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

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ABSTRACT: The main reaction mechanism that replaces the Al$_2$O$_3$ passivation layer on Al nanoparticles with an energetic AIH salt is demonstrated. The reaction mechanism is pH dependent and utilizes electrostatic forces that occur between the Al$_2$O$_3$ passivation layer and free hydrogen atoms (H$^+$) in solution. When Al particles are added to highly acidic solutions, free H$^+$ polarize the Al–O bonds in Al$_2$O$_3$, resulting in the formation of H$_2$O and free Al$^{3+}$ cations that are complexed by water molecules and exist as [Al(H$_2$O)$_6$]$^{3+}$ in aqueous solutions. The concentration of AIH is limited by the amount of [Al(H$_2$O)$_6$]$^{3+}$ that forms from the polarization reaction between free H$^+$ and the initial Al$_2$O$_3$ concentration. The proposed mechanism describes a stoichiometric reaction, but deviations from the stoichiometric reaction are expected with varying equivalence ratios (ER). The polarization mechanism is confirmed by measuring deviations in concentration of final AIH mixtures as a function of ER. A salt formation theory dependent on pH and pK$_a$ is used to demonstrate how the final AIH concentrations can be estimated at ER values that are not stoichiometric.

INTRODUCTION

Aluminum nanoparticles inherently include a 3–5 nm thick aluminum oxide (Al$_2$O$_3$) passivation shell. The Al$_2$O$_3$ shell acts as a barrier for oxygen diffusion reactions with the Al$^0$ core and also as a heat sink during combustion. Multiple studies have explored various passivation materials including fluoropolymers to reduce the effect of the Al$_2$O$_3$ diffusion barrier. Jouet et al. replaced the Al$_2$O$_3$ shell with perfluorotraffledacanoic (PFTD) acid, and Kim et al. extended this work to micron-scale Al particles using poly(tetrafluoroethylene) (PTFE). These polymers offer the potential of a highly reactive oxidizer, fluorine, in close proximity to the core enabling increased energy liberation upon Al reaction. Instead of a polymer, this study replaces the Al$_2$O$_3$ shell with an energetic salt: aluminum iodate hexahydrate (AIH). Aluminum iodate hexahydrate (AIH) is a reactive salt, and however, the mechanism of formation of Al$^{3+}$ during the AIH synthesis process is not well understood but of importance for the design of Al-based energetic materials with heightened reactivity.

There are two primary mechanisms for the formation of Al$^{3+}$ in acidic solutions. The first mechanism is field-assisted dissolution where the electromagnetic forces from applied voltages and ions in solution oxidize Al$^0$ to Al$^{3+}$ and pull Al$^{3+}$ across the Al$_2$O$_3$ passivation layer. This process is described by the following chemical reaction.

$$\text{Al(s)} \rightarrow \text{Al}^{3+}(\text{aq}) + 3\text{e}^- \quad (1)$$

The mechanism is demonstrated in Wu et al. The second mechanism for the formation of Al$^{3+}$ in acidic solutions is shown in reaction 2.

$$\text{Al}_2\text{O}_3(\text{s}) + 6\text{H}^+(\text{aq}) \rightarrow 2\text{Al}^{3+}(\text{aq}) + 3\text{H}_2\text{O} \quad (2)$$

Reaction 2 has been reported to have a minor role in the anodization process where an applied voltage is used to induce pore formation; however, reaction 2 may have a greater effect in situations where there is no applied potential across the Al and solution. The resulting formation of [Al(H$_2$O)$_6$]$^{3+}$ is also a key component in the formation of AIH and is discussed below. Aluminum iodate hexahydrate (AIH) is a reactive salt, and the formation of AIH can be explained using mathematical
descriptions of salt formation. Salt formation is a common and effective method for increasing solubility and dissolution rates of acidic and basic drugs.\textsuperscript{13} The mathematical descriptions of salt formation from drug delivery research can be applied to describe the formation of AIH. Serajuddin et al.\textsuperscript{14} showed that the formation of salts are related to the concentration, pH, and \( pK_a \) of the salt and acid (or base). The equations used to calculate solubility are shown in eqs 3a and 3b, where \( S \) is solubility of the acid or salt, \([A^-]\) is concentration of acid, \([AH]\) is concentration of acid or salt, and \( pK_a \) and pH are the pH of solution and \( pK_a \) of either the salt or acid (subscript \( s \) means saturated solution).

