were analyzed every hour via UV-Vis until the reaction ceased.
Table 9: MMH and AKGA concentrations for the different reactions in dilute and more concentrated solutions

<table>
<thead>
<tr>
<th></th>
<th>Reactions with Dilute Solutions</th>
<th>Reactions with Concentrated Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMH Sulfate/AKGA</td>
<td>Aqueous MMH/AKGA (1:1)</td>
</tr>
<tr>
<td>[MMH] (M)</td>
<td>0.00054</td>
<td>0.19</td>
</tr>
<tr>
<td>[AKGA] (M)</td>
<td>0.0039</td>
<td>0.0038</td>
</tr>
</tbody>
</table>

For kinetics at a more concentrated level, 1% v/v MMH concentration solutions were used by diluting portions from the 30% w/w previously obtained sample. A 0.19 M MMH solution was prepared and several concentrations of AKGA were prepared from a 2.0 M stock solution based on the ratio to be tested, 0.38, 0.29, and 0.21 M of AKGA solutions were obtained for the 2:1, 1.5:1, and 1.1:1 AKGA:MMH ratios respectively. The AKGA solution was added to a beaker on a stirring plate already containing the hypergol and allowed to react. Time was measured as the reaction was monitored via UV-Vis and spectra at 0, 30, 60, 90, 120, 180 and 240 minutes were obtained.

$^{13}$C NMR analysis was performed as another verification method for the formation of mPCA from the reaction of MMH and AKGA. A Varian VN-NMR 500 MHz (Palo Alto, California) with an 11.74T Oxford magnet was used. The $^{13}$C spectra were observed at 125.7 MHz with a 4.6 µs pulse (45 degrees), a one second acquisition time, and one second recycle delay. A concentrated standard solution, 0.50 M, was first prepared with the $^{13}$C labeled mPCA (obtained from NMHU) and analyzed. Then, a sample of the 30% w/w solution was taken and the concentration in molarity calculated in order to prepare a 1.1:1 AKGA:MMH ratio solution. Since the concentration of this 30% w/w sample was 6.5 M, a 7.2 M AKGA solution was prepared for the reaction. The sample was prepared with such high concentration to ensure a fast reaction and a clear spectrum with a low noise background. For the 0.50 M mPCA standard sample, 310 mg of alternating labeled mPCA were used in 4.0 mL of ultra-pure water. The 0.50 M AKGA standard was prepared by adding 150 mg of alternating labeled AKGA in
2.0 mL of ultra-pure water. Then, the reactants were mixed and allowed to react for NMR analysis. The amount of scans required for AKGA and MMH samples were 256 in order to obtain a clean spectrum. Five nm diameter NMR tubes from Wilmad were used as well as D₂O as locking solvent from Cambridge Isotope Labs. Specific ¹³C labeled material was obtained from New Mexico Highlands University with different labeling characteristics.

4.3 Results and Discussion

4.3.1 MMH Analysis via GC-NPD

Various modifications were performed to the method already used at NASA for fast and more appropriate analysis for UCF instruments. Several trials were first done in order to obtain accurate retention time for MMH until the method for analysis allowed clear separation of the HZ and MMH peaks. Figure 25 shows a sample of the retention time for MMH and Figure 8 (Section 3.3.1) shows a sample of the retention time for a mixture of HZ and MMH. The retention time at which MMH elutes was 5.5 min. Once this retention time was observed, a calibration curve (Figure 26) was run via NPD in order to obtain lower and higher limits of detection for MMH. Then, the reaction of MMH/AKGA was run to see how the hypergol concentration decreased as time progressed. In order to be able to see these hypergols within the NPD limits of detection, several dilutions in water and acetone had to be done. This method was also used to verify the time of completion of the reactions after the kinetics work was studied.
Figure 25: Sample chromatogram of a 0.0007 M MMH standard solution. Elution time for MMH was 5.5 minutes.

Figure 26: Sample calibration curve for MMH via GC-NPD
GC-NPD sensitivity makes the analysis challenging but with daily calibration curves the analysis was successfully achieved. The reaction was monitored with each of the HZ individually and with a combination of the two until no MMH was observed with the NPD. Figure 27 shows a chromatogram of a reaction of MMH with AKGA as time progresses at a 1.5:1 AKGA:MMH ratio. The dilution utilized in this reaction was 100 through all the reaction (minimum dilution that can be used as the sample has to be put into acetone for column analysis purposes). A last run was performed after 36 hours to ensure no MMH was present. Table 10 shows a summary of the mole balance between MMH reacted vs. mPCA formed in triplicate runs; the mole balance was 0.0181 ± 0.0003 vs. 0.019 moles or 95.3 ± 1.6 % conversion, which confirms that there are no other by-products formed, besides water, from the starting material.

**Chromatogram for the Reaction of MMH + AKGA at a 1.5:1 AKGA:MMH**

![Chromatogram for the Reaction of MMH + AKGA at a 1.5:1 AKGA:MMH Ratio](image)

*Figure 27: MMH disappearance in reaction with AKGA at a 1.5:1 AKGA:MMH ratio via GC-NPD. Elution time for MMH was 5.5 minutes*
Table 10: MMH and mPCA mole balance for the reaction of MMH and AKGA at a 1.5:1 AKGA:MMH ratio

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Run 1 MMH moles</th>
<th>Run 1 mPCA moles</th>
<th>Run 2 MMH moles</th>
<th>Run 2 mPCA moles</th>
<th>Run 3 MMH moles</th>
<th>Run 3 mPCA moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0191</td>
<td>0</td>
<td>0.0191</td>
<td>0</td>
<td>0.0191</td>
<td>0</td>
</tr>
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<td>30</td>
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<td>90</td>
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<td>0.0157</td>
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<td>0.000696</td>
<td>0.0176</td>
<td>0.000534</td>
<td>0.0176</td>
</tr>
</tbody>
</table>

**4.3.2 mPCA Analysis via UV-Vis**

GC-MS analysis was the first analysis method attempted for mPCA. The same specialized GC column for acid analysis previously used for the PCA analysis was used to analyze the compounds directly. This was not successful at least in part due to the high boiling point/decomposition temperature of mPCA and maximum temperatures allowed by the columns. The next effort was to use trimethylchlorosilane (TMCS) in combination with N,O-bis(trimethylsilyl)trifluoroacetemide (BSTFA) to produce a derivative that could be neatly observed using the GC-MS. This type of reaction produces a product that is less polar, more volatile, has increased thermal stability and therefore should produce better results for GC analysis. A standard procedure for silylation was followed (Sigma Aldrich, 1995). The primary negative issue with this method was sensitivity to humidity and the resulting inconsistencies in the analysis. The reaction must be run in nonaqueous solvent (pyridine was used for our experiments). The silylation compound itself is highly sensitive to moisture and thus extreme efforts were made to keep it in a dry environment. Even in laboratory controlled conditions, this proved to be difficult and the analysis (and quantification) of mPCA was not consistent using this method due to the silylation reagent being affected so quickly by any moisture in the environment. It was decided to pursue other methods for analysis of the two products of the reactions.
HPLC analysis was explored for mPCA and PCA. While this provides for a fast analysis, it does not effectively separate PCA and mPCA with a clean baseline, both necessary components for accurate quantitation. mPCA analysis was accomplished in only five minutes and without sample preparation but adequate separation of the two peaks (mPCA eluted at 1.3 min) proved difficult and could not be accomplished in the time period allotted for this work. When, mPCA was run separately on this instrument, the lowest level used in these experiments was 0.010 mM or approximately 1.56 ppm for mPCA. The solvent system used on the instrument was 70% acetonitrile and 30% water. Further optimization of this method could yield another method for rapid detection of both products.

A method for using UV-Vis proved to be fast, accurate, and with low limits of detection with limits of 0.40 x 10^{-5} M (0.62 ppm) for mPCA. There is no sample preparation necessary for this method and the sample can be pulled directly from the reaction vessel, poured into the cuvette and measured within two minutes. mPCA has a maximum peak wavelength of 272 nm. This method also provided linear calibration within the range needed for our experiments. AKGA can also be quantified using this method as it has UV absorption at 320 nm. Based on the fast analysis, limit of detection, and reproducibility, the UV-Vis method was chosen for further analysis of mPCA.

Quantitation had previously been based on calibration curves with water as the background. This was changed to using a 0.0038 M AKGA aqueous solution as the background for analysis as this will be the system used in all of the reactions for the remainder of the investigation. While the wavelength of absorbance measurements did not change, the linear equation used to quantify mPCA did change. Figure 28 and 29, shows the UV-Vis calibration for mPCA with AKGA as background.
Figure 28: UV-Vis spectrum of mPCA at different concentrations with AKGA aqueous solution as the background

Figure 29: Example of linear dynamic equation of mPCA standard with AKGA aqueous solution as the background
4.3.3 mPCA Formation from MMH Salt – Dilute Concentration

Early experiments were carried out with a high ratio of AKGA:MMH, as high as 15:1 as it was done with HZ/AKGA, and MMH salts (MMH sulfate) were used instead of solutions of MMH. Under these conditions the reaction could be modeled as a pseudo-first order reaction with the AKGA concentration essentially unchanged. The first study with MMH salt was done at pH 4.0 similar to work carried out with HZ. However, the reaction was proving to be so slow that the effort was abandoned. Kinetics studies were then performed at a pH of 2.5 to determine if lower pH would increase the reaction rate. Three different runs were performed for the MMH salt and AKGA, and it was observed that the reaction time does improve with this modification. The 0.00039 M MMH sulfate solution prepared was allowed to react; a sample was then analyzed in the UV-Vis at 0 min. mPCA forms more slowly so the reaction was monitored over a period of 6 hours with a final concentration of about 0.00017 M (25 ppm) MMH. mPCA reaches its saturation point after approximately 18 hours. Figure 30 shows the mPCA formation.

![mPCA Formation from MMH Salt](image)

Figure 30: UV-Vis spectrum of mPCA formation from MMH salt solution and AKGA at a pH of 2.5
### 4.3.4 mPCA Formation from MMH Solution 30% w/w Aqueous MMH

Based on previous work done with the MMH/AKGA system (Oropeza, 2011), it was concluded that the conversion rate and kinetics were not the same for the salts of MMH compared to an MMH aqueous solution. Aqueous MMH (30% by weight) was obtained from NASA laboratories and kinetics experiments continued using that solution as the stock MMH solution. Quantitation had previously been based on calibration curves with deionized water as the background. This was changed to using a 0.0038 M AKGA aqueous solution as the background solution for analysis.

The pseudo-first order reaction rate constant with respect to the product mPCA was obtained by monitoring the product formation in the reaction mixture of MMH and AKGA as analyzed via UV-Vis spectrophotometric analysis. The maximum absorbance wavelength for this product was detected at 272 nm. Three runs were made and an average rate constant was obtained with a value of 0.15 hr⁻¹, or 0.0025 min⁻¹, significantly lower than that of HZ. Table 11 shows the triplicate results of the different runs performed. Figure 31 also illustrates the average pseudo-first order kinetics for the formation of mPCA.

#### Table 11: Data of the pseudo-first order mPCA formation triplicate runs of the reaction of 0.0025 M MMH with 0.0038 M AKGA (15:1 AKGA:MMH ratio)

<table>
<thead>
<tr>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (hrs)</td>
<td>[mPCA] (ppm)</td>
<td>Time (hrs)</td>
</tr>
<tr>
<td>2</td>
<td>1.93</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>3.28</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>4.53</td>
<td>6</td>
</tr>
<tr>
<td>8</td>
<td>5.60</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>6.54</td>
<td>10</td>
</tr>
<tr>
<td>26</td>
<td>10.5</td>
<td>26</td>
</tr>
<tr>
<td>30</td>
<td>10.8</td>
<td>30</td>
</tr>
<tr>
<td>34</td>
<td>11.4</td>
<td>34</td>
</tr>
</tbody>
</table>

Rate constant = 0.00250  Rate constant = 0.00250  Rate constant = 0.00250
Kinetic data were also obtained for the formation of mPCA with the same 2:1 ratio of AKGA:MMH instead of the 15:1 ratio previously done. A 0.00025 M (11.5 ppm) MMH solution was prepared from a 30% w/w concentration of MMH in water. The total reaction volume prepared was 700 mL and the MMH and AKGA concentrations were calculated based on the total reaction volume. The reaction was performed with a 0.00050 M (73 ppm) AKGA solution. The same analysis procedure was followed for a 30-hour (1800 min) period of time. Figure 32 shows the maximum absorption of mPCA as the reaction progressed throughout the 30-hour period.
The following data, Table 12, shows a comparison of the absorbance of the 2:1 and 15:1 AKGA:MMH ratios as time progressed and the percentage difference of mPCA formation at each of the different ratios. Figure 33 also shows an overlay of the two different ratios as a form of comparison.

**Table 12: Comparison of the maximum absorbance of mPCA formation at 2:1 and 15:1 AKGA:MMH ratios and percent formation difference**

<table>
<thead>
<tr>
<th>Reaction time (min)</th>
<th>2 : 1 ratio</th>
<th>15 : 1 ratio</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0166</td>
<td>0.0715</td>
<td>76.8</td>
</tr>
<tr>
<td>120</td>
<td>0.105</td>
<td>0.412</td>
<td>74.4</td>
</tr>
<tr>
<td>240</td>
<td>0.191</td>
<td>0.695</td>
<td>72.5</td>
</tr>
<tr>
<td>360</td>
<td>0.270</td>
<td>0.954</td>
<td>71.7</td>
</tr>
<tr>
<td>480</td>
<td>0.348</td>
<td>1.18</td>
<td>70.4</td>
</tr>
<tr>
<td>600</td>
<td>0.422</td>
<td>1.37</td>
<td>69.3</td>
</tr>
<tr>
<td>1800</td>
<td>0.984</td>
<td>2.26</td>
<td>56.5</td>
</tr>
</tbody>
</table>
Figure 33: UV-Vis spectrum of mPCA formation kinetics overlay of the two different ratios, 15:1 and 2:1 AKGA:MMH ratios

With the tabulated absorbance for the 2:1 AKGA:MMH ratio and the calibration curve previously obtained, the concentration and actual yield after the 30 hour period were calculated considering the concentrations used and the total 700 mL volume.

**Theoretical yield:**

\[(0.000250 \text{ mole/L}) \times (0.700 \text{ L}) \times (1.00 \text{ mole mPCA / 1.00 mol MMH}) = 0.000175 \text{ mole mPCA}\]

**Actual yield:**

\[(0.000102 \text{ mole/L}) \times (0.700 \text{ L}) = 0.0000714 \text{ mole}\]

**Experimental yield:**

\[(0.0000714 \text{ mole} / 0.000175 \text{ mole}) \times 100\% = 40.8\%\]

### 4.3.5 mPCA Formation at 1% v/v from MMH Solution 30% w/w Aqueous

Following the previous, it was decided that working with higher MMH concentrations would be more pertinent to field tests and actual usage. Further kinetics and interference experiments were all based on a 1% by volume concentration of MMH in aqueous solution. Since the goal for this research is to
explore financially feasible alternatives to the current CA MMH treatment, the ratios of 2:1 (AKGA:MMH) and lower were examined for the remaining experiments.

