Replacing the Al$_2$O$_3$ Shell on Al Particles with an Oxidizing Salt, Aluminum Iodate Hexahydrate. Part I: Reactivity

Dylan K. Smith,$^{†}$ Daniel K. Unruh,$^{‡}$ Chi-Chin Wu,$^{§}$ and Michelle L. Pantoya$^{*†}$

$^{†}$Department of Mechanical Engineering, and $^{‡}$Department of Chemistry, Texas Tech University, Lubbock, Texas 79409, United States
$^{§}$Weapons and Materials Research Directorate, U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland 21005, United States

ABSTRACT: Improvements in the reactivity, measured in terms of flame speed, for aluminum-based energetic mixtures are increased by a factor of 2−3 by replacing the Al$_2$O$_3$ passivation layer of aluminum (Al) nanoparticles with aluminum iodate hexahydrate (AIH), an oxidizing salt. The Al−AIH nanoparticles are examined under transmission electron microscopy. An AIH passivation shell surrounding the Al core particle is a more reactive composite structure than Al$_2$O$_3$ passivation around Al which facilitates increased reaction rates with flame speeds as high as 3200 m/s. Flame speed measurements are used to show that reaction rates in AIH mixtures are determined by the AIH/Al$_2$O$_3$ ratio, oxygen balance, and β-HIO$_3$. Further optimization of these properties will ultimately boost significant increases in the reaction rates of the energetic materials presented in this article.

INTRODUCTION

Energetic materials contain stored chemical energy that is released upon ignition. Increasing the reaction rate of an energetic material will correspondingly increase the power delivered by the reaction. Monomolecular explosives contain relatively small levels of stored chemical energy (Figure 1) but can release that energy very quickly. These chemical reactions are triggered by kinetic mechanisms that spur bond breaking between atoms leading to fast reaction rates. Composites, on the other hand, are a mixture of fuel and oxidizer materials, discretely separated by a physical distance. These materials store a larger amount of chemical energy than monomolecular explosives (Figure 1) but are diffusion limited which inhibits the rate of energy release. Metallic fuels in composite energetic materials may have the potential to overcome limitations resulting from diffusion-based reaction mechanisms.

When metal fuels are mixed with metal oxides, the reactant mixture is commonly referred to as thermite (see example thermites in Figure 1). Mass diffusion kinetics for thermite reactions result in significant energy released relatively slowly compared with explosives.$^1$ For example, the heats of reaction for selected thermites and common explosives are presented in Figure 1 and show that the stored energy in thermites is significantly greater than that in explosives. However, flame speeds for thermites are generally below 1000 m/s while detonation velocities for explosives are above 7000 m/s.

Aluminum (Al) is a common fuel used in thermites due to its high energy density (16.4 kJ/g Al$_2$O$_3$)$^1$ when reacted with oxygen to form Al$_2$O$_3$. This reaction also happens naturally in an oxygen-containing environment producing an alumina passivation layer around unoxidized Al particles during synthesis. The passivation layer is inert and acts as a diffusion barrier and heat sink, reducing the total energy liberated and reaction rate in Al-based thermites.$^4$ Another limiting factor for energy release rates in composite materials is the large distance between fuel and oxidizer that is directly related to the size and shape of fuel and oxidizer particles. To decrease the limitations imposed by particle size, synthetic methods that produce...

Figure 1. Heat of reaction for selected thermites and explosives.$^{2,3}$ Solid bars are in units of kJ/cc, and hatched bars are in units of kJ/g.

Received: June 13, 2017
Revised: September 16, 2017
nanoscale Al particles have been utilized. Reduction of particle size has led to significant increases in reaction rates of thermites based on enhanced mass diffusion.\(^5\) However, the reduced size in Al nanoparticles also results in increased concentration of Al\(_2\)O\(_3\) limiting reaction rates in two ways: (1) Al\(_2\)O\(_3\) is an insulator and absorbs the energy that is produced upon reaction, and (2) Al\(_2\)O\(_3\) acts as a barrier in mass diffusion, inhibiting oxygen from reacting with unoxidized Al (Al\(^{3+}\)) in the core of Al nanoparticles. Therefore, reducing the limiting effects of the Al\(_2\)O\(_3\) layer can result in faster kinetics that approach those of common organic explosives.\(^9\)