\[
S_{\text{salt}} = [AH]_s(1 + 10^{pK_a - \text{pH}}) \tag{3a}
\]

**Figure 1.** Graphics representing conditions obtained from reaction 3 (normalized to AIH concentration). (a) Iodine loss (•) and AIH concentration (Δ) in final AIH mixtures representing condition 1. (b) Solid line is AIH concentration divided by initial \( Al_2O_3 \) (▲), and the dashed line is the maximum AIH concentration (condition 2). (c) Oxygen loss (□), AIH (Δ), and \( Al_2O_3 \) (○ shaded) representing conditions 3 and 4.
\[
S_{\text{acid}} = [A^-]_0 (1 + 10^{pH-pK_a})
\]  
(3b)

Derivations of eqs 3a and 3b are shown in Serajuddin et al.,14 along with detailed information on this mathematical formulation. In short, the formations of salts are determined by the max pH where the solubility of the salt and acid are equal. At pH max, both free acid and salt coexist as solids. If the pH of a saturated solution is lowered below pH max, salt will form. The solubility as a function of pH plots from Serajuddin et al.13,14 are used to mathematically describe the formation of AIH.

It is important to note that Smith et al. (Part I)7 focused on the reactivity of AIH mixtures and showed how the concentration of AIH, iodic acid, and material density affected the reactivity as measured by flame speed. Part II will focus on the synthesis conditions that affect the concentrations of AIH, Al²⁺, and iodic acids in AIH final mixtures. This will be accomplished by using concentration data from X-ray diffraction (XRD) analysis to predict species evolution that corresponds or deviates from established AIH reaction mechanisms and salt formation theory. The goal is to understand the synthesis method of AIH particles and determine the mechanism for how AIH increases reactivity in Al-based energetic materials. A better understanding of AIH could lead to enhanced reaction rates for Al-based energetic materials, possibly approaching that of molecular explosives.

■ EXPERIMENTAL AND THEORETICAL DEVELOPMENT

The samples discussed in this article are the same samples used in Smith et al.,7 and all details regarding mixing and testing are identical. For brevity, the reader is referred to Smith et al. for an in-depth explanation of the mixing and testing procedures.

In Smith et al.,7 a brief description on the formation of AIH was presented starting with the formation of Al³⁺ by electrostatic forces followed by hydrolysis of Al³⁺ to form aluminum hexahydrate [Al(H₂O)₆]³⁺. Smith et al.7 suggests that AIH replaces the Al₂O₃ passivation layer, and thus, a new mechanism for the formation of AIH from Al₂O₃ is proposed, following a similar mechanism presented by O’Sullivan.12 When Al₂O₃ comes into contact with highly acidic solutions, polarization of Al₂O₃ molecules results in the formation of Al³⁺ and water following reaction 4.12 Also, reaction 4 shows the polarization mechanism in reaction 2, with H₂O⁺ instead of H⁺, to form AIH.

\[
\begin{align*}
2\text{Al}_2\text{O}_3 + 12\text{H}_2\text{O}^+ + 12\text{I}_2\text{O}^- + 6\text{HIO}_3 \rightarrow & \quad (4a) \\
4\text{Al}^{3+} + 18\text{H}_2\text{O} + 12\text{I}_2\text{O}^- + 6\text{HIO}_3 \rightarrow & \quad (4b) \\
3[\text{Al}(\text{H}_2\text{O})_6]^{3+} + \text{Al}^{3+} + 12\text{I}_2\text{O}^- + 6\text{HIO}_3 \rightarrow & \quad (4c) \\
3([\text{Al}(\text{H}_2\text{O})_6]^{3+}(3\text{I}_2\text{O}^-)) + \text{Al}^{3+} + 3\text{I}_2\text{O}_5^- + 6\text{HIO}_3 \rightarrow & \quad (4d) \\
3([\text{Al}(\text{H}_2\text{O})_6]^{3+}(3\text{I}_2\text{O}^-)(2\text{HIO}_3)) + \left(\frac{1}{2}\text{Al}_2\text{O}_3\right)_{\text{s}} + \left(\frac{3}{2}\text{I}_2\text{O}_5\right)_{\text{s}} & \quad (4e) \\
+ \left(\frac{3}{4}\text{O}_2\right)_{\text{v}}
\end{align*}
\]

