



Brief Communications

Synthesis and reactive characterization of aluminum iodate hexahydrate crystals $[\text{Al}(\text{H}_2\text{O})_6](\text{IO}_3)_3(\text{HIO}_3)_2$



Dylan K. Smith^a, Michael N. Bello^a, Daniel K. Unruh^b, Michelle L. Pantoya^{a,*}

^a Department of Mechanical Engineering, Texas Tech University, Lubbock, TX 79409, United States

^b Department of Chemistry, Texas Tech University, Lubbock, TX 79409, United States

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ABSTRACT

A crystalline aluminum iodate acid salt has been synthesized from aluminum particles dissolved in iodic acid solution. The precipitate from solution is aluminum iodate hexahydrate $[\text{Al}(\text{H}_2\text{O})_6](\text{IO}_3)_3(\text{HIO}_3)_2$, as confirmed by X-ray diffraction (XRD) analysis. The method of synthesis first dissolves iodine oxide in water, creating an IO_3^- solution with $\text{pH} < 0.2$. Aluminum nanoparticles are added to the IO_3^- solution and aluminum iodate hexahydrate (AIH) crystals precipitate. The bulk density of the crystalline AIH and Al composite is dependent on the initial water to aluminum concentration ratio during synthesis. Reactivity is characterized in terms of flame speed with measurements purposefully designed to capture less than 1% light emission, resulting in speeds as high as 3200 m/s for AIH+Al composite with a calculated density of 3.43 g/cc.

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1. Introduction

Reactions between aluminum (Al) and iodine oxides (i.e., I_2O_5) have potential for significant energy generation [1] and can also produce products with diverse optical, piezoelectric, electro-optical, non-linear optical properties [2,3]. When water is added to I_2O_5 , an IO_3^- solution forms with composition dependent on the concentration of IO_3^- ions in solution and includes dimers, trimers, tetramers, and higher orders of polymerization defined by $\text{IO}_3(\text{HIO}_3)_n^-$, where n is a measure of polymerization [4]. As concentration increases during evaporation of the IO_3^- solution, polymerization and crystallinity increases until a solid HIO_3 crystal structure forms.

The complex bonding mechanism that influences iodic acid polymerization and crystallization has been used to synthesize hydrated aluminum iodate compounds [2,3]. Aluminum iodate hexahydrate ($[\text{Al}(\text{IO}_3)_3(\text{HIO}_3)_2 \cdot 6\text{H}_2\text{O}]$) is referred to as AIH for simplicity. Kidyarov et al. [2] synthesized pure $[\text{Al}(\text{IO}_3)_3 \cdot 6\text{H}_2\text{O}]$ by dissolving aluminum hydroxide, $\text{Al}(\text{OH})_3$, in a solution of iodic acid. The $[\text{Al}(\text{IO}_3)_3 \cdot 6\text{H}_2\text{O}]$ was then used as a starting reagent to synthesize $[\text{Al}(\text{IO}_3)_3 \cdot 8\text{H}_2\text{O}]$. It was also noted that AIH could be used as a starting reagent because it dissolves in water to form $[\text{Al}(\text{IO}_3)_3 \cdot 8\text{H}_2\text{O}]$. However, there is no mention of how to obtain or synthesize AIH. In Cradwick et al. [3] AIH was synthesized by creating the anion

salt, $[\text{Al}(\text{IO}_3)_2(\text{NO}_3) \cdot 6\text{H}_2\text{O}]$, using an $\text{Al}:\text{IO}_3^-$ ratio greater than 1:3. The nitrate was then removed from solution, leaving AIH. We assume Kidyarov et al. [2] used a similar procedure to produce AIH, but it was not reported. Characterizations such as X-ray diffraction (XRD) and neutron diffraction have been used to determine the crystal structure and estimate AIH optical and electric properties [2,3]. To the authors' knowledge, the synthesis of AIH has not been reported by mixing powders of Al and I_2O_5 in the presence of water. Furthermore, the reactivity of AIH has not been reported. The objective of this study is to use an iodic acid solution as a means for synthesizing an aluminum – iodate crystal and characterize its reactivity with aluminum powder.

2. Experimental

2.1. Synthesis

The synthesis method dissolves commercially available I_2O_5 powder, supplied by Sigma Aldrich (St. Louis, MO), in distilled water prior to mixing with 80 nm average diameter Al powder supplied by Novacentrix (Austin, TX). The 80 nm Al has an Al_2O_3 passivation layer such that the powder is approximately 80% Al, 20% Al_2O_3 . The solution created by mixing I_2O_5 powder in water is highly acidic and proper precautions should be taken when handling this solution. The I_2O_5 powder is not pure but comprised of multiple forms of iodine (V) oxides, primarily iodic acids (i.e. HIO_3 and HI_3O_8) [1,5]. When dissolved in water, iodine (V) oxides form an IO_3^- solution, eliminating the need to purify the commercial

* Corresponding author.