Halogenated oxidizers have been used to reduce the inhibiting effects of the Al\(_2\)O\(_3\) passivation layer.\(^1\) Halogens are electrophilic and can react exothermically with the Al\(_2\)O\(_3\) passivation layer in a reaction that has been coined "a pre-ignition reaction" (PIR).\(^3\) Recently, a PIR was observed at the surface of Al particles and produced by the exothermic reaction between the alumina passivation shell encapsulating aluminum particles and iodine, specifically, iodic acid (HIO\(_3\)).\(^8\) A relationship between flame speed and the concentration of water used during mixing of I\(_2\)O\(_5\) and Al nanoparticles had been discovered by Smith et al.\(^9\) The relationship is a result of the formation of aluminum iodate (AIH), (Al\((IO_3)_3(HIO_3)_2\)\(\cdot\)6H\(_2\)O).\(^7\) In fact, Al–AIH mixtures exhibited increased flame speeds compared to all other Al-containing thermites with measured flame speeds as high as 3200 m/s.\(^9\)

To begin to understand the heightened reactivity of AIH mixtures, one must examine the crystal structure of AIH. The crystal structure of AIH consists of aluminum hexahydrate (Al\((H_2O)_6^{3-}\)) cations, also referred to as hexaaquoaluminate-\((III)\),\(^6\) held in the pore space of an iodate framework through hydrogen bonds (see Figure 1 in Smith et al.\(^9\)). Since the oxidation state of Al in AIH is already 3+ (i.e., Al\(^{3+}\) is already oxidized), the energy released from forming Al\(_2\)O\(_3\) from AIH is significantly less (possibly endothermic) than that from forming Al\(_2\)O\(_3\) from Al\(^{3+}\). Due to Al in AIH already being oxidized (i.e., Al\(^{3+}\)), the increase in reactivity of these composite materials was not expected.\(^9\) Therefore, the increased flame speeds seen in AIH mixtures may be a result of a kinetically driven reaction that is related to the formation of AIH. This study expands our previous work of synthesizing Al–AIH\(^9\) nanoparticles by examining not only possible mechanisms controlling the increase in the reactivity of Al–AIH but also the crystalline structure of resultant composite nanoparticles under transmission electron microscopy (TEM). The objective is to analyze trends in reactivity as a function of AIH concentration in Al–AIH mixtures. The reactivity is assessed in terms of flame speed and reaction kinetics.

### EXPERIMENTAL SECTION

**Mixing Procedure.** The method of mixing involves completely dissolving commercially available I\(_2\)O\(_5\) supplied by Sigma-Aldrich (St. Louis, MO), in distilled water prior to mixing with Al nanoparticles. The commercially available I\(_2\)O\(_5\) is comprised of iodic acids\(^1\) (i.e., HIO\(_3\) and HI\(_3\)O\(_8\)) that dissolve in water along with I\(_2\)O\(_5\) to form an IO\(_3\)\(^–\) solution, eliminating the need to treat the sample prior to mixing. The I\(_2\)O\(_5\) was dissolved in a beaker with a magnetic stirrer rotating at 300 rpm in distilled water for 5 min before adding aluminum nanoparticles (~80 nm), supplied by Novacentrix (Austin, TX). Two separate reactivity studies are reported and are referred to as (1) the water to Al ratio study and (2) the equivalence ratio (ER) study. These two separate studies were designed to measure the effects of additional water concentration and initial mixing parameters on reactivity.

The water to Al ratio samples are identical to samples used in Smith et al.\(^9\) The samples in the ER study were mixed to produce an ER value (calculated from eq 1) ranging from 0.8 to 1.5 by keeping the ratio of water to Al constant at 1:1 wt % and the ratio of water to I\(_2\)O\(_5\) constant at 1:2.5 wt %. The 1:2.5 water to I\(_2\)O\(_5\) ratio is the reported saturation ratio of I\(_2\)O\(_5\) in water\(^12\) and is the lowest concentration of water needed to dissolve I\(_2\)O\(_5\).

**Reactivity Measurements.** The procedure and apparatus for measuring flame speed was previously discussed in Smith et al.\(^9\) but will be summarized here for completeness. The liquid solutions were poured into channels milled in an acrylic plate and placed in a low-humidity (i.e., <20% relative humidity) environment to dry. The 7 cm long channels were sealed using 1 cm wide acrylic plates adhered to the top of the channel filled with sample. The purpose of the "lid" was to direct energy propagation axially along the channel. Ignition was achieved at one end of sample using a nickel–chromium wire attached to a voltage generator. The channel filled with the sample and ignition source was placed in a blast chamber with a viewing port aligned with a high-speed camera positioned perpendicular to the direction of flame propagation. Image collection was performed using a Phantom v1611 high-speed camera (Vision Research Inc.) at 381,818 frames per second (fps) and at a resolution of 384 × 64 pixels. The intensity of light created by the reaction is greatest at the leading edge of the reaction. To view this location, the f-stop on the lens (i.e., f/32) and neutral density filters were coupled to block out >99% of the light emitted to prevent oversaturation of the camera sensor. Image analysis was performed with the Phantom camera control program to monitor flame propagation and measure velocity. The time and distance measurements were exported into a spreadsheet and plotted along with a linear curve fit. All data reported produced an \(R^2\) value greater than 0.95. Each experiment was performed in triplicate to establish repeatability.