At these lower concentrations, both AKGA and MMH have been determined to behave as first order reactants. The simplest second order takes into account only one reactant. Therefore, a kinetic model was chosen that takes into account the decrease as the reaction proceeds and all data relating to ratios of 2:1, 1.5:1, and 1.1:1 AKGA:MMH was treated with this model. The equation shown (Equation 3) below is the mathematical model used for experiments involving these lower concentrations:

$$k_t = \frac{1}{[MMH] - [AKGA]} \cdot \ln\left(\frac{[AKGA] \cdot ([MMH] - x)}{[MMH] \cdot ([AKGA] - x)}\right)$$

This model is used to calculate the kinetics for the 2:1 AKGA:MMH ratio and the results are shown in Figure 34.

Figure 34: Reaction of 1% by volume aqueous MMH with a 2:1 AKGA:MMH plotted using second order equation shown in Eq. 3

Optimization using lower AKGA:MMH ratios is reported in the following section.
4.3.6 AKGA Optimization of Treatment in the reaction of MMH and AKGA

Because AKGA is not a commodity chemical at this time, cost for the compound can be substantial. To obtain the most reasonable commercial cost for use of the chemical, optimization of the reaction to the lowest required ratio of AKGA:hypergol was necessary for acceptable degradation of the hypergol used. This section provides results for treatment optimization from 2:1 down to a 1.1:1 AKGA:MMH molar ratio. Figures 35 shows the graphically calculated rate constant with a 0.11 L/mole*min⁻¹ average value for mPCA formation after MMH (1% by volume or 0.19 M) reacts with AKGA at 2:1, 1.5:1, and 1.1:1 AKGA:MMH ratios.

![Graph showing second order mPCA formation kinetics at different AKGA:MMH ratios](image)

**Figure 35**: Second order mPCA formation kinetics comparing three different AKGA:MMH ratios. 2:1, 1.5:1, and 1.1:1

Reaction percentage yields were also calculated for mPCA formation based on the time of measurements. The calculations given below show the reaction yield at 120 min for mPCA formation at 2:1 and 1.5:1 AKGA:MMH ratio respectively, and the reaction yield at 180 min for the 1.1:1 ratio.
mPCA formation reaction yield at 120 min for 2:1 AKGA:MMH ratio:

Theoretical yield:

\[(0.190 \text{ mole/L}) \times (0.100 \text{ L}) \times (1.00 \text{ mole mPCA / 1.00 mole MMH}) = 0.0190 \text{ mole mPCA}\]

Reaction yield at 120 min:

\[(0.182 \text{ mole/L}) \times (0.100 \text{ L}) = 0.0182 \text{ mole PCA}\]

Experimental yield:

\[(0.0182 \text{ mole/0.0190 mole}) \times (100\%) = 95.8\%\]

mPCA formation reaction yield at 120 min for 1.5:1 AKGA:MMH ratio:

Theoretical yield:

\[(0.190 \text{ mole/L}) \times (0.100 \text{ L}) \times (1.00 \text{ mole mPCA / 1.00 mole MMH}) = 0.0190 \text{ mole mPCA}\]

Reaction yield at 120 min:

\[(0.163 \text{ mole/L}) \times (0.100 \text{ L}) = 0.0163 \text{ mole PCA}\]

Experimental yield:

\[(0.0163 \text{ mole/0.0190 mole}) \times (100\%) = 85.8\%\]

mPCA formation reaction yield at 180 min for 1.1:1 AKGA:MMH ratio:

Theoretical yield:

\[(0.190 \text{ mole/L}) \times (0.100 \text{ L}) \times (1.00 \text{ mole mPCA / 1.00 mole MMH}) = 0.0190 \text{ mole mPCA}\]

Reaction yield at 120 min:

\[(0.161 \text{ mole/L}) \times (0.100 \text{ L}) = 0.0161 \text{ mole PCA}\]

Experimental yield:

\[(0.0161 \text{ mole/0.0190 mole}) \times (100\%) = 84.7\%\]

Knowing the rate constant for mPCA appearance, a calculation of the time that MMH would take to be 99.9% converted at the 1.1:1 AKGA:MMH ratio can be obtained. Equation 4 shows the
mathematical time calculation for 99.9% MMH conversion. Based on Equation 3, the time required to achieve 99.9% conversion of MMH is approximately 36 hours and 53 hours.

\[
0.1900 \, \text{M} \times 0.9990 = 0.1898 \, \text{M}
\]

\[
\frac{1}{(0.1900 \, \text{M} - 0.2090 \, \text{M})} \times \ln \left( \frac{0.2090 \, \text{M} (0.1900 \, \text{M} - 0.1898 \, \text{M})}{0.1900 \, \text{M} (0.2090 \, \text{M} - 0.1898 \, \text{M})} \right) = (0.1063) \, t
\]

\[
t = 2213 \, \text{min} = \sim 37 \, \text{hrs}
\]

4.3.7 NMR Analysis Verification for the Formation of PCA after the Reaction of HZ and AKGA

As was done with HZ, $^{13}$C labeled material was also used for MMH confirmatory analysis.

Figure 36 shows an example of the mPCA labeling pattern used which is a combination of 50% of each of the structures shown; the same AKGA labeling pattern used in the analysis of HZ was used for MMH. This alternating pattern produces split peaks from the labeled $^{13}$C but less complicated to understand than when the material is fully labeled, therefore determining the identity of the species is simpler.

![mPCA molecule with different $^{13}$C label pattern (alternating pattern) for NMR analysis](image)

Figure 36: mPCA molecule with different $^{13}$C label pattern (alternating pattern) for NMR analysis

Standard labeled mPCA and AKGA were used as standard chromatograms for comparison in order to identify specific peaks for each of the products formed after the reaction of MMH with AKGA. Figure 22 (Section 3.3.7) shows the spectrum for a standard AKGA solution. For the MMH reaction with
labeled AKGA, a 1.1:1 AKGA:MMH ratio was chosen based on previous kinetics results. The 6.5 M MMH solution was used with the 7.2 M labeled AKGA; the reaction proceeded immediately due to the high concentration of the reactants. However, the reaction was allowed to take place for a week before the sample was drawn from the reaction mixture to insure reaction completion. Figure 37 shows the mPCA standard spectrum and Figure 38 shows the mPCA spectrum after its formation from MMH and AKGA. After comparing these two spectra it can be observed there is a residual of succinic acid from the AKGA synthesis. These peaks correspond to 30 and 180 ppm. The spectrum is very similar to that of PCA (Section 3.3.7) with a notable difference of a peak at 38 ppm (3) which corresponds to the non-labeled methyl group attached to the N.

![NMR spectra for standard mPCA alternating label pattern (0.50 M)](image)
Figure 38: NMR spectra for mPCA formed after the reaction of 6.5 M MMH (1% w/w) and 7.2 M AKGA at 1.1:1 AKGA:MMH ratio

4.3.8 Reaction of MMH at a 1.7% v/v with AKGA Aqueous Solution

In order to show the difference in reaction rates for each of the hypergol reactants, a reaction of MMH and AKGA was done at the same molar concentration of HZ (0.32 M) and AKGA at the 1.1:1 ratio (Section 3.3.6). The concentration of MMH used was 0.32 M (10240 ppm), which is 1.7% v/v instead of the 1% v/v previously used in the total reaction volume. The reaction was performed, and the concentration vs. time of mPCA formation was recorded in order to compare it with the PCA formation previously obtained. Figure 39 shows a comparison of the PCA and mPCA second order formation kinetics at the same concentration and same AKGA:hypergol ratio at 12 min.
A percent yield was also calculated for mPCA formed after 12 min and a comparison with PCA was performed. The calculations below show the mPCA reaction yield at 12 min which was found to be 55% in comparison to 84% for PCA at the same reaction time and same AKGA:hyperol ratio.

**mPCA reaction yield at 12 min for a 1.7% v/v MMH in the reaction mixture:**

**Theoretical yield:**

\[(0.320 \text{ mole/L}) \times (0.100 \text{ L}) \times (1.00 \text{ mole mPCA} / 1.00 \text{ mole MMH}) = 0.0320 \text{ mole mPCA}\]

**Reaction yield at 12 min:**

\[(0.176 \text{ mole/L}) \times (0.100 \text{ L}) = 0.0176 \text{ mole mPCA}\]

**Experimental yield:**

\[(0.0176 \text{ mole}/0.0320 \text{ mole}) \times (100\%) = 55.0\%\]
**PCA reaction yield at 12 min for a 1.1% V/V HZ in the reaction mixture:**

**Theoretical yield:**

\[(0.320 \text{ mole/L}) \times (0.100 \text{ L}) \times (1.00 \text{ mole PCA / 1.00 mole MMH}) = 0.0320 \text{ mole PCA}\]

**Reaction yield at 12 min:**

\[(0.0268 \text{ mole/L}) \times (0.100 \text{ L}) = 0.0268 \text{ mole mPCA}\]

**Experimental yield:**

\[(0.0268 \text{ mole/0.0320 mole}) \times (100\%) = 83.8\%\]

### 4.3.9 Reaction of Combination HZ and MMH with AKGA

The reaction of AKGA, HZ, and MMH all together at a 1.1:1 AKGA molar ratio to the addition of the hypergols’ concentration was done in order to observe how different in speed the reaction would behave and if there was any other change in the byproduct formation analysis. The same 100 mL total reaction volume was used with 25 mL of 1% v/v of HZ (0.32 M) and 25 mL of 1% v/v of MMH (0.19 M) which were added to a reaction beaker. After these two reactants were together, AKGA at a 1.1 ratio to the addition of both of the hypergols (0.56 M) was added to the same container and the reaction was allowed to proceed. Measurements were taken over time. **Figure 40** shows the formation of PCA and mPCA together. Although it was observed that the HZ dominated the reaction as the reaction was proceeding faster than MMH by itself, precipitation of the PCA did not start until one hour after the reaction started (compared to 12 minutes with AKGA and HZ alone), suggesting MMH was also affecting the reaction. Two peaks for this reaction were not detected but an overlap of the two maximum absorption wavelengths was observed, showing a maximum absorption wavelength at 264 nm.
Since the PCA started to precipitate after one hour, no more than 2 hours of readings were recorded. A percent yield was calculated at this time and the reaction was found to have an experimental yield of 73\% (hypergol conversion). Figure 41 shows a comparison of the formation of PCA and mPCA when only one of the hypergols reacts with AKGA and when they are formed together at the same AKGA:Hypergol ratio. It can be observed, as previously mentioned, that the maximum absorption wavelength shifts for both of the components. PCA was compared at 12 min, which is the time that PCA starts precipitating when it reacts by itself with AKGA and mPCA was compared at 60 min, which is the time that the precipitation starts when all components are together. When all the components are together, the formation of the product is slower than when only HZ and AKGA are present when comparing at 12 min. On the other hand the formation of the product is much faster after one hour if compared to MMH and AKGA by itself. Since HZ has an extra H, it is able to react faster. Therefore, AKGA is going to choose HZ as the first molecule for reaction. However, MMH has also an effect because the molecule is
going to still competing for the AKGA reaction. For this reason it is believed that HZ has a greater effect in the product formation.

![Comparison of PCA and mPCA Formation When Each is Formed Individually and Together](image)

**Figure 41**: PCA and mPCA comparison when they form individually and together after the reaction of HZ, MMH, and AKGA at same 1:1:1 Hypergol ratio

After an analysis was done based on the obtained results, for the combined hypergol experiment, a new experiment was performed in order to find out what ratio of HZ to MMH react when both of them are added in the same reaction mixture. Standard samples of the same concentrations of the PCA and mPCA were run via UV-Vis in order to see how the maximum absorption wavelength was affected based on the amount of PCA or mPCA added. Different ratios of both compounds were added and absorbance was measured; a concentration of $0.15 \times 10^{-6}$ M was used for PCA and mPCA. **Figure 42** shows how the maximum absorption changes based on the fixed different ratios. After observing that the 264 nm wavelength was obtained with a 80:20 PCA:mPCA ratio, a new calibration curve was constructed based on this ratio with concentrations that ranged from $0.025 \times 10^{-6}$ M to $0.25 \times 10^{-6}$ M. This calibration curve is shown in **Figure 43**.
Note: all the % yields calculated in the reaction of the two hypergols together with AKGA were calculated with this new calibration curve.

Figure 42: PCA and mPCA at different ratios and its maximum absorption wavelengths

Figure 43: Calibration curve for 80:20 PCA:mPCA ratio combination
CHAPTER 5: PROPOSED HZ/AKAGA MECHANISM TO FORM PCA
AND MMH/AKGA MECHANISM TO FORM MPCA

5.1 Introduction

In the previous chapters, determination of the formation kinetics of the byproducts for the reaction of HZ/MMH and AKGA were obtained with a second order formation, first order with respect of each of the reactants; meaning that both HZ/MMH and AKGA play an indispensable role in the reaction for the formation of the cyclic compounds. Even though both PCA and mPCA follow second order formation kinetics, it was observed that the reaction of MMH and AKGA was much slower than the HZ and AKGA reaction, so proposing a mechanism is crucial to understand the behavior of each of the reactants through the chemical transformation.

When available, the understanding of chemical mechanisms is of vital importance as it shows a step-by-step sequence of elementary reactions to demonstrate how a chemical change occurs. Some of these transformations happen under extreme conditions such as high or low temperatures, pressures, pH, with the addition of a catalyst, or they may happen spontaneously as the reaction of the hypergols and AKGA. The transformation of HZ or MMH with the addition of AKGA is a spontaneous and irreversible reaction that transforms the toxic and unstable hypergols into more stable organic compounds that do not depend on any conditions to keep its structure. When HZ and AKGA react, they form PCA, and when MMH and AKGA react the byproduct is mPCA.
5.2 Proposed Transformation Mechanisms for Byproduct Formation

5.2.1 HZ and AKGA proposed mechanism for PCA Formation

Based on the previous scheme (Figure 44), it is believed that the reaction of HZ and AKGA is favorable because the HZ molecule is a good nucleophile. In step A the ketone is attacked by the primary amine of HZ to form an imine. The oxygen in the ketone protonates under acidic media, and the carbonyl carbon goes through a quick nucleophilic attack by the pair of electrons of the primary amine. This carbon position is preferred due to the electrophilic character at such a carbon. In step B, one of the protons of the HZ is transferred from the nitrogen. In step C, the hydroxyl group is protonated to yield an oxonium ion which can be easily liberated as water. Again, the free pair of electrons in the nitrogen migrates towards...
the alpha carbon releasing water and leading to the formation of a hydrazone molecule. In step D, there is another rate determining step which happens fast by going through a nucleophilic attack of the other available nitrogen. This position is preferred as it will close into a stable six-membered ring. In step E, the hydroxyl group closest to the nitrogen gets protonated, forming once again an oxonium ion to be released as water. In the last step, step F, water deprotonates the hydroxyl group in order to obtain a stable ketone and forming the six-membered pyridizine-carboxylic acid ring.