Reaction 4a (initial reactants) and 4e (final products) represent the general global reaction for the formation of AIH from Al₂O₃ and reactions 4b, 4c, and 4d are the major intermediate steps needed to show the formation process of AIH from Al₂O₃. Each step in reaction 4 is shown as a forward reaction; however, it is suspected that many of the steps in reaction 4 are reversible and will reach an equilibrium state. The variables related to equilibrium conditions for reaction 4 are unknown; however, reaction 4 enables a comparison to measured concentration data (from XRD analysis) using specific details (conditions) that can be quantified as a function of equivalence ratio (ER) to validate reaction 4. Specifically, there are four conditions from reaction 4 as follows:

1. There is a 1:1 ratio of AIH concentration and iodine loss as shown in reaction 4e.
2. There is a maximum of 75% AIH concentration produced from initial Al₂O₃ shown by comparing initial concentration of Al₂O₃ (4a) and final concentration of Al₂O₃ (4c).
3. There is a 2:1 ratio of AIH concentration and oxygen loss as shown in reaction 4e.
4. There is a 6:1 ratio of AIH concentration to Al₂O₃ as shown in reaction 4e.

■ RESULTS AND DISCUSSION

The conditions from reaction 4 can be compared to concentrations of AIH mixtures as a function of equivalence ratio (ER) presented in Smith et al.,7 and the maximum calculated uncertainty for the XRD measurements is 7.5%. Therefore, the error bars in the following results (i.e., Figures 1–6) are not included but are noted to all have a maximum uncertainty of 7.5%. The graphs representing variations in AIH and Al₂O₃ concentration and iodine and oxygen loss are shown in Figure 1a–c as a function of ER. All graphs in Figure 1 are normalized to AIH concentrations to represent conditions 1–4. Because all graphs in Figure 1 are normalized to AIH concentration, the lines representing iodine loss (Figure 1a), oxygen loss (Figure 1c), and Al₂O₃ concentration (Figure 1c) will be the same as AIH concentration in an ideal situation.

Reaction 4 assumes a stoichiometric concentration of IO₃⁻ and Al₂O₃ to form from AIH, and deviations are expected when the ER varies from stoichiometric as shown in Table 1.

Table 1. Deviations between XRD Measurements Shown in Figure 1 and Expected Values from Reaction 3 Normalized to AIH Concentration

<table>
<thead>
<tr>
<th>condition</th>
<th>min</th>
<th>max</th>
<th>ave</th>
</tr>
</thead>
<tbody>
<tr>
<td>iodine loss</td>
<td>6%</td>
<td>16%</td>
<td>10%</td>
</tr>
<tr>
<td>AIH concentration</td>
<td>3%</td>
<td>12%</td>
<td>9%</td>
</tr>
<tr>
<td>oxygen loss</td>
<td>17%</td>
<td>78%</td>
<td>41%</td>
</tr>
<tr>
<td>Al₂O₃ concentration</td>
<td>2%</td>
<td>42%</td>
<td>15%</td>
</tr>
</tbody>
</table>

“Numbers in parentheses denote four conditions highlighted above.

In Table 1, the concentration of AIH has the smallest average deviation (9%), supporting the mechanism for formation of AIH shown in reaction 4. Three of the four average deviations in Table 1 are within 15% of the expected value from reaction 4 showing that, in general, the synthesis method that creates AIH follows the mechanism in reaction 4. The deviations from reaction 4 are caused by ancillary reactions that are occurring in solution as a result of difference in stoichiometry. Oxygen loss has the highest deviation because oxygen is in every molecule in solution, and most of the possible ancillary reactions will involve a transfer of oxygen. Iodine loss has the smallest deviation because it is involved in the least possible reactions.
One example of an ancillary reaction is seen in Al\(^0\) (Al\(_{\text{core}}\)) loss. The difference between Al\(^0\)\(_{\text{initial}}\) and Al\(^0\)\(_{\text{final}}\) is shown in Figure 2. Above an ER of 0.9, a significant portion of Al\(^0\) from the core is being oxidized (e.g., seen in Figure 2 as the difference between the two data points at ER 1.0). The most probable source of oxygen for the oxidation of Al\(^0\) is from iodic acid or water shown in reactions 5a and 5b.