**Oxygen Ratios.** For thermites, the fuel to oxygen ratio is reported as an equivalence ratio (ER), which is a ratio of the actual mass of fuel (Al\(^0\)) to mass of oxidizer over the stoichiometric mass of fuel to mass of oxidizer shown in eq 1.

\[
ER = \frac{m_f}{m_o} = \frac{m_f^{\text{actual}}}{m_f^{\text{stoich}}} 
\]

In eq 1, \(m_f\) is the fuel mass and \(m_o\) is the oxidizer mass. The fuel to oxidizer ratio increases as ER increases, and the stoichiometric ratio is 1.0. After mixing, the AIH crystals that formed were comprised of both Al and AIH making the determination of ER impossible assuming Al\(^{3+}\) in AIH forms Al\(_2\)O\(_3\). Therefore, fuel to oxidizer ratio for the mixture was determined by oxygen balance (OB) shown in eq 2. Oxygen balance is calculated in terms of 100 g of compound to determine the percent of oxygen excess or deficient for 100 g of a compound.

\[
\text{OB\%} = \frac{-1600}{M_c} \left[ 2X + \frac{Y}{2} + aM - Z \right] 
\]

In eq 2, \(M_c\) is the molecular weight of the compound, \(X\) is moles of carbon (i.e., 0 for this mixture since carbon is not
X-ray Diffraction. The samples used for powder XRD analysis were prepared identically to samples used for flame speed measurements. The data for each sample were collected on a Rigaku Ultima III powder diffractometer operated in continuous $\theta$–2$\theta$ mode from 15 to 60° 2$\theta$ with parallel beam geometry. The step size was 0.02° with a collection time of 2°/min. The MDI Jade V9.1.1 software provides both qualitative and quantitative data analysis used to estimate the oxygen balance of the AIH crystals formed.

Transmission Electron Microscopy. The AIH samples were further examined using TEM. The TEM specimens were prepared using high-purity ethanol as the medium via the freeze-drying method. The TEM specimens were examined using TEM. The TEM specimens were obtained by inserting an aperture of appropriate size into the back focal plane of the objective lens using a 25 cm camera length. The TEM images and SAD patterns obtained from TEM image. The selected aperture diaphragm (SAD) pattern was obtained by inserting an aperture of appropriate size into the back focal plane of the objective lens using a 25 cm camera length. The TEM images and SAD patterns obtained from TEM were analyzed by using the Digital Micrograph software (Gatan Inc.).

RESULTS AND DISCUSSION

The reactive natures of AIH mixtures were first reported in Smith et al. and initial XRD results were presented for AIH mixtures synthesized using various water to Al ratios. Previously reported concentration data for the AIH and Al mixtures were estimates due to an unidentified phase seen in the mixtures. The unidentified phase was later determined to be the rarely observed HIO$_3$. Details of the synthesis and single-crystal data for HIO$_3$ were reported in Smith et al. Concentration data for the various equivalence ratios (i.e., ER study) from initial mixing are tabulated in Tables 1 and 2, respectively, using quantitative XRD analyses and identification of peaks for HIO$_3$.

Table 1. Initial Mixing Concentrations

<table>
<thead>
<tr>
<th>ER</th>
<th>Al (mg)</th>
<th>Al$_2$O$_3$ (mg)</th>
<th>I$_2$O$_5$ (mg)</th>
<th>water (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>1611.2</td>
<td>402.8</td>
<td>3985</td>
<td>3608</td>
</tr>
<tr>
<td>1.2</td>
<td>1381.6</td>
<td>345.4</td>
<td>4272</td>
<td>3435.8</td>
</tr>
<tr>
<td>1.1</td>
<td>1298.4</td>
<td>324.6</td>
<td>4377</td>
<td>3373.8</td>
</tr>
<tr>
<td>1</td>
<td>1209.6</td>
<td>302.4</td>
<td>4487</td>
<td>3306.8</td>
</tr>
<tr>
<td>0.9</td>
<td>1116.8</td>
<td>279.2</td>
<td>4603</td>
<td>3237.2</td>
</tr>
<tr>
<td>0.8</td>
<td>1019.2</td>
<td>254.8</td>
<td>4725</td>
<td>3164</td>
</tr>
</tbody>
</table>