E-mail addresses: mpantoya@gmail.com, michelle.pantoya@ttu.edu (M.L. Pantoya).

Table 1

Relative weight percent of crystalline components of synthesized materials as a function of water to aluminum concentration ratios with resulting *R*-values as well as flame speed measurements.

| Water: Aluminum | Al(IO ₃) ₃ (HIO ₃) ₂ (H ₂ O) ₆ (%) | Al (%) | <i>R</i> (%) | Flame speed (m/s) |
|-----------------|--|--------|--------------|-------------------|
| 6:1 | 79.0 | 19.3 | 16.9 | 3062 ± 314 |
| 5:1 | 79.8 | 20.2 | 15.6 | 2168 ± 160 |
| 4:1 | 80.6 | 19.4 | 19.8 | 1860 ± 275 |
| 2:1 | 76.2 | 22.0 | 19.9 | 1786 ± 62 |

powder. The iodine (V) oxides were mixed with distilled water in a beaker on a magnetic stir plate with a stirrer rotating at 300 rpm for 5 min prior to adding the Al powder. Aluminum powder was then added to the iodine oxide solution and mixing was facilitated by the magnetic stirrer until the aluminum was dispersed in solution (<60 s). The equivalence ratio (ER) for initial mixing of the powders was fixed at 1.1 with varying water to aluminum concentration ratios, determined by total weight of Al reagent, of 6:1, 5:1, 4:1 and 2:1 wt%.

Equivalence ratio, ER, was initially used to determine the amount of I₂O₅ and Al used for synthesis. For compounds with fuel and oxidizer in the same molecule, an oxygen balance (OB) must be used instead of ER. Detailed calculations of OB are presented in the supplementary information portion of this paper.

2.2. Material characterization

Powder XRD was performed on the synthesized materials to determine crystal structure and final composition. Details on these experiments are in the supplemental information section of this paper.

The solution pH was measured using a Horiba F-74 pH meter before and after Al was added. The pH of the IO₃⁻ solution is highly acidic (i.e., pH < 0.2 for all samples shown in Supplementary Table S1) and at the lower limit of the testing capabilities for most pH meters.

To assess the reactive nature of the AIH crystals combined with Al, a new experimental design was used to enable comparison of flame speeds between different samples. Details of this apparatus are provided in the supplementary information section of this paper.

3. Results

The XRD results for the different water to aluminum concentrations used during synthesis are shown in Supplemental Fig. S1 and summarized in Table 1. The crystalline products observed by XRD are AIH, Al, and a small amount (i.e., <2%) unidentified phase. Given the uncertainty of the quantitative analysis, as reflected in the residual *R*-value of the analysis, we assume that the concentrations of AIH, Al, and the unidentified phase for the different samples are within error of each other. The concentration of the unidentified phase in the samples was small (i.e., < 2 wt%) and was not used in the oxygen balance calculations. The crystal structure for AIH is shown in Fig. 1. The density of AIH calculated from lattice parameters is 3.609 g/cm³. Table 1 includes flame speed measurements for a fixed ER of 1.1.

4. Discussion

The formation of AIH from Al in an IO₃⁻ solution involves multiple steps that are dependent on pH and the interactions of Al ions in the IO₃⁻ solution. The pH effect on Al can be illustrated using Pourbaix diagrams (Fig. S2) [6]. When Al is added to the IO₃⁻ solution, a process similar to electrolysis occurs by the electrical charges in the solution that pull Al³⁺ into solution [7]. When aqueous Al³⁺ is in an acidic solution, hydrolysis occurs and forms aque-

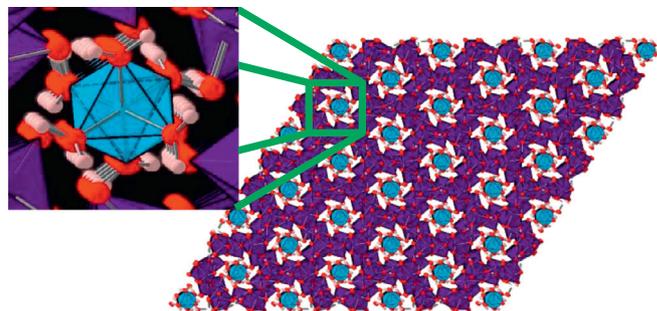


Fig. 1. Polyhedral view of the crystal structure of AIH. Iodine is purple, aluminum is blue, hydrogen is pink and oxygen is red. The box in the top left is a zoomed-in view of the pore space within the iodate framework that contains the Al(H₂O)₆³⁺ cation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

ous aluminum hexahydrate ([Al(H₂O)₆]³⁺) [8]; and, is shown in the inset of Fig. 1 with a net charge of 3⁺. As the solution reaches saturation, the IO₃⁻ in solution bonds with aluminum hexahydrate to balance the charge and form AIH precipitate. The product of synthesis using this method is a highly reactive mixture of AIH and Al.