\[
2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2 \quad (5a)
\]

\[
2\text{Al} + \text{HIO}_3 \rightarrow \text{Al}_2\text{O}_3 + \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{I}_2 \quad (5b)
\]

Figure 2 shows that iodine loss is less than expected from reaction 4 above an ER of 0.9. Since iodine loss is less than expected and Al\(_{\text{core}}\) oxidation is greatest at ER = 0.9, Al\(_{\text{core}}\) oxidation is likely from iodic acid or water. The difference between Al\(^0\)\(_{\text{initial}}\) and Al\(^0\)\(_{\text{final}}\) is shown in Figure 2. Above an ER of 0.9, a significant portion of Al\(^0\) from the core is being oxidized (e.g., seen in Figure 2 as the difference between the two data points at ER 1.0). The most probable source of oxygen for the oxidation of Al\(^0\) is from iodic acid or water shown in reactions 5a and 5b.
oxidation is most likely from water and follows reaction 5a. The ancillary reactions that have an effect on the deviations shown in Table 1 are complicated by pH of the solution.

In every graph in Figure 1, a significant change in the trends can be seen between ER of 0.9 and 1.0 that is a result of pH. Figure 3 shows the relation between iodine needed to form AIH and Al from Al2O3 in initial mixtures. Since the iodine in AIH solutions comes from iodide acid, Figure 3 indirectly shows a relation to pH. Figure 3 shows the relation between Al in Al2O3 and iodine needed to form AIH in initial mixtures (top) and concentration data for β-HIO3, HI3O8, and amorphous structure in final AIH mixtures (bottom). The solid black line in Figure 3 (top) is the total Al in initial mixtures including Al from Al2O3, and the gray line is 3/4 of Al in Al2O3 from initial mixtures. Both of these lines provide a reference for the Al that can be consumed from the Al2O3 shell according to reaction 3. In Figure 3, the double solid lines (solid □ markers) indicate the moles of iodine needed to form AIH from total iodine in initial mixing. The chemical formula for AIH is [Al(H2O)6]3+, (IO3)3−(HIO3)2 such that there are five iodine molecules for every Al molecule. The double solid line in Figure 3 is the total moles of iodine in 100 g of initial mixtures calculated from initial mixing concentrations divided by S (i.e., to normalize the concentration data to fit the Al lines and represents the amount of iodine needed to form AIH from the available Al in Al2O3 in the initial mixtures). The bottom section of Figure 3 shows the concentrations of β-HIO3, HI3O8, and amorphous material taken directly from the PXRD data in Smith et al.7

In Figure 3, we see that the line representing the amount of iodine needed to form AIH crosses (goes above) the full Al2O3 line (solid black line) between an ER of 0.9 and 1.0. When the iodine line crosses the full Al2O3 line, there is more iodine than is stoichiometrically needed to create AIH from the available Al in Al2O3. When compared to the concentration data for β-HIO3 and HI3O8, the iodine line crosses the full Al2O3 line at the same ER where concentrations of β-HIO3 and HI3O8 start increasing rapidly. The increase in β-HIO3 and HI3O8 is expected when the iodine line crosses the full Al2O3 line because at this point, there is more IO3− in solution than needed to form AIH. Conversely, when the iodine line crosses (goes below) the 3/4 Al2O3 line between an ER of 1.2 and 1.5, the concentration of amorphous materials starts to increase (◊ line in Figure 3 bottom). If we assume only 3/4 of Al from Al2O3 forms AIH (from reaction 4), the iodine crossing the 3/4 Al2O3 line at the same point the amorphous structure begins shows that when there is not enough iodine to form AIH, an amorphous structure forms. Since the formation of β-HIO3 and HI3O8 increases rapidly only after there is enough iodine to form AIH from all of the aluminum in the Al2O3 shell, all of the Al2O3 shell is reacting in the presence of the IO3− solution; however, amorphous formation starting after there is no longer enough iodine to form AIH from 3/4 Al in Al2O3 shows that only a portion (3/4) of the original Al2O3 forms AIH. All of the Al2O3 is initially reacting with IO3− in solution, but only 3/4 forming AIH further supports the mechanism for the formation of AIH shown in reaction 4. Since the significant difference in trends in Figure 1 occurs at the same ER where there is more iodine needed to form AIH, Figure 3 also shows that the change in trends at an ER of 0.9 are a result of pH.