The uncertainty based on standard deviation from variation between samples and accuracy of peak fitting is shown in parentheses in Table 2. The highest uncertainty in Table 2 is less than 5% (average uncertainty less than 7%), and a similar uncertainty is assumed in all figures where calculations were performed using the data from Table 2. The data from Table 2 coupled with flame speed measurements (see Figure 2) will be used to show that the increased reactivity seen in AIH mixtures appears to be the result of AIH replacing the Al$_2$O$_3$ passivation layer around the Al particles.

Structural Analysis of Al–AIH Nanoparticles via TEM. The structures of resultant Al–AIH nanoparticles are further examined under TEM and compared with that of bare Al nanoparticles. As an example, Figure 3 shows a TEM image of a bare Al nanoparticle at 2500X magnification. Distinct lattice fringes are exhibited in the core (see red arrows in Figure 3), indicating its strong crystallinity with a conformal and amorphous oxide layer with a measured thickness of approximately 4 nm. In contrast, Figure 4 shows high crystallinity in the outer shell of both Al–AIH nanoparticles (Figure 4a and b), as exhibited by the TEM images and their corresponding FFT plots in Figure 4a and b, respectively. These particles display superior single crystallinity throughout the entire particle from the Al core to the outer AlH shell exemplified by the parallel thin straight lines corresponding to lattice spacing. In comparison to the Al particle in Figure 3, no trace of remaining amorphous Al$_2$O$_3$ layer remains in both Al–AIH particles. The AlH layer on the outer shell surrounding the Al core also conforms perfectly with the crystallinity of the Al core such that the lattice fringes appear as thin parallel straight lines and are continuous throughout the core/shell structure. This is also confirmed by the FFT plots. In Figure 4b, the FFT diffraction spots also reveal the hexagonal nature of AIH crystals with additional diffraction spots.

Figure 5 displays a SAD pattern from Al–AIH nanoparticles at a relatively low magnification of 40kX. The pattern shows discrete diffraction spots rather than amorphous rings underscoring again the single crystallinity of Al–AIH nanoparticles. As demonstrated in the figure, the majority of high-intensity diffraction spots from Al–AIH match well with the corresponding (hkl) diffraction rings of a bulk Al crystal (where the values of h, k, and l are Miller indices) outlined as green circles. Nevertheless, several dimmer diffraction spots are also visible with low intensities. The d-spacing for those extra diffraction spots that do not belong to Al is estimated to be between 0.10 to 0.25 nm.

ER Study—Al$_2$O$_3$ Replaced by AIH. The formation process of AIH discussed in Smith et al. shows that AIH increases flame speeds but does not explain the reaction mechanism responsible for increased reactivity. Recall that AIH is a salt with aluminum hexahydrate [Al(H$_2$O)$_6$]$^{3+}$ interacting with the IO$_3^-$ framework through hydrogen-bonding interactions of the coordinating water molecules. The pH-dependent process that leads to the formation of [Al(H$_2$O)$_6$]$^{3+}$ uses oxygen from Al$_2$O$_3$ to form water and Al$^{3+}$. Since Al$^{3+}$ is oxidized and not expected to release energy (during the formation of Al$_2$O$_3$), the observed increase in flame speed is unexpected, and another mechanism is responsible for increased flame speeds. At this point we hypothesize that under the highly acidic (pH < 1) synthetic conditions, the Al$_2$O$_3$ passivation layer is being removed and replaced with AIH. To test this hypothesis the following figure (Figure 6) and analysis were used.

By calculating the moles of Al in 100 g of the initial mixture and the moles of AI in final AIH products using eqs 3–4a–4c, we can estimate the amount of AIH formed given the amount of Al available in Al$_2$O$_3$.