It is understood that the reaction of HZ and AKGA to form PCA happens very fast because the nitrogen doing the new nucleophilic attack in the second rate determining step of the mechanism (ring closure) has two available hydrogens instead of any other group that can affect its reactivity. This nitrogen is more reactive as it does not have any withdrawing group, which can deactivate the pair of electrons or cause steric hindrance when the ring closes. All such effects of withdrawing groups can slow down or prevent the reaction from occurring altogether.
5.2.2 MMH and AKGA mechanism

On the other hand, when MMH and AKGA react to form mPCA the step-by-step mechanism happens exactly the same way through the first 4 intermediate steps (Figure 45). When the reaction reaches the second rate determining step, step D, or the ring closure, the reaction slows down. In this step, the pair of electrons in the nitrogen going through nucleophilic attack on the carbon is less active than in the mechanism of PCA formation. This happens because the nitrogen has one hydrogen and one methyl group attached to it, acting as an electron withdrawing group. Therefore, the electron pair are weaker and at the same time the methyl group causes some steric hindrance when the ring starts closing, delaying the mPCA formation.
These proposed mechanisms happen through several suggested intermediate molecules that still need to be analyzed. The intermediate structure in the fifth step of the proposed mechanism is a hydrozone. After the formation of this hydrazone, the second rate determining step, step D, happens which is assumed to be what controls how fast the reaction happens.

Verification studies of the reaction mechanism will be approached using UDMH. Since this type of HZ has two methyl groups attached to one of the nitrogens, the closing of the ring will not happen as there are no available hydrogens to displace. The reaction will end in a hydrazone intermediate equilibrium structure.
CHAPTER 6: INVESTIGATION OF INTERFERENCES IN THE TREATMENT OF HZ AND MMH

6.1 Introduction

At this time, based on the hazards associated with handling and the flammability of HZ and MMH, NASA practices a neutralization technique which consists in the addition of a 14% w/w aqueous solution of CA to lower the vapor pressure and therefore minimize the off-gassing of its vapors. Also, the same 14% w/w CA solution is used with small amounts of IPA and an anti-foaming agent as a scrubber soup to entrap and neutralize HZ vapors. Under these characteristics the waste can be held on site for up to 90 days until it is sent off-site for incineration; this disposal technique costs NASA approximately $120K per year at KSC alone. The neutralization process is not a destruction process for these toxic hypergols and the reaction is reversible and pH dependent. After the waste gets shipped out and incinerated off-site, it promotes the formation of nitrogen oxide (NOx) gases which are regulated greenhouse gases leading to an air pollution problem. It also has a disadvantage as it has to be transported and an accidental release may happen putting the public and the environment in danger (Oropeza, 2011; Schmidt, 2001).

Since NASA-KSC currently uses the previously mentioned chemicals to stabilize and avoid fuming gases from the HZs mixture solutions at the moment of storage, it is important to analyze what would be the effect of the same compounds on the AKGA treatment method. Studies in the following sections provide data and interpretation of the effects of the silicone based AF, CA, and IPA on the kinetics and efficiency of the AKGA:hypergol reactions.

6.2 Experimental Procedure

For PCA and mPCA analysis via a UV-Vis spectrophotometer the same procedure as in section 3 was used. Standard reagent grade PCA and mPCA were taken to prepare aqueous solutions with
ultra-pure water and the respective interference (AF, CA, and/or IPA) as background. Solutions that varied from $0.4 \times 10^{-5}$ M to 0.002 M were obtained for PCA with a serial dilution by mixing the reagent in a stirring plate with a stirring bar from a 0.00050 M standard solution. The concentration of AKGA used was 0.0038 M and the concentrations used for mPCA vary from $0.4 \times 10^{-5}$ M to 0.003.0 M. When the AKGA solution was prepared in ultra-pure water, the interference was added and allowed to mix. For the AF agent 10 μL were added, for the CA 13.5 g were added, and for the IPA 4 mL were added; all of them in a total 100 mL volume reaction. Then, the PCA and/or mPCA solutions were made with these mixtures as background.

Since the AKGA:hypergol ratio was previously optimized in section 3 and 4, all interference testing was done with the 1.1:1 AKGA:hypergol ratio and the 1% v/v hypergol solutions. Same interferences were also used with the same amounts just described and added to the hypergol aqueous solution before the AKGA was mixed and allowed to react. The AKGA solution was added to a beaker with a stirring bar on a stirring plate already containing the HZ and/or MMH with the testing interference. Time was measured as the reaction was monitored via UV-Vis at the same intervals previously described.

6.3 Results and Discussion

6.3.1 CA Interference Testing in PCA or mPCA Formation

6.3.1.1 Calibration curves for PCA and mPCA formation in dilute solution with CA:

Calibration curves for PCA and mPCA were constructed one more time, but in this case, with a 0.0038 M AKGA and 14% v/v CA aqueous background in a 500 mL total volume. The solutions were obtained by preparing 0.00050 M PCA and mPCA concentration stock solutions of each of the reagents in the previously made AKGA/CA solution. Then, serial dilution was performed obtaining concentrations of 0.00030, 0.00020, 0.00010, 0.000050, 0.000025, 0.000013, and 0.0000040 M. Absorbance of each
sample was measured via UV-Vis. The maximum absorption wavelength was as previously observed in the other calibration curve; for PCA it was 260 nm and for mPCA it was 272 nm.

Three different runs were obtained for each of the concentrations and an average absorbance was calculated. Tables 13 and 14, and Figure 46 and 47 show the average tabulated data, as well as the calibration curves for each of the products.

Table 13: PCA average absorbance at different concentrations with AKGA and CA solution as background

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Max. Absorbance (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.400 x 10^{-3}</td>
<td>0.0291</td>
</tr>
<tr>
<td>0.130 x 10^{-4}</td>
<td>0.115</td>
</tr>
<tr>
<td>0.250 x 10^{-4}</td>
<td>0.228</td>
</tr>
<tr>
<td>0.500 x 10^{-4}</td>
<td>0.448</td>
</tr>
<tr>
<td>0.100 x 10^{-3}</td>
<td>0.893</td>
</tr>
<tr>
<td>0.200 x 10^{-3}</td>
<td>1.75</td>
</tr>
</tbody>
</table>

Table 14: mPCA average absorbance at different concentrations with AKGA and CA solution as background

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Max. Absorbance (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.400 x 10^{-5}</td>
<td>0.0414</td>
</tr>
<tr>
<td>0.130 x 10^{-4}</td>
<td>0.132</td>
</tr>
<tr>
<td>0.250 x 10^{-4}</td>
<td>0.261</td>
</tr>
<tr>
<td>0.500 x 10^{-4}</td>
<td>0.523</td>
</tr>
<tr>
<td>0.100 x 10^{-3}</td>
<td>1.04</td>
</tr>
<tr>
<td>0.200 x 10^{-3}</td>
<td>1.98</td>
</tr>
<tr>
<td>0.300 x 10^{-3}</td>
<td>2.83</td>
</tr>
</tbody>
</table>
Figure 46: PCA calibration curve with CA and AKGA background

![UV-Vis PCA Calibration Curve - CA+AKGA Background](image)

\[ y = 8.745.81x + 0.01 \]
\[ R^2 = 1.00 \]

Figure 47: mPCA calibration curve with CA and AKGA background

![UV-Vis mPCA Calibration Curve - CA+AKGA Background](image)

\[ y = 9.468.20x + 0.04 \]
\[ R^2 = 1.00 \]
6.3.1.2 CA interference in the formation of PCA – dilute solution:

Two different trials for PCA formation were performed with different percent amounts of CA: 7% and 14% (Figure 48 and 49), to observe the effect of it in the reaction kinetics. These two different percentages were chosen based on the regular practice used by NASA to observe if the amount of CA had a different effect. A solution of 700 mL contained 0.00025 M HZ, 0.00038 M AKGA and either 7% or 14% CA by volume. The CA was added to the HZ solution first and then the AKGA solution. After these three components reacted all together it was observed that as the concentration of CA increased, the reaction rate was much slower. Figure 50 shows the overlay graph of PCA formation under 7% and 14% CA effect. The formation of PCA was also compared with the already calculated PCA kinetics. The final concentration after a period of 4 hours with 7% CA was 0.00017 M and with 14% CA was 0.00015 M compared to 0.00025 M in regular (no CA) conditions; Figure 51 shows the overlay graph of the PCA formation with no CA and the 7% interference and Figure 52 shows the overlay graph of PCA kinetics with no CA and 14% interference. Table 15 also shows a summary of the absorbance and concentrations of all the different setups.

![PCA Formation with 7% Citric Acid Interference](image)

**Figure 48:** PCA formation with 7% w/w CA interference with dilute HZ solution
Figure 49: PCA formation with 14% w/w CA interference with dilute HZ solution

Figure 50: PCA formation comparison overlay with 7% and 14% w/w CA interference
Figure 51: PCA formation overlay in the absence and presence of 7% w/w CA interference

Figure 52: PCA formation comparison overlay in the absence and presence of 14% w/w CA interference
Table 15: Absorbance and respective concentration comparison of PCA formation without interference, 7% and 14% w/w CA interference

<table>
<thead>
<tr>
<th>Reaction time (hrs)</th>
<th>Regular Conditions</th>
<th>14% CA</th>
<th>7% CA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absorbance (au)</td>
<td>Concentration (M)</td>
<td>Absorbance (au)</td>
</tr>
<tr>
<td>0</td>
<td>-0.0390</td>
<td>-0.55 x 10^{-3}</td>
<td>0.141</td>
</tr>
<tr>
<td>1</td>
<td>1.05</td>
<td>0.12 x 10^{-3}</td>
<td>0.493</td>
</tr>
<tr>
<td>2</td>
<td>1.66</td>
<td>0.19 x 10^{-3}</td>
<td>0.791</td>
</tr>
<tr>
<td>3</td>
<td>2.04</td>
<td>0.24 x 10^{-3}</td>
<td>1.03</td>
</tr>
<tr>
<td>4</td>
<td>2.26</td>
<td>0.26 x 10^{-3}</td>
<td>1.25</td>
</tr>
</tbody>
</table>

6.3.1.3 CA interference in the formation of mPCA – dilute solution:

Since mPCA formation has shown to be already too slow (already shown in figures) in dilute solution and CA has shown to affect the speed of the reaction with PCA, a trial of mPCA formation was performed with 14% CA first (Figure 53), to observe the effect of CA on the reaction kinetics for this specific product. The same procedure was performed for the reaction and formation of mPCA. A solution of 700 mL containing 0.00025 M MMH, 0.00038 M AKGA and 14% w/w CA was done. The CA was added to the MMH solution first, and then the AKGA solution. After these three components reacted all together, it was observed that the CA also slowed down the reaction kinetics for production of mPCA. The formation of mPCA was also compared with the already calculated mPCA kinetics. The final concentration, after a period of 26 hours under the influence of 14% w/w CA was 0.00016 M compared to 0.00023 M with no CA present. Figure 54 shows the overlay graph of the mPCA formation with and without 14% w/w CA interference. Table 16 also shows a summary of the absorbance and concentrations of the mPCA formation with and without the addition of CA.
Figure 53: mPCA formation with 14% w/w CA interference with dilute MMH solution

Figure 54: mPCA formation comparison overlay in the absence and presence of 14% w/w CA
Table 16: Absorbance and respective concentration comparison of mPCA formation without interference and 14% w/w CA interference

<table>
<thead>
<tr>
<th>Reaction time (hrs)</th>
<th>Absorbance (au)</th>
<th>Concentration (M)</th>
<th>Absorbance (au)</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0697</td>
<td>0.630 x 10^{-3}</td>
<td>0.132</td>
<td>0.130 x 10^{-4}</td>
</tr>
<tr>
<td>4</td>
<td>0.695</td>
<td>0.710 x 10^{-4}</td>
<td>0.418</td>
<td>0.430 x 10^{-4}</td>
</tr>
<tr>
<td>8</td>
<td>1.37</td>
<td>0.140 x 10^{-3}</td>
<td>0.835</td>
<td>0.860 x 10^{-4}</td>
</tr>
<tr>
<td>12</td>
<td>1.38</td>
<td>0.140 x 10^{-3}</td>
<td>1.58</td>
<td>0.160 x 10^{-3}</td>
</tr>
<tr>
<td>16</td>
<td>1.61</td>
<td>0.170 x 10^{-3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>1.71</td>
<td>0.180 x 10^{-3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>2.20</td>
<td>0.230 x 10^{-3}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.3.1.4 CA interference in the formation of PCA – 1% v/v HZ solution:

After performing interference tests in dilute solution and observing that at these concentrations the reactions were too slow, 1% v/v solutions were used. This is the concentration usually obtained in the field samples at NASA, KSC. Based on this, CA was added to the same reaction mixture previously used at a 1.1:1 AKGA:HZ ratio. A 14% w/w CA amount was used on a 100 mL total volume reaction. The concentration of HZ used was 0.32 M and the concentration for AKGA was 0.35 M. The 1% v/v HZ was added to the reaction beaker and then the CA. The solution was allowed to mix until the CA was completely dissolved. Then, the AKGA solution was added and allowed to react. Figure 55 shows the PCA formation in the presence of CA and Figure 56 shows a comparison of the reaction with and without the 14% w/w CA interference.
Figure 55: PCA formation with 14% w/w CA interference in 1% by volume HZ solution (1.1:1 AKGA:HZ ratio)

Figure 56: PCA formation comparison overlay at 12 min in the absence and presence of 14% w/w CA interference in 1% by volume HZ solution
After the reaction was completed, it was observed that the CA had a slight effect in the formation of PCA. The percent yield without the CA was 85% while it was 78% in its presence at 12 minutes. This could be due to the effect that CA plays on the molecule, as it traps it to prevent the off-gassing. Therefore, this trapping of the molecule may prevent the reaction to happen at the same speed.

**6.3.1.5 CA interference in the formation of mPCA – 1% v/v MMH solution:**

The same procedure was used for mPCA interference analysis at higher concentration. CA was added to the same reaction mixture previously used at a 1.1:1 AKGA:MMH ratio. A 14% w/w CA amount was used based on the 100 mL total volume reaction. The concentration of MMH used was 0.19 M (8740 ppm) and the concentration for AKGA was 0.21 M (30514 ppm). The 1% v/v MMH aqueous solution was added to the reaction beaker and then the CA. The solution was allowed to mix until CA was completely dissolved. After the CA was dissolved the AKGA solution was added and allowed to react. Figure 57 shows the mPCA formation in the presence of the CA and Figure 58 shows a comparison of this reaction with and without the CA interference.