Reaction 4 assumes a stoichiometric mixture of Al2O3 and IO3−, and Figure 3 shows that the stoichiometric mixture for the formation of AIH occurs between an ER of 0.9 and 1.0. At an ER of 0.9, the Al2O3 and iodine loss have small deviations (Figure 1a and 1c) from the predicted mechanism. Figure 3 shows that when the ER is less than 0.9, there is more IO3− and H+ in solution than needed for reaction 4. Specifically, for a stoichiometric mixture, there are five HIO3 for every Al atom in Al2O3 and the 3H+ from the HIO3 go toward the formation of water from oxygen in Al2O3. In acidic solutions, pH is defined as the negative log of the hydronium ion concentration, and pKr is the pH where half of the H+ are dissociated from its conjugate base. In reaction 4, the formation of water from oxygen in Al2O3 takes the free hydrogen (Brønsted acid) to form water and leaves a Lewis acid (Al3+). The Al3+ cation is then coordinated by six water molecules under aqueous conditions, resulting in electron density being shifted from Al3+ to the oxygen in H2O. This electron distribution lowers the energy needed to dissociate O−H bonds in [Al(H2O)6]3+ by the amount of energy needed to dissociate 3H+ from 3HIO3.15,16 The energy density (energy required per dissociation of each free hydrogen per mole of water) in this reaction changes because there is no difference in total energy, but the energy is spread out over six water molecules in [Al(H2O)6]3+ instead of the three waters in the reaction between 3HIO3 and 3H2O. Because of the difference in energy density in the reaction described above, an apparent shift in pH and pKr is expected.17 Therefore, a mathematical model to describe the formation of AIH must be dependent on concentration, pH, and pKr. Additionally, deviations from the mechanism shown in reaction 4 can be explained by salt formation theory.

Salt Formation. Serajuddin et al. present a mathematical description of salt formation based on solubility and a maximum pH where salts can form. The solubility of a salt is calculated by using concentration, pKr, and pH as described previously in eqs 3a and 3b and can also be used to explain deviations from predicted concentrations as a function of the equivalence ratio (Table 1). Concentration and pH can be calculated from initial mixing parameters, and the pKr of HIO3 is 0.75; however, the pKr of HI3O8 cannot be measured because HI3O8 and HIO3 both dissolve into H3O+ and IO3− when in solution. Solubilities for both HIO3 and HI3O8 using eqs 3a and 3b are shown in Figure 4, and pKr for HI3O8 is estimated using the common ion effect based on an apparent pKr shift.

Figure 4. Solubility as a function of pH for HIO3 and HI3O8 calculated from eq 2a. Solid black line indicates solubility of HIO3 without pKr shift, and the long-dashed line indicates solubility of HIO3 with the pKr shift. Double black line indicates solubility of HI3O8 without pKr shift, and the short-dashed line indicates solubility of HI3O8 with the pKr shift.
discussed in Serajuddin et al.14 By definition, the common ion effect is responsible for a change in solubility of an ionic precipitate when a soluble compound containing one of the ions in the precipitate is added to the solution in equilibrium with the precipitate.14 This common ion effect is demonstrated in Table 2 when different “qualities” of water were mixed with I₂O₅ and then precipitated. Ion chromatography (IC) analysis was performed on the water samples, and PXRD quantitative analysis was performed on the precipitates. Table 2 supports the hypothesis that when Cl⁻ and SO₄²⁻ ions are present in high concentrations, the IO₃⁻ solution precipitates out as HI₃O₈ instead of HIO₃. The relative humidity during precipitation was not measured; however, all samples were mixed within 10 min of each other and dried within a 10 cm radius of each other. Therefore, effect of relative humidity should be negligible between samples.