$$\text{Mol}_1 = \frac{\text{wt} \% \times 100 \ g}{\text{MW}_1}$$  \hspace{1cm} (3)
The subscript $i$ in eq 3 represents the species that contain Al (i.e., Al$_2$O$_3$, AIH, and Al$^0$ from the core of the particle). Mol$_i$ is moles of each species, wt % is the weight percent (shown in Tables 1 and 2) from initial mixing (subscript initial) or concentration data obtained from XRD measurement (subscript final), and MW is molecular weight. In eq 3, Mol$_i$ represents the moles of species in initial and final mixtures (i.e., Al$_2$O$_3$, AIH, and Al$^0$ from the core of the particle). From the number of molecules in each mixture, the number of atoms (i.e., Al, iodine(I), and oxygen (O)) can be calculated by adding the number of atoms in each molecule. The calculation of the number of atoms used to show AIH replacement of the Al$_2$O$_3$ shell in Figure 6 is shown in eqs 4a−4c. The total initial Al (Al$_{\text{tot,initial}}$) including Al from Al$_2$O$_3$ (black line in Figure 6) is calculated using eq 4b; the Al from final mixtures (Al$_{\text{Al-HI}}$, dashed line in Figure 6) including Al from AIH is calculated using eq 4c.

$$Al_{\text{tot,initial}} = \text{Mol}_{\text{Al,initial}} + 2 \times \text{Mol}_{\text{Al}_2\text{O}_3,\text{initial}}$$

### Table 2. Final Concentration Data Obtained from XRD Measurements with Standard Deviation in Parentheses

<table>
<thead>
<tr>
<th>ER</th>
<th>AIH (%)</th>
<th>Al$^0$ (%)</th>
<th>H$_2$O$_3$ (%)</th>
<th>β-HIO$_3$ (%)</th>
<th>amorphous (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>10.5% (2.0)</td>
<td>16.3% (2.8)</td>
<td>0%</td>
<td>0%</td>
<td>73% (3.1)</td>
</tr>
<tr>
<td>1.2</td>
<td>72.7% (5.2)</td>
<td>22.8% (1.6)</td>
<td>4.0% (0.5)</td>
<td>0.5% (0.1)</td>
<td>0%</td>
</tr>
<tr>
<td>1.1</td>
<td>76.1% (4.3)</td>
<td>20.0% (1.1)</td>
<td>3.0% (0.4)</td>
<td>0.9% (0.1)</td>
<td>0%</td>
</tr>
<tr>
<td>1</td>
<td>77.9% (4.7)</td>
<td>18.8% (1.1)</td>
<td>1.3% (0.2)</td>
<td>2.1% (0.2)</td>
<td>0%</td>
</tr>
<tr>
<td>0.9</td>
<td>57.8% (3.4)</td>
<td>18.6% (1.1)</td>
<td>11.6% (0.7)</td>
<td>11.9% (0.7)</td>
<td>0%</td>
</tr>
<tr>
<td>0.8</td>
<td>53.2% (2.1)</td>
<td>16.6% (0.7)</td>
<td>1.9% (0.2)</td>
<td>28.4% (1.1)</td>
<td>0%</td>
</tr>
</tbody>
</table>

Figure 2. Flame speeds (●), AIH (Δ), aluminum (○), HIO$_3$ (+), H$_2$O$_3$ (×), and amorphous (◊) concentrations as a function of ER. In all figures, dashed lines indicate concentration (wt %) and the solid line indicates flame speeds (m/s).

Figure 3. TEM image of Al$_2$O$_3$ passivated Al nanoparticle at 250k× magnification. The high crystallinity of the Al core is exhibited by distinct lattice fringes as indicated with red arrows. The thickness of amorphous oxide layer is measured as approximately 4 nm.

Figure 4. TEM image of Al−AIH nanoparticles: (a) at 500k× magnification and (b) at 600 k× magnification. The particles display superior single crystallinity from the Al core to the outer AIH shell exemplified by the parallel thin straight lines corresponding to lattice spacing. The inset shows the corresponding FFT plots in which a straight line drawn from a set of diffraction pair is perpendicular to the respective set of lattice fringes.

Figure 5. SAD pattern acquired from Al−AIH nanoparticles. The green circles highlight the diffraction rings of a bulk Al crystal with each ring specified by its (hkl) Miller index.

