A Metal Inorganic Framework Designed as a Propellant Burn Rate Modifier

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The kinetics of a strategically synthesized burn rate enhancer (BRE) are investigated in its reaction with ammonium perchlorate (AP). The BRE is designed for multifunctionality by 1) producing reactive gases that couple with AP gas production; 2) trapping reactive gases with high surface area; and 3) exposing metal cations to incite exothermic reactions at a temperature coincident with AP decomposition. This study advances inorganic synthesis by introducing a metal inorganic framework (MIF) composed of an aluminum cation (Al+3) surrounded by inorganic "linker" molecules of oxidizing species. To increase surface area, a porous, amorphous MIF (a-MIF) is synthesized by controlling solution properties of an acid-base precipitation reaction. Upon gas generation, high surface area and aluminum-rich surface of a-MIF accelerate AP decomposition and induce an exothermic reaction that is otherwise endothermic in thermal equilibrium analysis. AP decomposition rate is advanced by reducing peak onset temperature and increasing decomposition rate with addition of a-MIF (i.e., from 17% min⁻¹ at 401 °C to 18% min⁻¹ at 365 °C). Enthalpy of AP decomposition increases from +240 J g^{-1} to -1040 J g^{-1} . Results introduce an approach for increasing the decomposition rate of solid oxidizers by demonstrating a recipe for designing and synthesizing an MIF.

1. Introduction

Ammonium Perchlorate (AP) is a commonly used oxidizer in solid propellant applications due to its high oxidizer content, stability under storage conditions, and energetic potential.^[1,2] Experiments using differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA) study AP decomposition processes and analyze reaction kinetics under equilibrium conditions that inform nonequilibrium reaction dynamics. The decomposition of AP can proceed through two mechanisms.^[2–6]

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The first is endothermic dissociation of AP into ammonia (NH_3) and perchloric acid $(HClO_4)$, as shown in Reaction (1)

$$NH_4ClO_4(s) \rightarrow NH_3(g) + HClO_4(g)$$
 (1)

The second is the redox decomposition of the gaseous products from AP dissociation (i.e., Reaction (2)) having an exothermic energy balance. Reaction (2) is an example of dissociated species that maximizes heat release through H_2O formation, since N_2 and O_2 can further react endothermically to form nitrogen oxides.

$$\begin{split} \mathrm{NH}_3(g) + \mathrm{HClO}_4(g) &\to 0.5\,\mathrm{N}_2(g) \\ &\quad + 2\mathrm{H}_2\mathrm{O}\,(g) + 0.5\,\mathrm{Cl}_2(g) + \mathrm{O}_2(g) \end{split} \mbox{(2)}$$

Upon decomposition, Reaction (1) and (2) can overlap in time.^[4] Whether the overall decomposition process is net exothermic or endothermic depends on whether gas-phase products from Reaction (1) are confined to react exothermically or escape without reaction.

Figure 1 shows a concept sketch describing the stages of AP decomposition under open and confined equilibrium conditions. In the first stage, AP shows an endothermic phase change. Following phase change and in an open environment, an exothermic Stage 2 occurs followed by an endothermic Stage 3 (see Figure 1). Stage 2 exothermicity is driven by the highly porous sponge-like morphology of decomposing AP that creates increased surface area for exothermic interface reactions including products from Reaction (1),^[4] such as Reaction (2).

Stage 3 is net endothermic because, as the pores grow, surface area is removed to eventually allow gases to escape without sufficient exothermic reaction (see Figure 1, blue solid line).^[4,7] The stage-wise behavior in an open environment assumes that AP particles are of sufficient size, usually in the micrometerrange, so that enough surface area exists to manifest these stages. Confinement (dashed line, Figure 1) during AP decomposition influences participation of gas-phase species. In a confined environment, decomposition is exothermic owing to contributions from gas-phase reactions trapped by confinement, either within pores or within the confined volume.^[4]

Open environment thermal equilibrium experiments are useful in testing the surface influence of a burn rate modifier to increase decomposition rate and increase exothermicity in





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Figure 1. Concept sketch of stages of AP decomposition in open and confined environments. After Stage 1 phase change, and Stage 2 exothermic reaction, open and confined environments induce different responses. Open environments have a Stage 3 endothermic decomposition phase because gases produced in Stage 2 escape. Confined environments have an exothermic decomposition process since confinement forces exothermic reactions from decomposition gases.

the later AP endothermic decomposition stage. Exothermic enhancement occurs either by gas adsorption and heterogeneous catalysis of gaseous products with AP dissociated species^[8] or by direct reaction of the additive with AP decomposition products.^[9]

Many studies in the past two decades have focused on improving combustion of AP using additives, called burn rate enhancers (or burn rate modifiers).^[2,8–15] Burn rate enhancers are typically added to AP in small concentrations, that is, up to 10 wt%. Energetic additives have been tested in amounts up to 50% or greater.^[13,15] Key metrics for improved AP combustion include increased mass decomposition rate and exothermic heat released.^[2,16] Thermal equilibrium experiments using DSC–TGA are often used to quantify decomposition rates and exothermicity because experiments require only a few mg of material and data provide insight on reaction kinetics that contribute to global nonequilibrium burn rates.