Table 2. Low-Level IC Anion Analysis (ppm)

<table>
<thead>
<tr>
<th>name</th>
<th>Fl</th>
<th>Cl</th>
<th>NO₂⁻</th>
<th>Br</th>
<th>NO₃⁻</th>
<th>PO₄</th>
<th>SO₄</th>
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</tr>
<tr>
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<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>76.3</td>
<td>HI₂O₅</td>
</tr>
</tbody>
</table>

Figure 5. (Top) Solubility as a function of pH for HIO₃ and HI₃O₈ calculated from eq 2a with an apparent pKₛ shift so HI₃O₈ solubility crosses HIO₃ solubility at an ER of 1.0. AIH solubility is estimated by fitting the AIH solubility line at pH max (AIH solubility and HIO₃ solubility are equal) to the point where an amorphous structure begins (ER 1.2 bottom). Shaded area labeled AIH formation represents the pH range where AIH will form. (Bottom) Concentration of β-HIO₃ (+), HI₃O₈ (×), and amorphous (◊) structure from XRD measurements.
probability of formation for each of the species (i.e., HIO₃ or H₃IO₈), and the greater the distance between the solubility line and 0, the greater the probability that HIO₃ or H₃IO₈ will form. By comparing the solubility lines with and without an apparent pKₐ shift, Figure 4 shows that formation of H₃IO₈ is never favored over HIO₃ in low ion solutions, but when the ion effect is taken into account, H₃IO₈ becomes favored when the pH is above ~0.95.

The mathematical model shown in Figure 4 provides an excellent way to quantify the common ion effect and explain what is occurring in Table 2. This method for estimating the pKₐ of H₃IO₈ can be extended to AIH mixtures as a function of ER study by examining concentration as a function of solubility (Figures 5 and 6) and can help explain the deviations from the final AIH concentrations (Table 1) as predicted by reaction 4.

Figure 5 shows solubility as a function of pH for HIO₃ and H₃IO₈ in the calculated pH range for the ER study in the top plot and concentrations of β-HIO₃, H₂IO₇°, and amorphous material as a function of ER (bottom plot). In Figure 5, the apparent pKₐ shift is fixed so the HIO₃ solubility line crosses the H₃IO₈ solubility line at an ER of 1.0, the point where HIO₃ concentration increases and H₃IO₈ concentration starts to decrease. The maximum pH corresponding to AIH formation is labeled as max pH in Figure 5 and is where the solubility lines for AIH and HIO₃ intersect. Below the max pH, AIH will precipitate from solution. Because AIH will only form below the max pH, the AIH solubility line in Figure 5 is fit so pH max is below the pH (and equivalent ER) where an amorphous structure begins to form (ER of 1.1). When the apparent pKₐ shift is fit to an ER of 1.0, and the solubility of AIH is fit to an ER of 1.2, Figure 5 can explain all of the iodic acid concentrations that were measured. Between an ER of 1.0 and 1.2, HIO₃ and H₃IO₈ concentrations are similar to the distance between the respective solubility lines and the solubility line of AIH. When the HIO₃ and H₃IO₈ solubility lines cross, the distance between the solubility lines and AIH line follows a similar trend as HIO₃ and H₃IO₈ concentrations (Figure 5 bottom, ER of 0.9 and 0.8).

Figure 5 shows how the solubility as a function of pH accounts for the iodic acid concentrations seen in the AIH mixtures but cannot solely account for AIH concentrations seen in AIH mixtures. Figure 6 (bottom) shows that AIH concentration decreases with ER from stoichiometric conditions and the difference between the HIO₃ line and AIH solubility line is greater than the concentrations seen in AIH mixtures. The discrepancies in AIH concentrations in Figure 6 are a result of using measured data to fit the apparent pKₐ shift and AIH solubility. The pKₐ for H₃IO₈ is estimated from a critical point where HIO₃ concentration increases and H₃IO₈ decreases (ER 0.9) and the solubility of AIH can be estimated because pH max was fit to the point where amorphous structure formation begins. Using this method to fit the apparent pKₐ shift and AIH solubility gives average solubility between the two fitting points and not the solubility for each individual ER. The solubility calculations in Figure 6 are only estimates used to show how salt formation theory can be used to explain deviations from eq 3.