Figure 6) is calculated using eq 4b; the Al from final mixtures (Al$_{\text{Al-HI}}$, dashed line in Figure 6) including Al from AIH is calculated using eq 4c.
the AIH compound is heated to 135 °C, the water molecules are driven off, allowing acidic Al³⁺ to react exothermically with iodate species in AIH to form Al₂O₃ and I₂ gas. The lower onset temperature (135 °C) and exothermic Al³⁺ reaction in AIH significantly lower the apparent activation energy resulting in faster reaction rates and greater total energy generated when compared to Al⁰ reactions involving the Al₂O₃ passivation layer. Reaction rates are also affected by the large concentration of oxygen from AIH reactions and reduced distance between oxygen and Al⁰. Since AIH replaces the Al₂O₃ shell, the spacing between Al⁰ in the core and oxygen is reduced when compared to Al reactive mixtures with the Al₂O₃ passivation layer. The reaction to form Al₂O₃ from AIH is overoxidized (12.5 extra moles of oxygen for every mole of AIH). The abundance of oxygen and small spacing between available oxygen from the AIH reaction and unoxidized Al⁰ (Al⁰) can significantly increase reaction rates. The combination of decreases in apparent activation energy, reduced limitations from the Al₂O₃ diffusion barrier, and shortened distance between Al⁰ and oxygen from AIH reactions all account for the significant reactivity increases seen in AIH mixtures.

Significant differences in reaction behavior have also been observed in AIH mixtures that are related to concentrations of AIH, Al⁰, iodic acids, and overall densities of the mixtures. In Smith et al.,⁹ flame speeds increased from 1757 to 3132 m/s for AIH mixtures at a fixed ER of 1.1 when the initial water to Al ratio varied from 2:1 to 6:1. It was suggested that the dramatic increase in observed reactivity by increasing the initial water to Al ratio was caused by concentration differences or differences in density of the final material. In Smith et al.,⁹ it was assumed that concentrations of AIH and Al⁰ were the same for the different water to Al ratios. This assumption was necessary because β-HIO₃ had not been indexed causing high uncertainties in the quantitative analysis of the XRD measurements. Figure 7a shows the average concentration data (with uncertainties) for all samples (i.e., 2:1, 4:1, 5:1, and 6:1 water to Al ratio) with an ER of 1.1, and Figure 7b shows corresponding flame speeds for the same mixtures as a function of varying

Figure 6 shows that Al₄H₉final is between Al₄tot,initial and Al₄core,final indicating that AIH forms from Al in the Al₄O₃ passivation layer and that AIH replaces the Al₂O₃ passivation layer. The initial total Al is used to show the upper limit, and the final core Al⁰ is used to show the lower limit since the Al₂O₃ passivation layer is amorphous and cannot be detected by XRD measurements. However, the initial Al particles have an average diameter of 80 nm with an Al₂O₃ passivation shell that is 4 nm thick (as shown in Figure 3).¹⁵ If it is assumed that no Al leaves as vapor during synthesis, the difference between Al₄AIH,final and Al₄core,final is the amount of AIH formed during synthesis, and the amount of final Al₂O₃ is the difference between the Al₄tot,initial and Al₄AIH,final in Figure 6.

Replacement of Al₂O₃ with AIH increases reactivity of the composite material by replacing an inert oxidation barrier (i.e., Al₂O₃) with an energetic salt (AIH), thereby increasing the amount of oxygen that can react with elemental Al⁰ (Al₄core) and decreasing the distance between Al⁰ and oxygen. In nanoparticle Al oxidation reactions with an Al₂O₃ passivation layer, the oxidation of Alcore starts at the melting temperature of Al (approximately 660 °C depending on particle size). Volumetric expansion from molten Al allows oxygen to diffuse through the Al₂O₃ passivation layer, oxidizing molten Al from the core of Al nanoparticles.¹⁶ In this way, Al₂O₃ acts as a diffusion barrier limiting the amount of oxygen that can react with Al from the core of the particle. Also, when the temperature of Al particles is raised to the melting temperature of Al metal, heat is absorbed by the Al₂O₃ passivation layer, a natural heat sink. By creating oxygen diffusion limitations and absorbing heat, the Al₂O₃ passivation layer raises the apparent activation energy of the system and lowers the total energy generated by Al⁰ oxidation reactions.

In AIH, Al³⁺ and IO₃⁻ are separated by a water ring in aluminum hexahydrate, [Al(H₂O)₆]³⁺. Al³⁺ in AIH has vacant 3s and 3p orbitals that allow Al³⁺ to act as a Lewis acid. When

\[ \text{Al}^{0\text{core,final}} = \text{Mol}_{\text{Al,final}} \]  
\[ \text{Al}^{\text{AIH,final}} = \text{Mol}_{\text{Al,final}} + \text{Mol}_{\text{AIH,final}} \]
The Journal of Physical Chemistry C

Figure 7. (a) Average concentration data for AIH, Al\(^0\), and \(\beta\)-HIO\(_3\) for fixed ER = 1.1 but for all water to Al ratios (i.e., 2:1, 4:1, 5:1, and 6:1 water to Al ratio). Error bars are the standard deviations in four samples. Data shows concentrations do not change as a function of the water to Al ratio. (b) Flame speed as a function of initial water to Al ratio. All samples were mixed at an initial ER of 1.1.

water concentrations. The small error bars in Figure 7a confirm that the concentration of AIH, Al\(^0\), and \(\beta\)-HIO\(_3\) are statistically the same in all samples with an ER = 1.1. Figure 7b shows increases in flame speed as water to Al ratio increases are not caused by differences in concentration but instead assumed to be a result of differences in density of the final material.