![mPCA Formation with CA as Interference at 1.1:1 AKGA:MMH](image)

**Figure 57:** mPCA formation with 14% w/w CA interference with a 1% by volume MMH solution (1.1:1 AKGA:MMH ratio)
Figure 58: mPCA formation comparison overlay at 180 min in the absence and presence of 14% w/w CA interference with 1% by volume MMH solution

After the reaction was completed, it was observed that the CA has some effect in the formation of mPCA; the reaction was delayed by approximately one hour and the percent yield was reduced. The percent yield in the presence of the CA was 78% after a 240 min period of time while it was 85% without its presence in a 180 min period. The percent yield obtained at the same 180 min was 75% when CA is present.

6.3.2 IPA Interference Testing in PCA or mPCA Formation

6.3.2.1 Calibration curves for PCA and mPCA formation in dilute solution with IPA:

Calibration curves for PCA and mPCA were constructed once again, in this case with a 0.0038 M (147.5 ppm) AKGA and 4% v/v IPA background in a 500 mL volume. The solutions were obtained by preparing a 0.00050 M (71 ppm for PCA and 78 ppm for mPCA) concentration stock solution of each of the reagents in the previously made AKGA/CA solution. Then, serial dilution was performed obtaining concentrations of 0.00030, 0.00020, 0.00010, 0.000050, 0.000025, 0.000013, 0.0000040 M (42.6, 28.4,
14.2, 7.1, 3.6, 1.8 ppm for PCA and 46.8, 31.2, 15.6, 7.8, 3.9, 2.0 ppm for mPCA). Absorbance of each sample was measured via UV-Vis. The maximum absorption wavelength was the same as previously observed in the other calibration curve. For PCA it was 260 nm and for mPCA it was 272 nm.

Three different runs were obtained for each of the concentrations and an average absorbance was calculated. Tables 17 and 18, and Figure 59 and 60 show the average tabulated data as well as the calibration curves for each of the products.

**Table 17: PCA average absorbance at different concentrations with AKGA and IPA solution as background**

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Max. Absorbance (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.00 x 10^{-6}</td>
<td>0.0192</td>
</tr>
<tr>
<td>1.30 x 10^{-5}</td>
<td>0.0260</td>
</tr>
<tr>
<td>2.50 x 10^{-5}</td>
<td>0.0639</td>
</tr>
<tr>
<td>5.00 x 10^{-5}</td>
<td>0.146</td>
</tr>
<tr>
<td>1.00 x 10^{-4}</td>
<td>0.298</td>
</tr>
<tr>
<td>2.00 x 10^{-4}</td>
<td>0.612</td>
</tr>
<tr>
<td>4.00 x 10^{-4}</td>
<td>1.22</td>
</tr>
</tbody>
</table>

**Table 18: mPCA average absorbance at different concentrations with AKGA and IPA solution as background**

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Max. Absorbance (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.00 x 10^{-6}</td>
<td>0.0418</td>
</tr>
<tr>
<td>1.30 x 10^{-5}</td>
<td>0.123</td>
</tr>
<tr>
<td>2.50 x 10^{-5}</td>
<td>0.238</td>
</tr>
<tr>
<td>5.00 x 10^{-5}</td>
<td>0.470</td>
</tr>
<tr>
<td>1.00 x 10^{-4}</td>
<td>0.930</td>
</tr>
<tr>
<td>2.00 x 10^{-4}</td>
<td>1.82</td>
</tr>
<tr>
<td>4.00 x 10^{-4}</td>
<td>2.67</td>
</tr>
</tbody>
</table>
Figure 59: PCA calibration curve with IPA and AKGA background

Figure 60: mPCA calibration curve with IPA and AKGA background
6.3.2.2 IPA in the formation of PCA – dilute solution:

IPA was added to the reaction mixture to observe the effect on the kinetics of PCA formation, as it was previously done with CA. The amount of IPA added to the solution was 4% v/v (28 mL) of the total reaction mixture, 700 mL. It was observed that IPA lowers the reaction rate as it happens with CA but to a smaller extent. Figure 61 shows the overlay graph of PCA formation under IPA effect and the kinetics of PCA formation with no IPA present. Table 19 also shows a comparison of the different absorbance and concentrations with the different interferences. The final concentration after a period of 4 hours under the influence of IPA was 0.00021 M (30.4 ppm) compared to 0.00027 M (37.7 ppm) with no IPA present.

![PCA Formation in the Absence and Presence of IPA Interference Overlay](image)

Figure 61: PCA formation comparison overlay in the absence and presence of IPA interference in dilute HZ solution
### Table 19: Absorbance and respective concentration comparison of PCA formation with 7% and 14% w/w CA and IPA interferences

<table>
<thead>
<tr>
<th>Reaction time (hrs)</th>
<th>Regular Conditions</th>
<th>IPA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absorbance (au)</td>
<td>Concentration (M)</td>
</tr>
<tr>
<td>0</td>
<td>-0.0390</td>
<td>-5.54 x 10^{-6}</td>
</tr>
<tr>
<td>1</td>
<td>1.05</td>
<td>1.22 x 10^{-3}</td>
</tr>
<tr>
<td>2</td>
<td>1.66</td>
<td>1.94 x 10^{-4}</td>
</tr>
<tr>
<td>3</td>
<td>2.04</td>
<td>2.38 x 10^{-4}</td>
</tr>
<tr>
<td>4</td>
<td>2.26</td>
<td>2.65 x 10^{-4}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Absorbance (au)</th>
<th>Concentration (M)</th>
<th>Absorbance (au)</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.141</td>
<td>1.56 x 10^{-5}</td>
<td>0.118</td>
<td>1.29 x 10^{-3}</td>
</tr>
<tr>
<td>0.493</td>
<td>5.69 x 10^{-5}</td>
<td>0.567</td>
<td>6.56 x 10^{-5}</td>
</tr>
<tr>
<td>0.791</td>
<td>9.19 x 10^{-5}</td>
<td>0.944</td>
<td>1.10 x 10^{-4}</td>
</tr>
<tr>
<td>1.03</td>
<td>1.20 x 10^{-4}</td>
<td>1.23</td>
<td>1.43 x 10^{-4}</td>
</tr>
<tr>
<td>1.25</td>
<td>1.46 x 10^{-4}</td>
<td>1.47</td>
<td>1.71 x 10^{-4}</td>
</tr>
</tbody>
</table>

### 6.3.2.3 IPA in the formation of mPCA - dilute solution:

As it was done with PCA, IPA was also added to the reaction mixture to observe the effect on mPCA formation. The amount of IPA added to the solution was one more time was 4% v/v (28 mL) of the total reaction mixture, 700 mL. In this case, it was observed that IPA speeds up the reaction rate, the opposite of what happens with PCA formation and IPA. Figure 62 shows the overlay graph of mPCA formation with IPA present effect and the formation of mPCA without its presence. Table 20 also shows a comparison table of the different absorbances and concentrations with different interferences. The final concentration after a period of 18 hours with IPA present was 0.00025 M (38.2 ppm) compared to 0.00018 M (27.6 ppm) with no IPA added.
Figure 62: mPCA formation comparison overlay in the absence and presence of IPA interference in dilute MMH solution
Table 20: Absorbance and respective concentration comparison of mPCA formation with CA and IPA interferences

<table>
<thead>
<tr>
<th>Reaction time (hrs)</th>
<th>Regular Conditions</th>
<th>Isopropanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absorbance (au)</td>
<td>Concentration (M)</td>
</tr>
<tr>
<td>0</td>
<td>0.0697</td>
<td>6.29 x 10^{-6}</td>
</tr>
<tr>
<td>4</td>
<td>0.695</td>
<td>7.14 x 10^{-5}</td>
</tr>
<tr>
<td>8</td>
<td>1.37</td>
<td>1.42 x 10^{-4}</td>
</tr>
<tr>
<td>12</td>
<td>1.38</td>
<td>1.43 x 10^{-4}</td>
</tr>
<tr>
<td>16</td>
<td>1.61</td>
<td>1.67 x 10^{-4}</td>
</tr>
<tr>
<td>18</td>
<td>1.71</td>
<td>1.77 x 10^{-4}</td>
</tr>
<tr>
<td>26</td>
<td>2.20</td>
<td>2.28 x 10^{-4}</td>
</tr>
</tbody>
</table>

14% CA

<table>
<thead>
<tr>
<th>Absorbance (au)</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.132</td>
<td>1.28 x 10^{-5}</td>
</tr>
<tr>
<td>0.418</td>
<td>4.26 x 10^{-5}</td>
</tr>
<tr>
<td>0.835</td>
<td>8.60 x 10^{-5}</td>
</tr>
<tr>
<td>0.841</td>
<td>8.66 x 10^{-5}</td>
</tr>
<tr>
<td>1.02</td>
<td>1.06 x 10^{-4}</td>
</tr>
<tr>
<td>1.11</td>
<td>1.15 x 10^{-4}</td>
</tr>
<tr>
<td>1.58</td>
<td>1.64 x 10^{-4}</td>
</tr>
</tbody>
</table>

6.3.2.4 IPA in the formation of PCA – 1% v/v HZ solution:

IPA was also studied in more concentrated hypergol solutions and its effects were observed. IPA was added to the same reaction mixture composition used for CA at a 1.1:1 AKGA:HZ ratio. A 4% v/v IPA was used based on the 100 mL total volume reaction. The concentration of HZ used was 0.32 M (10240 ppm) and the concentration for AKGA was 0.352 M (51392 ppm). The 1% v/v HZ was added to the reaction beaker and then the IPA. The solution was mixed and AKGA solution was added and allowed to react. Figure 63 shows the PCA formation in the presence of the IPA and Figure 64 shows a comparison of the reaction with and without the IPA interference.
Figure 63: PCA formation with 4% v/v IPA interference in 1% by volume solution (1.1:1 AKGA:HZ ratio)

Figure 64: PCA formation comparison overlay at 12 min in the absence and presence of 4% v/v IPA interference in 1% by volume HZ solution (1.1:1 AKGA:HZ ratio)
After the reaction was completed, it was observed that the IPA has no effect in the formation of PCA. The reaction yield was 85% with and without the presence of IPA present at 12 min 1.1:1 AKGA:HZ ratio.

**6.3.2.5 IPA in the formation of mPCA – 1% v/v MMH solution:**

In order to keep comparing the kinetics in the different products and the effect of the interferences in its formation, IPA was also studied with mPCA in more concentrated MMH solution. IPA was added to the same reaction mixture used at a 1.1:1 AKGA:MMH ratio. A 4% v/v IPA was used based on the 100 mL total volume reaction. The concentration of MMH used was 0.19 M (8740 ppm) and the concentration for AKGA was 0.21 M (30514 ppm). The 1% v/v MMH aqueous solution was added to the reaction beaker followed by the addition of IPA. The solution was mixed and AKGA solution was added and allowed to react. Figure 65 shows the mPCA formation in the presence of the IPA and Figure 66 shows a comparison of the reaction with and without the interference at 180 min.

![mPCA Formation with IPA as Interference at 1.1:1 AKGA:MMH](image)

**Figure 65:** mPCA formation with 4% v/v IPA interference in 1% by volume MMH solution (1.1:1 AKGA:MMH ratio)
Figure 66: mPCA formation comparison overlay at 180 min in the absence and presence of 4% v/v IPA interference in 1% by volume MMH solution (1.1:1 AKGA:MMH ratio)

After the reaction was completed, it was observed that the IPA does not have any considerable effect in the formation of mPCA. The percent yield with the IPA present was 83% and it was 85% without its presence for the 1.1:1 AKGA:MMH ratio.

6.3.3 AF Interference Testing in PCA or mPCA Formation

6.3.3.1 Calibration curves for PCA and mPCA formation in dilute solution with AF:

Calibration curves for PCA and mPCA were constructed one more time but in this case with a 0.0038 M (147.5 ppm) AKGA and a 0.01% v/v silicone based AF background in a 500 mL volume. The solutions were obtained by preparing a 0.00050 M (71 ppm for PCA and 78 ppm for mPCA) concentration stock solutions of each of the reagents in the previously made AKGA/AF solvent. Then, serial dilution was performed obtaining concentrations of 0.00030, 0.00010, 0.000050, 0.000025, 0.000013, 0.0000040 M (42.6, 14.2, 7.1, 3.6, 1.8 ppm for PCA and 46.8, 15.6, 7.8, 3.9, 2.0 ppm for mPCA); absorbance of each sample was measured via UV-Vis. The maximum absorption wavelength
was once again the same as previously observed in the other calibration curves. For PCA it was 260 nm and for mPCA it was 272 nm.

Three different runs were obtained for each of the concentrations and an average absorbance was calculated. Tables 21 and 22, and Figure 67 and 68 show the average tabulated data as well as the calibration curves for each of the products.

Table 21: PCA average absorbance at different concentrations with AKGA and AF solution as background

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Max. Absorbance (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.00 x 10^{-6}</td>
<td>0.0294</td>
</tr>
<tr>
<td>1.30 x 10^{-5}</td>
<td>0.127</td>
</tr>
<tr>
<td>2.50 x 10^{-5}</td>
<td>0.272</td>
</tr>
<tr>
<td>5.00 x 10^{-5}</td>
<td>0.556</td>
</tr>
<tr>
<td>1.00 x 10^{-4}</td>
<td>1.12</td>
</tr>
<tr>
<td>3.00 x 10^{-4}</td>
<td>2.98</td>
</tr>
</tbody>
</table>

Table 22: mPCA average absorbance at different concentrations with AKGA and AF solution as background

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Max. Absorbance (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.00 x 10^{-6}</td>
<td>0.0472</td>
</tr>
<tr>
<td>1.30 x 10^{-5}</td>
<td>0.127</td>
</tr>
<tr>
<td>2.50 x 10^{-5}</td>
<td>0.233</td>
</tr>
<tr>
<td>5.00 x 10^{-5}</td>
<td>0.475</td>
</tr>
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</table>
Figure 67: PCA calibration curve with AF and AKGA background

Figure 68: mPCA calibration curve with AF and AKGA background
6.3.3.2 AF interference in the formation of PCA – 1% v/v HZ solution:

The AF was analyzed as a last possible interference. This silicone based AF is only use in small amounts to prevent foaming from bacteria (8 oz. per 600 gal = 0.01% v/v) grown on the scrubber towers. It was observed that this compound may affect the product formation in the field samples when some of the investigation of the scrubber liquors was started. Even though the amount added is small, it still needs to be analyzed as it can cause alterations in the reaction of the HZs and the acid. This work was performed under the same conditions used for CA and IPA interferences. A 1% v/v HZ solution was prepared at a 1.1:1 AKGA:HZ ratio; the HZ used was 0.32 M (10240 ppm) and the concentration for AKGA was 0.35 M (51392 ppm). A 0.01% or 10 µL of AF were added to a 100 mL volume. The HZ was added to the beaker and then the white, thick AF. The solution was mixed until the AF was completely dissolved and no cloudiness was observed. Then, the AKGA solution was added and allowed to react.