Aluminum iodate hexahydrate may serve as an oxidizer for the Al powder, contributing to the high flame speeds (Table 1). The speed of sound has not been measured for the AIH compound; however, the velocities achieved in this study are well above generally accepted detonation velocities (>1000 m/s) [9].

Aluminum hexahydrate plays an important role in the reactivity of AIH-Al mixtures. When solutions that contain Al(H₂O)₆³⁺ and IO₃⁻ are placed on a heating pad at 110 °C, iodine vapor is released from the liquid solution. However, in samples without Al in the solution, iodine gas is not released when heated under the same conditions. The current hypothesis is that when the solution mixtures are not heated, IO₃⁻ hydrogen bonds to water molecules on the aluminum hexahydrate during evaporation of excess water molecules to form AIH crystals. Conversely, when the same solution mixtures are heated above the boiling point of water, the aluminum hexahydrate molecules are dehydrated and Al in solution reacts directly with iodine oxide to produce iodine gas.

Table 1 shows that reactivity increases as the initial water to aluminum ratio used during synthesis increases. The difference in reactivity between samples with different water to aluminum ratios is assumed to be a result of differences in concentration and density. The samples containing initial water to aluminum ratios of 6:1, 5:1, and 4:1 show final AIH and Al concentrations that are statistically similar (less than 1.6% difference). The resulting OB for these samples is -3.05%, indicating a fuel rich mixture. The 2:1 sample had a slightly lower concentration of AIH (76%) and higher concentration of Al (22%), which gives an OB of -7.8%, indicating an even more fuel rich mixture. While the water to aluminum ratio used during synthesis may slightly affect the concentration of AIH, proportionally affecting the OB, the differences in OB alone may not account for the large differences observed in flames speeds between the 2:1 (1786 ± 62 m/s) and 6:1 (3062 ± 314 m/s) samples.

The density of the AlH+Al composite can be estimated using a weighted average approach proposed by Nielsen et al. [10] shown in Eq. (1) where P can be any material property (i.e. density), n is a mixing parameter, X is wt% and the subscripts A and B denote different materials (i.e., AlH and Al).

$$P^n = P_A^n X_A + P_B^n X_B \quad (1)$$

When $n=1$, the standard weighted average TMD equation is obtained which assumes a completely dense sample with no pore space. When $n=1$, the theoretical maximum density for the 6:1 and 2:1 samples are 3.43 and 3.33 g/cm³, respectively. The bulk density, however, may vary with initial water to aluminum concentration ratio. For example, the mixture formed from the 2:1 sample is difficult to handle because any external force (i.e., as in picking up the crystal for measurements of the dimensions) causes the composite to fracture into a powder. Conversely, the 6:1 sample forms a stronger composite that is difficult to fracture by hand. These observable differences in composite strength may be related to the bulk density (and porosity) of the composite which is a result of the degree of structural order within the composite (i.e., crystallinity). With the assumption that a higher level of crystallinity (and an increase in bulk density of the composite), then n in Eq. (1) is a measure of crystallinity and increases as the water to aluminum concentration ratio decreases. The increased crystallinity and bulk density of the samples reduces convective influences (with less porosity) but increases conductive influences and results in higher flame speeds. This is in contrast to what is usually seen with powder mixtures that exhibit higher flame speeds in highly porous loose powder media compared with pressed pellets. The differences between the crystallinity and bulk density are difficult to measure because of the reactive nature of these materials.

Synthesis of AlH is facilitated by an acid-Al reaction described using Pourbaix diagrams. Pourbaix diagrams are used to explain this process because applied potentials will affect the Al-acid reaction. Further studies are on-going to determine the effects of an applied potential, the effects of water to aluminum ratio on the concentrations of AlH and Al, and to develop a safe, reliable method for determining the crystallinity and density of the AlH products.

5. Conclusions

Aluminum iodate hexahydrate $(\text{Al}(\text{IO}_3)_3(\text{HIO}_3)_2(\text{H}_2\text{O})_6)$ was synthesized by dissolving commercially available I_2O_5 in water

prior to mixing with Al powder. The IO_3^- solutions are highly acidic (i.e., $\text{pH} < 0.2$), thereby pulling Al^{3+} ions into solution prompting the formation of AlH crystals. This synthesis approach produced an 80/20 mixture of AlH and Al, respectively. The mixture was highly reactive, as demonstrated with flame speeds as high as 3200 m/s. To fully understand how the synthesis parameters affect crystal formation, structure, and reactivity, further characterization studies are ongoing.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2017.01.012.

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