Examination of Figures 2 and 6 and 7 does not lead to a conclusive relationship between flame speed and AIH concentration. Figure 8 shows the measured flame speed as a function of ER, oxygen balance, and concentrations of AIH, Al\(^0\), and iodic acids. There are three clear trends shown in Figure 8a and b:

- AIH concentration significantly decreases at an ER of 0.9 compared to an ER of 1.0 (Figure 8a).
- There is a linear relation between OB and flame speed (Figure 8b).
- \(\beta\)-HIO\(_3\) concentration increases at an ER of 0.9 and 0.8 (Figure 8c).

Figure 8a shows flame speed, oxygen balance, and AIH concentration as a function of ER (between an ER of 0.8 and 1.5). The oxygen concentrations of AIH, Al\(^0\), and iodic acid are all accounted for when calculating OB, and in general, there is a parabolic relationship between OB and flame speed.\(^{18}\) Figure 8b shows an almost linear relation between OB and flame speed (\(R^2 = 0.92\)) for a range of ER. Figure 8c shows flame speed, OB, AIH, HIO\(_3\), and H\(_2\)O\(_3\) concentration as a function of ER between an ER of 0.8 and 1.1. Figures 8a and 8c show that the concentration of AIH is less at an ER of 0.8 and 0.9 when compared to concentrations of AIH at an ER of 1.0, 1.1, and 1.2. The HIO\(_3\) and H\(_2\)O\(_3\) concentration increases rapidly (Figure 8c) at an ER of 0.8 and 0.9 compared to ER of 1.0, 1.1, and 1.2. The ER range in Figure 8c is reduced because of the amorphous structure beginning at an ER of 1.5 (see Figure 2). The composition of the amorphous structure cannot be determined; thus, accurate fuel to oxygen ratios (OB) cannot be calculated, and OB for an ER of 1.5 is an estimate.

The linear relation between OB and flame speed (Figure 8b) is unexpected because there is normally a parabolic trend between OB and reactivity with the greatest reactivity seen with a slightly fuel rich mixture. With the assumption that the greatest reactivity will be seen where OB is slightly fuel rich (ER = 1.0), it is unexpected to see increased reactivity at an ER of 0.8 and 0.9 compared to ER of 1.0. The increase in flame speed corresponds with decreased AIH concentrations (below ER = 1.0) and decreased \(\text{Al}_2\text{O}_3\) concentrations (Figure 8). Figure 8 shows \(\text{Al}_2\text{O}_3\) concentration in the final AIH mixtures determined by the distance between dashed line and solid black line. The concentration of \(\text{Al}_2\text{O}_3\) is greater at an ER of 1.0 compared to an ER of 0.9 and can account for the increase in flame speed at ER = 0.9. Smith et al.\(^{19}\) (see Figure 3 from ref 19) show that all the initial \(\text{Al}_2\text{O}_3\) reacts with the acidic solution but only a portion forms AIH. The \(\text{Al}_2\text{O}_3\), that forms as a byproduct of AIH formation may not be a uniform layer and may be less of a diffusion barrier than the original \(\text{Al}_2\text{O}_3\) layer. In this way, \(\text{Al}_2\text{O}_3\), that forms as a byproduct of AIH formation will act mainly as a heat sink and not a diffusion barrier. Another factor that influences the difference in flame speed between an ER of 0.9 and 1.0 is the amount of Al\(^0\). Al\(^0\) is a fuel for AIH reactions, and reducing the amount of Al\(^0\) will reduce the amount of total energy generation. Concentrations of iodic acids, \(\beta\)-HIO\(_3\) at an ER of 0.8 and both \(\beta\)-HIO\(_3\) and H\(_2\)O\(_3\) at an ER of 0.9, are highest when flame speeds are highest. All of these aspects, OB, concentration of AIH, \(\text{Al}_2\text{O}_3\), Al\(^0\), and iodic acids, need to be considered when examining concentration effects on flame speed. Because there is no direct relationship between flame speed and concentration of AIH or \(\text{Al}_2\text{O}_3\), we propose that, in general, reactivity is directly related to relative concentration of AIH and \(\text{Al}_2\text{O}_3\) shown in Table 3 as AIH to \(\text{Al}_2\text{O}_3\) ratio. Table 3 shows that, in general, higher AIH/\(\text{Al}_2\text{O}_3\) ratios have faster flame speeds when OB is considered. In Table 3, there is a linear relation between AIH to \(\text{Al}_2\text{O}_3\) ratio and flame speed between an ER of 1.1 and 0.9. At an ER of 1.2, AIH to \(\text{Al}_2\text{O}_3\) ratio increases but flame speed significantly decreases; however, OB also decreases significantly. The decrease in flame speed between an ER of 1.1 and 1.2 that does not follow the AIH to \(\text{Al}_2\text{O}_3\) ratios relation to flame speed can be explained by the significant decrease in OB. At an ER of 0.8, flame speeds continue to increase, but AIH to \(\text{Al}_2\text{O}_3\) ratio decreases and OB increases. We propose that the increase in flame speed between an ER of 0.9 and 0.8 is a result of increased concentrations of iodic acids, specifically, \(\beta\)-HIO\(_3\). The reason why \(\beta\)-HIO\(_3\) increases flame speed is unknown and requires further study.