Figure 69 shows PCA formation in the presence of the AF and Figure 70 shows a comparison of the reaction with and without the AF interference at 8 min. In this opportunity, only 8 minutes of reaction were recorded as the precipitate started forming.
Figure 69: PCA formation with 0.01% v/v AF interference in 1% by volume HZ solution (1.1:1 AKGA:HZ ratio)

Figure 70: PCA formation comparison overlay at 8 min in the absence and presence of 0.01% v/v AF interference in 1% by volume HZ solution
After the reaction was completed, it was observed that the silicone based AF does not have a great effect in the formation of PCA. The percent yield at 8 min without the AF was 77% while it was 62% in its presence.

6.3.3.3 AF interference in the formation of mPCA – 1% v/v MMH solution:

The same procedure previously used for PCA was used for mPCA and AF interference. A silicone based AF was added to the same reaction mixture previously used at a 1.1:1 AKGA:MMH ratio. A 0.01% v/v AF amount was used based on the 100 mL total volume reaction. The concentration of MMH used was 0.19 M (8740 ppm) and the concentration for AKGA was 0.21 M (30514 ppm). The 1% v/v MMH aqueous solution was added to the reaction beaker and then the 10 µL AF. The solution was mixed until it was completely dissolved. After the AF was dissolved the AKGA solution was added and allowed to react. Figure 71 shows the mPCA formation in the presence of the AF and Figure 72 shows a comparison of this reaction with and without the AF interference.

![Graph](image_url)

**Figure 71:** mPCA formation with 0.01% v/v AF interference in 1% by volume MMH solution (1.1:1 AKGA:MMH ratio)
After the reaction was completed, it was observed that the AF had some effect in the formation of mPCA; the reaction was enhanced increasing the percent yield in the same period of time. The percent yield in the presence of the silicone base AF was 89% after a 180 min while it was 85% without its presence in the same period.

6.3.4 Combination of CA and IPA Interference Testing

Previous analysis showed interference of CA or IPA in the formation of PCA and mPCA from two different hypergol solutions, one diluted and other more concentrated (1% v/v hypergol). The results of the kinetics study for the formation of these two products showed to have better response in the more concentrated solution, also it has more similarity to current NASA practices. An optimization of the amount of AKGA needed was as well found in low proportion to the hypergol used. For this reason, following studies were only done with the higher concentration of hypergol (1% v/v) and the AKGA optimized amount (1.1:1 AKGA:hypergol).
6.3.4.1 CA and IPA interference in the formation of PCA – 1% v/v HZ solution:

CA and IPA were added to the same reaction mixture used with a 1.1:1 AKGA:HZ ratio. A 14% w/w of CA and a 4% v/v IPA were used on 100 mL total reaction volume. The concentration of HZ used was 0.32 M (10240 ppm) and the concentration for AKGA was 0.35 (51392 ppm) M. The 1% v/v aqueous HZ solution was added to the reaction beaker followed by adding CA and the IPA simultaneously. The solution was mixed until CA was dissolve. Then, the AKGA solution was added and allowed to react. Figure 73 shows the PCA formation in the presence of the both of the interferences and Figure 74 shows a comparison of the reaction with and without the interferences at 12 min.

![PCA Formation with IPA and CA as Interferences at 1.1:1 AKGA:Hz](image)

Figure 73: PCA formation with CA and IPA interferences in 1% by volume HZ solution (1.1:1 AKGA:HZ ratio)
After the reaction was completed, it was observed that the combination of CA and IPA does not have any different effect on the reaction as to when each was added individually. There is still a slight delay of the reaction caused by the IPA. The percent yield in the presence of both of the interferences was 80%. It was 85% when only CA was present, 78% when only IPA was present, and 84% without the presence of them in the same period of time with a 1.1:1 AKGA:HZ ratio.

6.3.4.2 CA and IPA interference in the formation of mPCA – 1% v/v MMH solution:

CA and IPA were added to the same reaction mixture used at a 1.1:1 AKGA:MMH ratio. A 14% w/w of CA and a 4% v/v IPA were used in a 100 mL reaction volume. The concentration of MMH used was 0.19 M (8740 ppm) and the concentration for AKGA was 0.21 M (30514 ppm). The 1% v/v MMH was added to the reaction beaker followed by the addition of CA and IPA simultaneously. The solution was mixed until CA was completely dissolved. Then, the AKGA solution was added and allowed to react. Figure 75 shows the mPCA formation in the presence of the both of the interferences and Figure 76 shows a comparison of the reaction with and without the interferences at a 180 min.
Figure 75: mPCA formation with CA and IPA interference in 1% by volume MMH solution (1.1:1 AKGA:MMH ratio)

Figure 76: mPCA formation comparison overlay at 180 min in the absence and presence of CA, IPA, and CA+IPA interferences in 1% by volume MMH solution (1.1:1 AKGA:MMH ratio)
After the reaction was completed, it was observed that the combination of CA and IPA does not have any different effect on the reaction as to when each was added individually. There is still a delay of the reaction caused by the CA, by about an hour. The reaction yield in the presence of both of the interferences was 75% in a 240 min. It was 75% with only CA, 83% with only IPA, and 85% without their presence in 180 min.

6.3.5 Combination of CA, IPA, and AF Interference Testing

6.3.5.1 CA, IPA, and AF interference in the formation of PCA – 1% v/v HZ solution:

The silicone based AF agent, the CA, and the IPA were added to the same reaction mixture used with 1.1:1 AKGA:HZ ratio. A 0.01% v/v of AF, 14% w/w of CA, and a 4% v/v IPA were used in 100 mL. The concentration of HZ was 0.32 M (10240 ppm) and the concentration for AKGA was 0.35 M (51392 ppm). The 1% v/v aqueous HZ solution was added to the reaction beaker and then all the interferences all together. The solution was mixed and the CA to dissolve. Then, the AKGA solution was added and allowed to react. Figure 7 shows the PCA formation in the presence of all the interferences and Figure 78 shows a comparison of the reaction with and without the interferences at 12 min.
Figure 77: PCA formation with CA, IPA, and AF interference in 1% by volume HZ solution (1.1:1 AKGA:HZ ratio)

Figure 78: PCA formation comparison overlay at 12 min in the absence and presence of CA, IPA, AF, CA + IPA, and CA + IPA + AF interference in 1% by volume HZ solution (1.1:1 AKGA:HZ ratio)

It was witnessed that the combination of AF, CA, and IPA does not have any considerable effect on the reaction as to when they were added individually. There is still a slight delay of the reaction caused
by the CA. The percent yield in the presence of all the interferences was 80%, the same as when only CA and IPA are present. It was 85% with only CA, 78% with IPA was present, and 84% without the presence of them in the same period of time with the 1.1:1 AKGA:HZ ratio.

6.3.5.2 CA, IPA, and AF interference in the formation of mPCA – 1% v/v MMH solution

The same interferences were also added to the same reaction mixture used at a 1.1:1 AKGA:MMH ratio. A 0.01% v/v of antifoaming, 14% w/w of CA, and a 4% v/v IPA were used based on the 100 mL total volume reaction. The concentration of MMH used was 0.19 M (8740 ppm) and the concentration for AKGA was 0.21 M (30514 ppm). The 1% v/v aqueous MMH solution was added to the reaction beaker followed by all the interferences at the same time. The solution was mixed and CA dissolved before adding the AKGA solution. The reaction was allowed to proceed and data was recorded. Figure 79 shows the PCA formation in the presence of all the interferences and Figure 80 shows a comparison of the reaction with and without the interferences at 120 min.

Figure 79: mPCA formation with CA, IPA, and AF interference in 1% by volume MMH solution (1.1:1 AKGA:MMH ratio)
Figure 80: mPCA formation comparison overlay at 180 min in the absence and presence of CA, IPA, AF, CA + IPA, and CA + IPA + AF interference in 1% by volume MMH solution

After the reaction was completed, it was observed that the combination of all the possible interferences had no different effect on the reaction as to when they were added individually. There is still a delay of the reaction caused by the CA, by about an hour. The reaction yield in the presence of all interferences was 77%. It was 75% with only CA, 83% with only IPA, and 85% without their presence in a 180 min period.

6.3.6 CA, IPA, and/or AF Interference Testing in PCA and mPCA (together) Formation

6.3.6.1 CA interference in the formation of PCA and mPCA (together) – 1% v/v HZ and MMH solutions:

CA was tested as an interferent for the reaction mixture of HZ, MMH and AKGA. The AKGA was added at a 1.1 mole ratio to the addition of the concentration of the components in the mixture. A 14% w/w CA amount was used based on the 100 mL total volume reaction. The concentration of HZ used was 0.32 M (10240 ppm), the MMH concentration was 0.19 M (8740 ppm) and the total concentration for AKGA was 0.561 M (81906 ppm). The 1% v/v aqueous solutions of HZ and MMH were added to the
reaction beaker and then the CA. The solution was allowed to mix until CA was completely dissolved. After the CA was dissolved, the AKGA solution was added and allowed to react. **Figure 81** shows the mixture of PCA and the mPCA formation in the presence of CA. It was observed that PCA formation dominates the reaction but showed a slight change in the maximum absorption wavelength from 262 nm to 264 nm. The maximum absorption wavelength at which mPCA absorbs was not detected even after a 24 hours period of time, although the 2 nm movement in the maximum absorption may indicate an overlap between the two components. **Figure 82** shows a comparison of the reaction of the two hypergols individually and together with CA. The mixture is compared with two different graphs, one is the PCA formation with the presence of CA when only HZ is added at 12 min, and the other is the mPCA formation with the CA when only MMH is present at 60 min formation.

![PCA and mPCA Formation with CA as Interference](image_url)

**Figure 81**: Formation of combined PCA and mPCA with CA interference in 1% by volume HZ and MMH solutions (1.1:1 AKGA mole ratio to the addition of the hypergols)
The formation of PCA and mPCA together is delayed when CA is present in the reaction mixture. Also, as it was mentioned in Section 4.3.9 HZ seems to dominate the reaction, showing a greater formation of PCA and being unable to detect any formation of mPCA as the maximum absorption wavelengths may overlap and only a slight change in the absorbance was noted.

6.3.6.2 IPA interference in the formation of PCA and mPCA (together) – 1% v/v HZ and MMH solutions:

IPA was added to the same reaction mixture as described in the CA experiments above. A 4% v/v IPA was used in 100 mL total reaction volume. The concentration of HZ was 0.32 M (10240 ppm), the MMH concentration was 0.19 M (8740 ppm) and the concentration for AKGA was 0.56 M (81906 ppm), which is 1.1 mole ratio to the addition of the concentration of both hypergols. The 1% v/v HZ and MMH were added to the reaction beaker and then the IPA. The solution was mixed and AKGA solution was added and allowed to react. Figure 83 shows the PCA and mPCA formation in the presence of the IPA and Figure 84 shows a comparison of the reaction of the two hypergols with IPA. The mixture is
compared with two different graphs, one is the PCA formation (at 12 minutes) with the presence of IPA when only HZ is added, and the other is the mPCA formation (at 60 minutes) with the IPA when only MMH is present.

Figure 83: Formation of combined PCA and mPCA with IPA interference in 1% by volume HZ and MMH solutions (1.1:1 AKGA mole ratio to the addition of the hypergols)
As observed before, HZ seems to dominate the reaction. The maximum absorption wavelength shifts about 4 nm and the maximum absorption wavelength for mPCA formation was not detected. As noted earlier, the wavelength shift for PCA could indicate that both compounds are represented by an overlay of the curves. Also, the amount of precipitate formed in this reaction was greater than the one usually observed when no interferences are present in the reaction mixture. This is likely due to a decreased solubility of PCA in the IPA solution, as PCA is less soluble in IPA than in water. The precipitate was weighed and compared to the PCA obtained in the 1.1:1 AKGA:HZ reaction. Usually an amount of about 2.5 g is obtained when HZ reacts with the AKGA; in this case the amount weighed was 4.2 g, which is almost double the amount.

Based on these observations, HPLC was run with this sample to observe if mPCA was present in the precipitate as well. After running HPLC with both of the developed methods for PCA and mPCA detection (previously obtained), no mPCA was found to be present. Only the presence of PCA was
observed with a retention time of 1.11 minutes. Several solutions with different concentrations of the dissolved precipitate were used to ensure the presence of this component. A saturated solution was finally used and only PCA was found in the precipitate.

6.3.6.3 AF interference in the formation of PCA and mPCA (together) – 1% v/v HZ and MMH solutions:

The silicone based AF was added to the reaction mixture of HZ, MMH and AKGA together. The AKGA was added at a 1.1 mole ratio to the addition of each of the components in the mixture. A 0.01% v/v amount of AF was added in 100 mL volume reaction. The concentration of HZ used was 0.32 M (10240 ppm), the MMH concentration was 0.19 M (8740 ppm), and the total concentration for AKGA was 0.56 M (81906 ppm). The 1% v/v HZ and MMH aqueous solutions were added to the reaction beaker with the AF allowing it to dissolve. Then, the AKGA solution was added and allowed to react. Figure 85 shows the PCA and the mPCA formation in the presence of the AF and Figure 86 shows a comparison of the PCA and mPCA formation in the absence and presence of the different interferences at 120 min.

![PCA and mPCA Formation with AF as Interference](Figure 85: Formation of combined PCA and mPCA with AF interference in 1% by volume HZ and MMH solutions (1.1:1 AKGA mole ratio to the addition of the hypergols))
The formation of the PCA-mPCA product gets enhanced when the AF is added to the reaction mixture. The percent yield at 120 minutes when only the AF is added was 77% versus 64% when only CA is added, or 70% when only IPA is added. Also the percent yield of the product is lower when no interferences are present with a 73% reaction yield.

6.3.6.4 CA and IPA interference in the formation of PCA and mPCA (together) – 1% v/v HZ and MMH solutions:

CA and IPA were added to the reaction mixture of HZ, MMH and AKGA together at a 1.1 mole ratio of the addition of the hypergols’ concentration. A 14% w/w CA and a 4% v/v IPA amounts were used based in 100 mL volume. The concentration of HZ used was 0.32 M (10240 ppm), the MMH concentration was 0.19 M (8740 ppm), and the total concentration for AKGA was 0.56 M (81906 ppm). The 1% v/v HZ and MMH aqueous solutions were added to the reaction beaker with the two interferences. Finally, the AKGA solution was added and allowed to react. Figure 87 shows the PCA and
the mPCA formation in the presence of the CA and IPA and Figure 88 shows a comparison of the PCA and mPCA formation with only CA and only IPA in comparison to all of them together. The observations regarding the formation of the products are the same as it was previously described. Moreover, when all of the components are together the formation of the products is slower, the same as when only CA is present.