In Figure 3, we showed that at an ER of 0.9, there was more IO₃⁻ than needed to form AIH from Al₂O₃, the result is more H⁺ in solution, thereby reducing the common ion effect. This reduction in the common ion effect and its relation to AIH concentration are shown in Figure 6.

Figure 6 shows that the concentration of AIH is reduced when the solubility of HIO₃ is reduced. When there are more IO₃⁻ than the stoichiometric mixture in reaction 4, IO₃⁻ becomes less soluble. When IO₃⁻ is less soluble, pH max (intersection of AIH solubility and IO₃⁻ solubility) shifts, and the distance between the AIH solubility line and 0 is reduced. It is important to note that the solubility plots shown are estimates based on two fitting points at different ERs. For solubility plots based on measurements, the solubility lines will shift at every ER. In Figure 4, the HIO₃ and H₂IO₇° solubility lines without the pKₐ shift represent an ER of 0, and the HIO₃ and H₂IO₇° solubility lines with a pKₐ shift represent an average solubility between an ER of 1.0 and 1.2 (fitting points). Figure 4 shows the general trend that is expected of HIO₃ solubility resulting from the common ion effect in AIH synthesis using this mixing procedure. As ER and pH increase, HIO₃ solubility increases up to the stoichiometric mixture in reaction 3. The relation between HIO₃ solubility and ER is used in Figure 6 to estimate AIH concentrations. Using the trend in HIO₃ solubility from Figure 4 and adjusting the pH max in Figure 6 based on HIO₃ solubility only works if the solubility of AIH is directly related to that of HIO₃. Figure 2 in Li et al. shows the assumption that pH max of salt with a conjugate free base (IO₃⁻) is directly dependent on the solubility of the free base. The solubility trend in Figure 2 of Li et al. closely follows the trend expected in AIH mixture using Figure 4 to estimate the common ion effect and Figure 6 to calculate concentration of AIH. Using the methods described in Figures 4–6, final

![Figure 6](image URL)
concentrations of AIH mixtures can be estimated and used to optimize AIH mixtures for maximum reactivity.

CONCLUSIONS

The basic reaction mechanism that replaces the Al₂O₃ passivation layer with AIH reactive salt is presented in reaction 3. The reaction mechanism is pH dependent and utilizes electrostatic forces that occur between the Al₂O₃ passivation layer and H⁺ in solution. When Al particles are added to highly acidic solutions, H⁺ polarize the Al–O bonds in Al₂O₃. When the Al–O bonds are polarized, H₂O is formed from H⁺ and oxygen in Al₂O₃ resulting in the formation of [Al(H₂O)₆]³⁺. Concentration of AIH is limited by the amount of [Al–(H₂O)₆]³⁺ that forms from the polarization reaction between free hydrogens and initial Al₂O₃. The reaction mechanism describing the formation of AIH results in conditions that are used to support the validity of this mechanism. Iodine loss is expected to be the most accurate condition from the reaction mechanism, and the average deviation seen from PXRD measurements is 10%, supporting the polarization mechanism for the formation of AIH.

The polarization mechanism shown in reaction 4 assumes a stoichiometric mixture, and deviations from this mechanism are a result of varying ER. The final concentrations of AIH mixtures can also be estimated from salt formation theory by calculating the solubility as a function of pH and pKMₐ. The reaction mechanism includes a step that forms a Lewis acid from a Brønsted acid that will appear as a shift in pKMₐ. The shift in pKMₐ is used to demonstrate how salt formation theory can estimate final AIH concentrations. The basic reaction mechanism and salt formation theory can be used to tailor AIH concentrations to independently study the effects of AIH concentrations on reactivity. Independently studying the effects of concentration on AIH mixtures could result in increasing the reactive power with flame speeds higher than the 3200 m/s already measured.

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Notes
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REFERENCES