It is interesting to note that \(\beta\)-HIO\(_3\) is stable in AIH mixtures. Smith et al. show that \(\beta\)-HIO\(_3\) is metastable when aged for a period of 8 days after being ground for powder XRD measurements. The AIH samples shown here were aged after being ground for a period of months, and \(\beta\)-HIO\(_3\) did not convert into \(\alpha\)-HIO\(_3\).
AIH increases reactivity in Al energetic materials by replacing the Al₂O₃ passivation layer that naturally forms on Al particles with AIH. The Al₂O₃ acts as a heat sink and oxygen diffusion barrier, and replacement of the Al₂O₃ passivation layer with AIH significantly reduces the diffusion barrier and facilitates Al oxidation. The Al−AIH single-crystalline structure without the amorphous Al₂O₃ layer was carefully assessed and examined under TEM. The images revealed distinct single crystalline lattice fringes throughout the entire particle from the Al core to the outer AIH shell with perfect conformity. Also, FFT plots confirm the crystallinity, and the SAD pattern confirms that distinct diffraction spots have lattice spacing consistent with those of a bulk Al crystal. The reaction to form Al₂O₃ from AIH is extremely overoxidized (i.e., 12.5 mol of extra oxygen for every mole of AIH), and replacement of the Al₂O₃ passivation

Figure 8. (a) Flame speeds (●), OB (−), and AIH concentration (△) as a function of ER. (b) Flame speed as a function of OB. Dashed line is a linear fit with R² value of 0.92. (c) Zoom-in of Figure 8a between ER of 0.8 and 1.1 with HIO₃ (+) and HI₃O₈ (□).
layer with AIH increases the available oxygen and reduces the distance between unreacted Al in the core and oxidizer. The combined effects of reducing the diffusion barrier and reduced distance between fuel and oxidizer result in flame speeds as high as 3200 m/s in Al–AIH mixtures.

Flame speed is affected by the concentrations of AIH, Al\(^{0}\), Al\(_2\)O\(_3\), and iodic acids of Al–AIH mixtures. In general, higher ratios of AIH to Al\(_2\)O\(_3\) increase flame speeds. Since oxygen is supplied by iodic acids in AIH mixtures, the effects of iodic acids on flame speed can be summarized by oxygen balance. Decreases in flame speed are seen when the AIH to Al\(_2\)O\(_3\) ratio is relatively high and oxygen balance is significantly away from stoichiometric. An increase in reactivity is seen when oxygen balance is 2.6% and AIH to Al\(_2\)O\(_3\) ratio is less than 2.0 at an ER of 0.8. At an ER of 0.8, \(\beta\)-HIO\(_3\) concentration is the highest reported, and the increase in reactivity at ER 0.8 could be a result higher concentrations of \(\beta\)-HIO\(_3\).

### AUTHORS INFORMATION

**Corresponding Author**
*Phone: 806-834-3733. E-mail: michelle.pantoya@ttu.edu.*

**ORCID**
Michelle L. Pantoya: 0000-0003-0299-1832

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**
The authors are grateful for support from the Army Research Office under award W911NF-14-0250 and encouragement from our program manager, Dr. Ralph Anthenien. We are also grateful to Dr. Jennifer Gottfried from ARL for constructive feedback on this work.

### REFERENCES