![PCA and mPCA Formation with CA and IPA as Interference](image)

**Figure 87:** Formation of combined PCA and mPCA with CA and IPA interferences in 1% by volume HZ and MMH solutions (1.1:1 AKGA mole ratio to the addition of the hypergols)
Figure 88: Formation of combined PCA and mPCA comparison overlay at 120 min with CA, IPA, and CA+IPA (1.1:1 AKGA mole ratio to the addition of the hypergols)

The formation of PCA and mPCA together is affected when CA is present in the reaction, mixture slowing down the formation kinetics. This happens because CA is trapping the molecules, also MMH is competing with HZ to react with AKGA, however HZ stills reacting faster based on the hydrogens availability. There is a greater formation of PCA even though mPCA also affects the product formation with a shift in the maximum absorption wavelength to 264 nm. The following calculations show the reaction yield at 180 min with the 80:20 PCA:mPCA ratio formation and its respective calibration curve. Measurements of product formation were taken only for the first 3 hours as there was precipitate formed after this period.

**PCA-mPCA reaction yield at 180 min:**

**Theoretical yield:**

\[(0.512 \text{ mole/L}) \times (0.100 \text{ L}) \times (1.00 \text{ mole PCA-mPCA} / 1.00 \text{ mole HZ/MMH}) = 0.0512 \text{ mole PCA/mPCA}\]

**Reaction yield at 180 min:**

\[(0.332 \text{ mole/L}) \times (0.100 \text{ L}) = 0.0332 \text{ mole PCA/mPCA}\]
Experimental yield:

\[(0.032 \text{ mole}/0.051 \text{ mole}) \times (100\%) = 64.8\%\]

6.3.6.5 CA, IPA, and AF interference in the formation of PCA and mPCA (together) – 1% v/v HZ and MMH solutions:

In this final portion, all the interferences in combination with the hypergols and the AKGA were studied in order to be as close as possible to a real world scenario. The AKGA was added once again at a 1.1 mole ratio to the addition of each of the components in the mixture, as this was the optimized ratio (Sections 3.3.6 and 4.3.6). The concentration of HZ used was 0.32 M (10240 ppm), the MMH concentration was 0.19 M (8740 ppm) and the concentration for AKGA was 0.56 M (81906 ppm). The 1% v/v HZ and MMH were added to the reaction beaker in combination with the three interferences and mixed. AKGA was then added and allowed to react. Figure 89 shows the PCA and mPCA formation in the presence of the three interferences and Figure 90 shows a comparison of the reaction of the two hypergols in its absence and presence at 180 min. The complete mixture (all components together) is compared with other combination of interferences.

![PCA and mPCA Formation with AF, CA, and IPA as Interferences](image)

Figure 89: Formation of combined PCA and mPCA with CA, IPA, and AF interferences in 1% by volume HZ and MMH solutions (1.1:1 AKGA mole ratio to the addition of the hypergols)
Figure 90: Formation of combined PCA and mPCA comparison overlay at 120 min with CA, IPA, AF, CA + IPA, and CA + IPA + AF in 1% by volume solution (1.1:1 AKGA mole ratio to the addition of the hypergols)

The formation of PCA and mPCA together is affected when CA is present slowing down the formation kinetics. Also, as previously mentioned HZ once again dominates the reaction, showing a greater formation of PCA although there is still a movement in the maximum absorption wavelength to 264 nm. The following calculations show the reaction yield at 180 min with the 80:20 PCA:mPCA ratio formation and its respective calibration curve. Measurements of product formation were taken only for the first 3 hours as there was formation of precipitate.

*PCA-mPCA reaction yield at 180 min:*

**Theoretical yield:**

\[
(0.512 \text{ mole/L}) \times (0.100 \text{ L}) \times (1.00 \text{ mole PCA-mPCA / 1.00 mole HZ/MMH}) = 0.0512 \text{ mole PCA/mPCA}
\]

**Reaction yield at 180 min:**

\[
(0.332 \text{ mole/L}) \times (0.100 \text{ L}) = 0.0332 \text{ mole PCA/mPCA}
\]

**Experimental yield:**

\[
(0.0332 \text{ mole} / 0.0512 \text{ mole}) \times (100\%) = 64.8\%
\]
CHAPTER 7: FIELD TESTING OF SCRUBBING LIQUOUR SAMPLES CONTAINING INTERFERENCES

7.1 Introduction

High volumes of HZ and MMH contaminated fuel streams are processed at KSC. These HZs are considered highly toxic and potentially carcinogenic. Consequently, the toxic streams are currently treated and contained in a scrubber liquor mixture containing the previously analyzed 14% CA and 3-4% IPA as well as 0.01% AF agent. The purpose of this neutralizer is to reduce the vapor pressure, effectively immobilizing the HZ molecules in solution. They remain immobilized for as long as the solution acidity at ambient temperature conditions are maintained. If the solution pH shifts to basic or temperature increases (such as in an accidental fire incident), the trapped fuel molecules are liberated, and will off-gas from the solution presenting a safety hazard to personnel.

The use of AKGA to treat fuel waste streams containing HZs with AKGA would be beneficial to NASA/KSC and verification of the efficiency of treatment with actual samples taken from the scrubbers on-site is an important step in this direction. The goal is to determine if the already proven laboratory-scale treatment of AKGA can be effectively replicated in the field by first analyzing some of the current stored scrubber liquors.

7.2 Experimental Procedure

Three different samples were first obtained from NASA-KSC for analysis. Later a fresher sample with higher hypergols concentrations was also obtained. The sample bottles were refrigerated upon receiving and a small amount (approximately 60 mL) of each one was transferred into a different container for testing. The next step was to determine the concentration of HZ and MMH in each of the samples with the NPD method previously obtained for HZs analysis. Daily calibration curves with a mixture of the two hypergols were prepared with concentrations varying from $0.1 \times 10^{-4}$ M to $0.003$ M of
each of the components in reagent grade acetone. Then, the liquors were diluted in acetone at different ratios until finding the best one for analysis of both hypergols. Dilutions from 100,000 to 100 were performed and analyzed in the NPD. Once the HZ and MMH concentrations were obtained, a 1.1 AKGA mole ratio to the addition of the hypergols was prepared in ultra-pure water. The scrubber liquors were first filtered in order to remove any impurities and cloudiness from the solution with a 45 µm suspended particulate matter (SPM) filter. A 50 mL aliquot of the scrubber liquor (each one independently) was added to the beaker while stirring followed by the addition of the aqueous AKGA solution. The reaction was monitored by UV-Vis to observe PCA and/or mPCA formation at 0, 12, 24, 60, and 120 minutes.

As a verification method, the reactions were also monitored via NPD in order to observe the decrease in HZ and MMH concentration as the reaction progressed. Areas under the curve were recorded at each specific time and analyzed with the previously obtained calibration curves. For this analysis, the reactions were allowed to proceed for 24 hours to ensure complete reaction of the HZs with the AKGA. A final chromatogram was obtained to see if there were any HZs left in the reaction. A mole balance was also performed with the previously obtained data.

7.3 Results and Discussion

7.3.1 Aged Scrubber Liquor Samples

The first three samples were obtained for initial testing. These field waste solutions were identified by KSC personnel as VS-1 with a deep orange color, VS-3 with a yellow color, and a LT-66 with a dark burgundy color. These names are given to the mixtures based on the location of the scrubber tower where the liquors are contained before shipment. The pH for the samples varied between 2.3 and 2.8, the darker the color the more acidic. VS-1 had a fresh liquor load from September 2012 with very low concentrations of HZs. VS-3 was a liquor from October 2013 also with low HZ concentration. The LT-66 had approximately 3000 gallons and an additional 400 lbs of CA.
Since the samples have been stored for a while, the components of the liquors contained low concentrations of the HZs at different pHs and different unknown organics. The liquor samples’ different colors may be attributed to the growing bacteria at the scrubber towers where the liquors are contained and stored during treatment and before shipment. The GC-NPD analysis method previously obtained (Sections 4.31 and 5.3.1) was used for HZ and MMH concentration calculations in order to add the right amount of AKGA for treatment. Due to the presence of all the other unknown organics, the two peaks for HZ and MMH were not clearly identified in the chromatograms. For liquors VS-1 and LT-66 several peaks were obtained with unidentified origin. HZ and MMH were clearly identified in the liquor VS-3, however, its concentration was too low for AKGA treatment at the field scale. Based on these results, the effort was abandoned with the three field samples described above and a new one was prepared by NASA and shipped to UCF laboratories.

7.3.2 Fresh Scrubber Liquor Sample

As it was mentioned in the previous section, the first three samples received for analysis were not treated with AKGA as the concentrations of HZ and MMH were either not clearly identified or the hypergol concentration was too low for AKGA treatment, Based on these results, a new scrubber liquor was prepared at NASA-KSC with higher concentrations of hypergols.

In order to process the liquor and analyze for HZ and MMH concentrations, the previously obtained method for HZ and MMH analysis via GC-NPD was used (Section 3.3.1 and 4.3.1). An aliquot of the sample was diluted into acetone 100 times; Figure 91 shows a chromatogram of the scrubber liquor at the dilution factor previously stated. The two peaks for HZ and MMH are clearly detected at 5.1 minutes for HZ and at 5.5 minutes for MMH. Based on this chromatogram the concentration of MMH is lower than the HZ concentration, which agrees with the report given by KSC laboratories at the moment of the liquor shipment.
Several runs on different days were done with different calibration curves (Figure 92 – sample calibration curve) to ensure the hypergols concentrations were correct. Therefore, the AKGA amount added was calculated for a 1.1:1 AKGA molar ratio treatment to the addition of the hypergols. Table 23 shows the different runs with the concentrations obtained for each of the hypergols on three different days. The HZ concentration was calculated to be $0.447 \pm 0.033$ M and the concentration for MMH was calculated to be $0.0551 \pm 0.0019$ M. With these concentrations of AKGA required was calculated to be $0.552$ M concentration.
Figure 92: HZ/MMH combination solution standards calibration curve sample via GC-NPD
### Table 23: HZ and MMH calculated concentration in scrubber liquor

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<td><strong>[MMH] (mM)</strong></td>
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<td>0.590</td>
<td>0.520</td>
</tr>
<tr>
<td></td>
<td>0.533</td>
<td>0.550</td>
<td>0.559</td>
</tr>
<tr>
<td></td>
<td>0.527</td>
<td>0.589</td>
<td>0.560</td>
</tr>
<tr>
<td>*<em>[MMH]<em>100fd (mM)</em></em></td>
<td>53.5</td>
<td>59.0</td>
<td>52.0</td>
</tr>
<tr>
<td></td>
<td>53.3</td>
<td>55.0</td>
<td>55.9</td>
</tr>
<tr>
<td></td>
<td>52.7</td>
<td>58.9</td>
<td>56.0</td>
</tr>
<tr>
<td><strong>[MMH] (M)</strong></td>
<td>0.0535</td>
<td>0.0590</td>
<td>0.0520</td>
</tr>
<tr>
<td></td>
<td>0.0533</td>
<td>0.0550</td>
<td>0.0559</td>
</tr>
<tr>
<td></td>
<td>0.0527</td>
<td>0.0589</td>
<td>0.0569</td>
</tr>
</tbody>
</table>

After the reactants were analyzed and the average concentration for AKGA was calculated, the solutions were mixed in a beaker and allowed to react. The formation of the product was monitored once again with the UV-Vis. As it was expected the formation of PCA was faster since the concentration of HZ was about 9 times higher than the concentration of MMH. This was observed in the UV-Vis as the maximum absorption was always monitored at 260 nm (which is the maximum absorption for PCA alone). However, the presence of MMH delayed the reaction and the precipitate started forming after one day. **Figure 93** shows some pictures of the reaction of the scrubber liquor and the AKGA through five
days. The last picture to the right shows some of the PCA precipitate that was formed after the fifth day. The UV-Vis spectrum for the formation of the byproducts is shown in Figure 94. Also, the PCA/mPCA moles formed vs. the HZ and MMH moles reacted are summarized in Table 24; all the analysis was done with a new calibration curve constructed for the 90:10 PCA:mPCA ratio as this would be the ratio present between the two hypergols. However, the maximum absorption wavelength of the by-product is 260 nm.

Figure 93: Pictures of the reaction of the fresh scrubber liquor and AKGA at a 1.1:1 AKGA molar ratio to the addition of the hypergols
Figure 94: UV-Vis spectrum of the byproduct formation after the reaction of a fresh sample of scrubber liquor and AKGA at a 1.1:1 AKGA mole ratio to the addition of the hypergols’ concentration

Table 24: Summary of the PCA/mPCA moles formed vs. HZ and MMH moles reacted at 1.1:1 AKGA molar ratio to the addition of the hypergols’ concentration

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>HZ moles</th>
<th>MMH moles</th>
<th>PCA/mPCA moles</th>
<th>Total moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0447</td>
<td>0.0055</td>
<td>0</td>
<td>0.0502</td>
</tr>
<tr>
<td>12</td>
<td>0.00197</td>
<td>0.00246</td>
<td>0.0134</td>
<td>0.0178</td>
</tr>
<tr>
<td>24</td>
<td>0.00115</td>
<td>0.00134</td>
<td>0.0147</td>
<td>0.0172</td>
</tr>
</tbody>
</table>

When the scrubber liquor was treated with AKGA at the optimized 1.1:1 AKGA mole ratio to the addition of the hypergols concentration, it was observed that a mole balance was not accurately obtained when adding the moles of HZ and MMH reacted vs. the moles of byproduct formed. The experiment was repeated over five times to avoid any possibility of systematic and human errors however the same results were obtained. There is a clear disappearance of the hypergols to the point of being below the NPD limits of detection (Figure 95), but the formation of the byproduct is extremely slow after the first hour of reaction. The maximum absorbance increased very little over the measured time.
Figure 95: NPD chromatogram of HZ and MMH disappearance in a field sample scrubber liquor after AKGA treatment at a 1.1 AKGA molar ratio to the addition of the hypergols’ concentrations after two hours
So, what could be possibly happening to the byproduct formation? Several ideas have been considered to obtain the best explanation for the poor mole balance. One of the ideas was to repeat the experiment several times to eliminate the possibility of human or instrumental error. Even though this was tried several times, the same data was obtained. Other ideas that have been discussed but not yet experimented include:

- The presence of bacteria in the scrubber liquor. Rueda et al. in 2013 stated that bacteria are able to use PCA as a carbon source and biodegrade the PCA molecule. This usually happens under neutral pH as very acidic ones may kill it. The addition of AKGA acidifies the water considerably; however some bacteria may survive in these acidic conditions. UV-Vis analysis as well as $^{13}$C labeled NMR will be used in order to validate this hypothesis.

- Whatever is causing the color of the scrubber liquor may be causing some interference in the product formation or measurement. The removal of the color was already approached by doing filtration with 0.45 µm filters with unsuccessful results. Another idea is that the color may be caused by the presence of metals (oxides) that can react with the product once formed. Sulfuric acid is being used to show if there is precipitation of metals. Charcoal is also being used to remove the color of the solution.

- There may be presence of other organics in the liquor that are interfering with the byproduct measurement. Although disappearance of reactants has been already successfully tested with the NPD, a deeper analysis of the byproduct formation needs to be approached using other analysis instrumentation and methodologies.
8.1 Introduction

The objective of this portion of the study was to obtain additional data to verify the previous studies done with PCA and mPCA biodegradation. A microbial study was previously approached by Rueda et.al in 2013. The addition of PCA to groups of bacteria showed an increase in the oxygen depletion in samples containing 2 and 5 mg/L of PCA with 2.46 and 5.43 mg/L respectively of O$_2$ consumed. This represents 67% of degradation for the 2 mg/L sample and 59% degradation for the 5 mg/L sample with respect to the theoretical oxygen demand after the 28 days experimental time. It was theorized that the microbes, in the presence of PCA and under the experimental conditions, were able to use carbon as a source of energy causing the consumption of O$_2$ to increase considerably (Rueda J, 2014).

On the other hand, the addition of mPCA was not toxic or inhibitory to the activated sludge (AS) after 7 days at a concentration 5 mg/L. These experiments showed no increase in the oxygen consumption in samples after 28 of incubation when compared to the control; therefore, it was determined that no degradation of mPCA occurred based on the theoretical oxygen demand. These preliminary results indicated that the microbes in the activated sludge (AS) samples were not able to use mPCA as an alternative source of energy or grow within the experimental conditions (incubation period, temperature, humidity, pH, and concentration of suspended solids). Figure 96 is a representation of the theoretical percent degradation of PCA, mPCA, and the control based on oxygen consumption (Rueda J, 2014).
Figure 96: Biodegradation percentage of PCA, mPCA, and KHP (KHP was used as reference to validate experiment at given conditions (Rueda J, 2014).

Since groups of bacteria in the presence of PCA showed a considerable consumption of oxygen in comparison to its theoretical oxygen demand and biodegradation above 50% in the 28 days of experiment, more studies to confirm the use of PCA as an energy source were needed. For this experiment labeled $^{13}$C PCA material was used with NMR analysis. This specially labeled material would allow the identification of PCA characteristic peaks before and after exposure with AS. If the microorganisms were really using PCA carbon as an energy source, the spectra of the PCA molecule would show some changes in its structure by changing the position of its characteristic NMR carbon labeled peaks. One of the changes expected was the formation of carbon dioxide from the carboxylic acid carbon of the PCA molecule.

PCA showed consumption of oxygen but mPCA did not, so more studies were also needed to confirm these preliminary results indicating mPCA was not biodegradable and if it was, identification of possible degradation products was needed. For this experiment, alternate labeled $^{13}$C mPCA material was
used with NMR analysis to follow any possible degradation. This specially labeled material would allow the identification of mPCA characteristic peaks before and after exposure to AS over a 28 day period.

Biodegradation tests using activated sludge-water samples from the Cape Canaveral Air Force Station Water Treatment Plant were used in order to verify that the same species of microbes that PCA wastes would be exposed to on site are capable of biodegrading PCA.

8.2 Experimental Procedure

The effect of PCA and mPCA on the biological treatment efficiency of a wastewater treatment plant was evaluated according to the method described in EPA OPPTS 835.3110 Ready Biodegradability-Closed Bottle Test, January 1998 (EPA 712-C-98-076). Activated sludge-water samples were first collected at the Cape Canaveral Air Force Station Water Treatment Plant. The sample was taken from the effluent of the reactor after re-aeration in the close loop reactor splitter box located before the clarifiers. The sample was taken to UCF laboratories immediately to ensure survival of the living organisms. The activated sample was homogenized in a blender for 20 seconds and then allowed to settle for 20 minutes. The supernatant was removed to increase the concentration of suspended solids. The sample was once again allowed to settle for another 20 min and more supernatant was removed. Then, 20 mL of the sample were taken to analyze the mixed liquor suspended solids (MLSS) concentration. For this calculation the 20 mL were filtrated with a 45 µm fiber glass filter under vacuum. The filter was then removed and dried in the oven at 100 °C for 30 min. Total MLSS was determined by the difference in weight of the filter before and after filtration and drying. In order to obtain the amount of AS needed in the solutions based on the EPA method, the bacterial count per milliliter was computed using Equation 5:

\[
\frac{0.03 \, g}{L} \times \frac{1 \, (L)}{MLSS \, (g)} \times \text{Dilution Factor} \, (mL) = \text{MLSS volume} \, (mL)
\]
Simultaneously, a mineral solution was prepared. To prepare 1 L of the mineral solution, 100 mL of each of the four mixtures listed below (a, b, c, and d) were prepared in water. A 10 mL volume of solution a was added to 800 mL of water. Then, 1 mL of solutions b, c, and d were added to the same flask and filled to the mark with more water.

- **Solution a** (pH ~7.4): 0.85 g of potassium dihydrogen orthophosphate (KH$_2$PO$_4$), 2.18 g of dipotassium hydrogen orthophosphate (K$_2$HPO$_4$), 3.34 g of disodium hydrogen orthophosphate dehydrate (Na$_2$HPO$_4$.2H$_2$O), and 0.05 g of ammonium chloride (NH$_4$Cl).
- **Solution b**: 3.64 g of calcium chloride dehydrate (CaCl$_2$.2H$_2$O)
- **Solution c**: 2.25 g of magnesium sulfate heptahydrate (MgSO$_4$.7H$_2$O)
- **Solution d**: 0.025 g of iron (III) chloride hexahydrate (FeCl$_3$.6H$_2$O) and 0.04 g of EDTA

A 0.035 M (5000 ppm) concentration of alternating $^{13}$C labeled PCA solution was prepared. Since PCA is slightly soluble in water, the solution had to be sonicated for two hours. This solution was prepared with the mineral water as solvent and analyzed using NMR. Then, the calculated amount of MLSS was added to the mixture and immediately placed in the apparatus shown in **Figure 97** to avoid any exposure to carbon dioxide from the environment. The round bottom, three-neck flask with the amber-colored solution contains the labeled material with the AS in mineral water. Ultra-pure, zero air (Airgas Orlando, Florida) was flowed into Flask A through a glass-frit diffuser inserted into the solution. The gas exit of Flask A emptied into Flask B through another glass-frit diffuser into a solution of 1.0 M NaOH. This flask served as a CO$_2$ trap where CO$_2$ coming from the microbial degradation of PCA would form carbonate ion (CO$_3^{2-}$) in solution which could be analyzed via NMR. The gas exit from Flask B then enters a final trap composed of a tube packed with molecular sieves and carbon to trap any volatiles that might be formed from the microbial degradation of PCA. A sample from Flask A solution was taken every 7 days for 28 days and at the end a sample of the Flask B solution was also taken for CO$_2$ analysis via NMR. The activated carbon was also analyzed by NMR after extraction with ethanol.
A 0.032 M (5000 ppm) concentration of alternating $^{13}$C labeled mPCA solution was also prepared. This solution was prepared with mineral water (the same described for the PCA experiments) as solvent and analyzed using NMR. The calculated amount of MLSS was added to the mixture and immediately placed in the apparatus shown in Figure 97, which was the same set up used for PCA biodegradation analysis. The round bottom, three-neck flask with the clear-yellow solution to the left (Flask A) contained the labeled material with the AS in mineral water. mPCA did not cause immediate foaming in the mixture as PCA did. A sample from Flask A solution was taken every 7 days for 28 days and on day 28 a sample of the Flask B solution (1.0 M NaOH solution-CO$_2$ trap) was also taken for CO$_2$ analysis via NMR. The activated carbon from the volatiles trap was also analyzed by NMR after extraction with ethanol.
8.3 Results and Discussion

8.3.1 Bacterial Biodegradation of PCA

The 0.035 M alternating $^{13}$C labeled PCA solution was analyzed using NMR (Figure 98) as a baseline spectrum in order to observe the molecule’s characteristic peaks and be able to later identify changes in it. The main characteristic peaks for this molecule are at 20 ppm which corresponds to the CH$_2$ next to the C attached with double bond to the N (1); the peak at about 26 ppm corresponds to the C that forms the ketone next to the labeled CH$_2$ (2); the peak at about 146 ppm corresponds to the C attached with double bond to the N (3); the peak at about 166 ppm corresponds to the carboxylic acid (4); and the peak at about 172 ppm corresponds to the carbon amide (5).

![Figure 98: Standard 0.035 M $^{13}$C alternating labeled PCA solution in mineral water with activated sludge](image)

One of the most important observations to discuss was the reaction witnessed when the MLSS was added to the PCA solution. When the microbes were added to the solution and the flask was sealed with air flow, and the solution began to form foam at the top of the flask. For this reason the air flow had
to be reduced to prevent the solution from going to Flask 2. The foam formation was observed through all 28 days of experiment, see Figure 99.

Figure 99: $^{13}$C labeled PCA solution in mineral water after addition of activated sludge

When the day one sample was analyzed using the NMR (Figure 100), the characteristic peaks for PCA were almost gone. The only two carbon labeled peaks left were at 20 and 26 ppm (carbons 1 and 2 from Figure 98) but very small. A new peak was observed immediately, specifically from carbon 4, but slightly upfield of where it appears in the PCA spectrum (~169 ppm instead of 166 ppm). One of the characteristics of this new peak, besides being tall, was that it appears as a singlet instead of a doublet as shown on PCA peaks. This was expected as the carbon dioxide should come from the labeled carboxylic acid carbon after degradation of the PCA molecule and it should not show as a doublet as there are no other labeled carbons around it. When day seven was analyzed (Figure 101), the same peaks were still observed with the difference that the new peaks located at 60 and 74 ppm were taller. The height of the peaks may correspond to impurities of the sample or pieces of the PCA molecule after degradation by microorganisms, a further study to find masses could be performed in order to identify the new pieces.
Days 14, 21, and 28 (Figure 102) showed exactly the same spectra, which indicates that the microbes may do the biodegradation work in the first days of contact with PCA. All these samples were run overnight to ensure the minimum noise in the baseline so all the peaks, including the smallest ones, could be clearly observed.

Figure 100: NMR spectrum of $^{13}$C labeled PCA solution in mineral water in the presence of activated sludge – Day 1
As previously mentioned, a sample of the NaOH aqueous mixture (Flask B) used as a trap for the carbon dioxide not dissolved in the solution of Flask A, was analyzed via NMR at the end of the 28
period (Figure 103). In this sample, a singlet peak at 171 ppm is clearly observed which indicates the presence of carbon dioxide (as carbonate). The peak moved to this position as the pH of the NaOH was very basic and extreme pH can cause small variations to the position of the peaks. In order to verify if the peak really corresponded to carbon dioxide, the NaOH solution was spiked with ethanol which should show peaks at 18 and 58 ppm, these two peaks were also moved to the left by a small amount based on the basic pH.

![NMR spectrum of NaOH sample at the completion of the biodegradation experiment – Day 28](image)

Figure 103: NMR spectrum of NaOH sample at the completion of the biodegradation experiment – Day 28

Taking in consideration this new approach to verify biodegradation of PCA by microorganisms as well as the biodegradation studies completed by Rueda’s et al. in 2013, it can be determined that bacteria are actually able to use carbon as an energy source yielding an increase in its oxygen demand levels. Supplementary work needs to be performed in order to verify if bacteria are able to completely digest the pieces of PCA molecule not observed anymore in the NMR spectra. Moreover, the effect of bacteria on $^{13}$C labeled mPCA (next section) needs to be analyzed to observe it proficiency under different experimental conditions.

### 8.3.2 Bacterial Biodegradation of mPCA

The 0.032 M alternating $^{13}$C labeled mPCA solution was analyzed using NMR (Figure 104) as a baseline spectrum in order to observe the molecule’s characteristic peaks and be able to later identify
changes in it. The main characteristic peaks for this molecule are as follows: a peak at 20 ppm which corresponds to the CH$_2$ next to the C attached with double bond to the N (1); the peak at 26 ppm corresponds to the C that forms the ketone next to the labeled CH$_2$ (2); the peak at 146 ppm corresponds to the C attached with double bond to the N (3); the peak at 166 ppm corresponds to the carboxylic acid (4); the peak at 172 ppm corresponds to the carbon amide (5); and the peak at 38 ppm corresponds to the unlabeled methyl group (6).

Figure 104: Standard 0.032 M $^{13}$C alternating labeled mPCA solution in mineral water with activated sludge

As opposed to what happened with PCA in solution with the microorganisms, mPCA did not have any observable reaction when the MLSS was added to the mineral aqueous mixture. As soon as the microbes were added to the solution, the flask was sealed and a slow zero-air flow was started. Foam formation was never observed through the 28 days of experiment.

When the day one sample was analyzed using the NMR (Figure 105), the characteristic peaks for mPCA were still unchanged. The spectrum showed all the peaks at the same positions, with the same
intensities and no new peaks were observed. Samples were pulled from the experimental set up every seven days for 28 days and NMR spectra remained exactly the same through this time period. The NMR spectrum of the mPCA sample at day 28 is shown in Figure 106.

Figure 105: NMR spectrum of $^{13}$C labeled mPCA solution in mineral water in the presence of activated sludge – Day 1

Figure 106: NMR spectrum of $^{13}$C labeled mPCA solution in mineral water in the presence of activated sludge – Day 28

As previously mentioned, a sample of the NaOH aqueous mixture (Flask B) used as a trap for the carbon dioxide that could pass from the solution of Flask A, was also analyzed via NMR at the end of the
28 period (Figure 107). In this sample, a singlet peak at 169 ppm is clearly observed which indicates the presence of carbon dioxide (as carbonate). The peak moved to this position as the pH of the NaOH was very basic and extreme pHs can cause small variations to the position of the peaks. In order to verify if the peak really corresponded to carbon dioxide, the NaOH solution was spiked with ethanol which should show peaks at 18 and 58 ppm, these two peaks were also moved to the left by a small amount based on the basic pH.

Figure 107: $^{13}$C NMR spectrum of Flask 2 (NaOH solution) after day 28 of experiment

Taking into consideration this new approach to verify biodegradation of mPCA by microorganisms as well as the biodegradation studies completed by Rueda, et al. in 2013, it can be determined that AS microbes are not capable of using the carbon from mPCA as an energy source as efficiently as with PCA. It is possible that the extra methyl group on the mPCA causes steric hindrance for microbial activation of the molecule and interferes with the degradation process. However, it does appear that after 28 days the microbes are capable of attacking the carboxylic acid group on the mPCA.
The remainder of the molecule (mPCA without the carboxylic group) was not identified indicating it may be completely consumed by the microbes or is not in a concentration high enough to see using NMR analysis.
CHAPTER 9: REACTION ENTHALPIES OF FORMATION

9.1 Introduction

The application of a different technology for the treatment of HZs for fuel waste streams at NASA, KSC involves many different important factors to keep under consideration. Therefore, a complete study of the reactants, the products, and the actual reaction is of great importance before used for field-scale handling of the waste materials. After having a better understanding of how the reaction of HZ and MMH with AKGA proceeds, and after doing a deeper study of its mechanism, kinetics, and reversibility, the heat capacity also gives us a more clear view of how the reaction will behave in the field if AKGA is added as the treating methodology.

Calorimetry is the process in which heat exchange from a chemical reaction or from a physical change is measured. A simple calorimeter consists of a thermometer attached to a metal compartment which is full of water suspended above the combustion chamber. There are more complex calorimetric equipment that are capable of measuring the change of heat in a reaction that dependent on different factors, such as pressure, type of reactants, temperature, etc. A bomb calorimeter is a constant-volume calorimeter used to measure the heat of reaction of a specific reaction. Since the calorimeter is isolated from the rest of the universe, the reactants will work as the system and the vessel and water as the surroundings. For this specific part of the research an isothermal bomb calorimeter calibrated with water at 35°C was used to measure the change in temperature of the reactions and observe if these would behave as endothermic or exothermic.

The change of heat (ΔH) in the reaction of HZ or MMH (MMH) with AKGA to form PCA or mPCA, respectively was measured. In order to gather data on the reactions, the heat capacity of the bomb calorimeter had to be determined with the blank solution in use. When no interferences were used the
blank used was water with a heat capacity of 418.0 J/°C. When the interferences were used the heat capacity for the blank solutions were: water and CA, 409.6 J/°C, water and IPA 418.1 J/°C, and water, CA and IPA 405.6.

9.2 Experimental Procedure

Procedure for this section was the same as procedure for interference section (Section 5). Reaction vessel was the bomb calorimeter instead of the beaker with the stirring bar. A temperature probe was inserted inside the calorimeter for temperature readings and recorded into the computer.

9.3 Results and Discussion

9.3.1 Reaction Enthalpy of Formation for PCA After the Reaction of HZ and AKGA

First, the temperature of 50 mL of 0.32 M (10240 ppm) HZ was measured in the bomb calorimeter container. In a separate beaker, the temperature of 50.0 mL 0.352 M AKGA (51392 ppm) was measured. AKGA was added to the bomb calorimeter container and the temperature was recorded for 12 minutes. The rise in temperature recorded was from 27.2°C to 28.4°C. Figure 108 shows the temperature change profile for this reaction. Once the temperature change in the reaction was obtained, the $\Delta$heat per mole of compound was calculated (Equation 6) and it was found to be 18.6 KJ/mol.
Figure 108: Temperature profile for PCA formation in 12 minutes with a 1% by volume HZ solution

\[ \Delta H = q(J/mole) \times \Delta T \]

Where \( q \) = heat capacity of calorimeter, \( \Delta T \) = change in temperature during reaction, and \( \Delta H \) = molar enthalpy of reaction.

\( \Delta T = 1.2 \, ^\circ C \)

\( q = \Delta T (q/°C) = 1.2 \, °C \times (418.0 \, J/°C) = 501.6 \, J \)

at 12 min PCA formed = 0.027 mole

\( q/mole = (501.6 \, J / 0.02700 \, mole) / 1000 \, J/KJ = 18.60 \, KJ/mole \)

9.3.2 Reaction Enthalpy of Formation for mPCA After the Reaction of MMH and AKGA

A bomb calorimeter was used in order to measure the change of heat (\( \Delta H \)) in the reaction of MMH with AKGA to form mPCA. First, the temperature of 50 mL of 0.19 M MMH (8740 ppm) was measured in the bomb calorimeter container. In a separate beaker, the temperature of 50.0 mL 0.210 M
AKGA (30514 ppm) was measured. AKGA was added to the bomb calorimeter container and the temperature was recorded for 12 minutes. The rise in temperature recorded was from 25.4°C to 26.2°C. Figure 109 shows the temperature change profile for this reaction. Once the temperature change in the reaction was obtained, the Δheat per mole of compound was calculated and it was found to be 35.5 KJ/mol.

![mPCA Formation Temperature Profile](image)

**Figure 109: Temperature profile for mPCA formation in 30 minutes with a 1% by volume MMH solution**

\[ \Delta T = 0.8 \, ^\circ\text{C} \]

\[ q = \Delta T \left( \frac{q}{^\circ\text{C}} \right) = 0.8 \, ^\circ\text{C} \times (418.0 \, \text{J/}^\circ\text{C}) = 334.4 \, \text{J} \]

at 30 min mPCA formed = 0.01100 mole

\[ q/\text{mole} = \frac{334.4 \, \text{J}}{0.01100 \, \text{mole}} / 1000 \, \text{J/KJ} = 30.44 \, \text{KJ/mole} \]

### 9.3.3 Reaction Enthalpy of Formation with HZ, MMH, and AKGA in the Presence of Interferences

#### 9.3.3.1 Enthalpy of formation with HZ, MMH, AKGA, and CA interference:

The same bomb calorimeter previously used to measure the change of heat in the reaction of HZ
with AKGA was used. In this case the calibration of the calorimeter was done with water and CA but no considerable change was observed in comparison to the calibration done with just water. The change in the temperature for just water was 0.9 °C and the change in the temperature with the CA was 1.1 °C. The previous set up for this reaction was repeated; 100 mL total volume reaction was added into the bomb calorimeter but in this case with a 14% by weight of CA. 25 mL of 1% v/v of HZ (0.32 M or 10240 ppm) and 25 mL of 1% v/v of MMH (0.19 M or 8740 ppm) were added first to the container and temperature was measured. In a separate beaker, the AKGA was prepared (0.561 M or 81906 ppm) and temperature was measured. AKGA solution was added to the bomb calorimeter and temperature was recorded for 12 minutes. The average of the rise in temperature was recorded as ΔT = 2.5 °C. Figure 110 shows an example of the temperature change profile for this reaction. Once the temperature change in the reaction was obtained, the heat per mole of compound was calculated and it was found to have an average of 31.6 KJ/mol.

![PCA-mPCA Formation with CA as Interference](image)

**Figure 110:** Temperature profile for PCA and mPCA formation in 12 minutes with CA as interference
ΔT = 2.5 °C

\[ q = \Delta T \left( \frac{q}{°C} \right) = 2.5 °C \times (409.6 \text{ J/°C}) = 1024.0 \text{ J} \]

at 12 min PCA-mPCA formed = 0.03200 mole

\[ \frac{q}{\text{mole}} = \frac{(1024.1 \text{ J} / 0.03200 \text{ mole})}{1000 \text{ J/KJ}} = 32.00 \text{ KJ/mole} \]

9.3.3.2 Enthalpy of formation with HZ, MMH, AKGA, and IPA interference:

The same procedure previously used was employed for the IPA interference in the reaction of the hypergols and AKGA. In this case the calibration of the calorimeter was done with water and IPA and a greater effect was observed for the change in the temperature. The change in the temperature for just water was 0.9 °C, with the CA was 1.1 °C, and with the IPA was 1.4 °C. Previous set up for this reaction was done once again; 100 mL total volume reaction was added into the bomb calorimeter but in this case with a 4% by volume of IPA. 25 mL of 1% v/v of HZ (0.32 M 10240 ppm) and 25 mL of 1% v/v of MMH (0.19 M or 8740 ppm) were added first to the container and temperature was measured. In a separate beaker the AKGA solution was prepared (0.561 M or 81906 ppm) and temperature was measured. The AKGA solution was added to the bomb calorimeter and the temperature was recorded for the 12 minutes. The average of the rise in temperature was recorded as

\[ \Delta T = 5.8 °C. \text{ Figure 111 shows an example of the temperature change profile for this reaction. Once the temperature change in the reaction was obtained the heat per mole of compound was calculated and it was found to have an average of 75.8 KJ/mol.} \]
Figure 111: Temperature profile for PCA and mPCA formation in 12 minutes with IPA as interference

\[ \Delta T = 5.9 \, ^\circ C \]

\[ q = \Delta T (\frac{q}{C}) = 5.9 \, ^\circ C \times (418.1 \, J/\circ C) = 2466.8 \, J \]

at 12 min PCA-mPCA formed = 0.03200 mole

\[ \frac{q}{mole} = \frac{2466.8 \, J}{0.03200 \, mole} \times \frac{1000 \, J}{1 \, KJ} = 77.10 \, KJ/mole \]

9.3.3.3 Enthalpy of formation with HZ, MMH, AKGA, CA, and IPA interference:

The same procedure previously used was applied for the interference of IPA and CA together for the reaction of the hypergols and AKGA. The calibration of the calorimeter was done with water IPA and CA and no greater effect in the temperature change was observed than for water and IPA alone. The change in the temperature was 1.4 °C. The previous set up for this reaction was used: 100 mL total reaction volume was added into the bomb calorimeter, in this case with a 4% v/v of IPA and 14% w/w of CA. 25 mL of 1% v/v of HZ (0.32 M or 10240 ppm) and 25 mL of 1% v/v of MMH (0.19 M or 8740 ppm) were mixed with the CA and the IPA and then added to the container and temperature was measured. In a separate beaker, the AKGA solution was prepared (0.561 M or 81906 ppm) and
temperature was measured. Then, AKGA was added to the bomb calorimeter and temperature was recorded for 12 minutes. The average of the rise in temperature recorded was $\Delta T = 2.4 \, ^\circ C$. Figure 112 shows an example of the temperature change profile for this reaction. Once the temperature change in the reaction was obtained the heat per mole of compound was calculated and it was found to have an average of 30.4 KJ/mol.

Figure 112: Temperature Profile for PCA and mPCA formation in 12 minutes with CA and IPA interferences

$\Delta T = 2.4 \, ^\circ C$

$q = \Delta T \cdot (q/°C) = 2.4 \, ^\circ C \cdot (405.6 \, J/°C) = 973.4 \, J$

at 12 min PCA-mPCA formed = 0.03200 mole

$q$/mole = (973.4 J / 0.03200 mole) / 1000 J/KJ = 30.40 KJ/mole
Table 25 summarizes the data for the heat of formation per mole of the formed by-products in the absence and presence of field interferences:

Table 25: Heat of formation per mole of individual and combine byproducts in the absence and presence of CA and/or IPA

<table>
<thead>
<tr>
<th></th>
<th>ΔT (°C)</th>
<th>q (J)</th>
<th>q/mole (KJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCA (12 min)</td>
<td>1.2</td>
<td>501.6</td>
<td>18.60</td>
</tr>
<tr>
<td>mPCA (30 min)</td>
<td>0.80</td>
<td>334.4</td>
<td>30.44</td>
</tr>
<tr>
<td>PCA + mPCA + CA (12 min)</td>
<td>2.5</td>
<td>1024</td>
<td>32.00</td>
</tr>
<tr>
<td>PCA + mPCA + IPA (12 min)</td>
<td>5.9</td>
<td>2467</td>
<td>77.10</td>
</tr>
<tr>
<td>PCA + mPCA + CA+IPA (12 min)</td>
<td>2.4</td>
<td>973.4</td>
<td>30.40</td>
</tr>
</tbody>
</table>
CHAPTER 10: CONCLUSIONS

AKGA treatment was successfully applied in samples of 1% by volume HZ and MMH at in the presence and absence of common field interferences. The treatment was also successful in field scrubber liquor samples after proving the following:

- Characterization and quantitation of HZ and MMH was possible through GC-NPD. The calculation of the HZ/MMH concentration remaining in the reaction mixture after the reaction time obtained from kinetics studies was conducted, allowing for the calculation of the moles of HZ remaining at a specific time. This mole calculation in combination with the PCA/mPCA mole calculation from UV-Vis analysis, resulted in the expected mole balance as almost complete transformation of the reactants into the product of interest was obtained.

- Characterization and quantification of PCA and mPCA with a 0.0038 M AKGA as a background was possible via UV-VIS with a 260 nm wavelength for PCA and 272 nm wavelength for mPCA. HPLC was used as a qualitative verification method. UV-Vis was used as quantitative method for product determination. Calibration curves and linear equations were obtained for PCA and mPCA which allowed for the quantification of the products during kinetics experiments.

- Pseudo-first-order reaction rate constants were obtained for the formation of PCA and mPCA when AKGA was added in excess (15:1 AKGA:Hypergol ratio). After the AKGA was optimized and hypergols were used in concentrations resembling field applications, the reactions were found to follow second order kinetics, first order with respect of each of the reactants. HZ was found to be 84% converted after a 12 min period for the lowest ratio, 1.1:1 with an average 0.88 L/mole*min\(^{-1}\) rate constant. MMH was found to be 85% converted after a
180 min period for the lowest ratio, 1.1:1 with an average 0.11 L/mole*min\(^{-1}\) rate constant.

- Calculations for HZs reaction time completion were possible based on the rate constants determined and the mathematical models. A conversion of 99% for each of the hypergols will be obtained after 2 hours and 44 min for HZ and 36 hours and 53 min for MMH.

- Calibration curves with backgrounds that included interferences and the associated linear fit equations were obtained for PCA and mPCA, which allowed for the quantification and characterization of the products for comparison when interferences are present in the reaction mixture.

- CA was found to have a slight delay in the reaction kinetics of PCA and mPCA formation; which was expected as the acid traps the HZ molecules to lower the vapor pressure. On the other hand, IPA and the silicone based AF were not found to have any significant effect in the formation of PCA and/or mPCA.

- When HZ, MMH and AKGA are all together in the same reaction, there is a delay in the formation of the products. Although HZ dominates the reaction as it proceeds faster than when only MMH is present, there is also a shift in the maximum absorption wavelength to 264 nm, which indicates that some amount of MMH is also reacting to form products showing an overlap of the wavelengths.

- In the case of HZ and MMH together, when CA, IPA, and the AF are added independently as well as when they are added together they cause a delay in the product formation. Based on this delay, the reaction yield at the same compared time is smaller.

- Application of AKGA treatment to field samples needs to be further studied as the formation of
the byproduct is almost negligent after one hour and then after 5 days of reaction. However, the disappearance of the HZ and MMH fuels was successfully achieved within the first hour of reaction within the NPD limits of detection.

- Biodegradation studies were performed to validate Rueda et al. work in 2013. Using $^{13}$C NMR to track labeled PCA and mPCA material, it was determined that bacteria are able to use the PCA molecule as a carbon source degrading or breaking down the molecule into smaller pieces. Though, bacteria were not able to use mPCA as a carbon source and the molecule does not break into smaller pieces as PCA does.
REFERENCES