One example of a burn rate enhancer is nanosized titanium dioxide (n-TiO₂). Particles of n-TiO₂ were studied by Reid et al.^[8] to increase AP decomposition rate and overall exothermicity. They analyzed DSC–TGA data and derived metrics (e.g., decomposition rate and exothermicity) for performance that correlated with increased propellant burn rates. Burn rate enhancers, like TiO₂, can work through heterogeneous catalysis by trapping the gases from AP decomposition (Stage 1 in Figure 1) thus enabling exothermic reactions,^[8] or by direct reaction with AP decomposition products.^[9]

Ideal metal oxide formulation development for burn rate enhancer applications requires higher oxidizer concentration than TiO_2 to add to overall gas generation capability. Also, lessons learnt from studying TiO_2 , like high porosity helps trap gases to increase exothermic potential, should also be exploited. Motivation to provide increased functionality to burn rate enhancer design inspired the development of a metal inorganic framework (MIF). Like metal organic frameworks (MOFs) composed of a metal cation and organic ligands, MIF is introduced

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here to explain the purposeful design of a similar molecular structure. The MIF is composed of two main components: a metal cation and an inorganic molecular structure called a linker shown in **Figure 2**. The aluminum cation combines with a hexahydrate– iodate–iodic acid linker to form $[Al(H_2O)_6](IO_3)_3(HIO_3)_2$, aluminum iodate hexahydrate iodic acid, abbreviated AIH. The strong ionic bonds within the molecular structure may identify AIH as a metal salt, but the MIF concept can extend beyond salts and include covalent bonds. The abundance of oxidizer species in the inorganic linker makes the MIF useful as a burn rate enhancer or can be useful as a standalone solid oxidizer for energetic applications.

An MIF called AIH was recently synthesized from an acid-base precipitation reaction and studied for its energetic properties and diverse applications.^[17-20] For example, AIH can replace the Al₂O₃ passivation shell on Al particles and act as a burn rate enhancer by lowering the Al particle ignition threshold.^[18] The AIH passivation shell on Al particles decomposes at relatively low temperatures (i.e., 120-195 °C) to readily expose pyrophoric Al to surrounding oxidizers and rapidly react. The gasification and removal of the AIH shell at low temperatures (i.e., <400 °C) is a key process accelerating aluminum oxidation. Overall, the AIH coating on Al particles enables production of greater power from metal combustion. AIH also has a noncentrosymmetric P63 structure that promotes piezoelectric electromechanical activation.^[21] P63 iodate structures have also shown promise for nonlinear optical applications such as second-harmonic generation where photonic energy is amplified.^[22]

There are features about the molecular structure of an MIF that make it a good candidate as burn rate enhancer. First, the inorganic linker begins decomposition at temperatures in the range of AP decomposition such that intermediate gas-phase reactions may offer pathways for greater and more rapid AP decomposition and added thrust. Second, the main gas-phase decomposition products from AIH are oxidizers including iodine and oxygen gases^[20,23,24] and released at relatively low temperatures (i.e., below 400 °C) to interact exothermically with ammonia and chlorate gases. Third, upon MIF linker decomposition and gas generation, Al⁺³ cations are exposed at temperatures coinciding with AP gas-phase decomposition with further potential for promoting heterogeneous exothermic reactions.

The goal of this study was to synthesize an MIF and examine its effectiveness as a burn rate enhancer. The hypothesis is that an MIF combined with AP will introduce multifunctional



Figure 2. Schematic of a MIF that includes a metal cation linked through an inorganic structure. The MIF shown here is aluminum iodate hexahydrate iodic acid, AIH $[AI(H_2O)_6](IO_3)_3(HIO_3)_2$.



reactions that enable additional chemical pathways to effectively increase AP decomposition rate and exothermicity. The goal was accomplished by synthesizing an MIF based on AIH (see Figure 2) and tailoring synthesis to produce crystalline and amorphous AIH. The amorphous AIH (a-AIH) increased porosity and accessible metal cations ideal for catalyzing AP decomposition by 1) exposing metal cations to induce heterogeneous surface reactions and 2) trapping reactive gases. Therefore, a-AIH is the focus of this study.

Mechanisms for reactions observed through thermal equilibrium diagnostics are based on DSC–TGA data of two MIFs: amorphous and crystalline AIH. Comparing a-AIH to AIH helped differentiate between combustion-enhancing effects of gas-phase reactions relative to heterogeneous reactions with exposed surface cations in higher concentration for a-AIH.

Results show promise for an MIF as a multifunctional burn rate enhancer not only for its high surface area but also accessible metal cations to incite exothermic reactions and increase AP decomposition rate and exothermicity. The key processes responsible for combustion enhancement also provide insight on strategies targeting material synthesis in ways that will exploit burn rate enhancer properties for advanced propellant technologies. Important material properties include high surface area, metal cation-rich surfaces, and timely release of reactive gases to further promote propellant combustion.

2. Experimental Section

2.1. Materials and Synthesis

This study examined powders composed of ammonium perchlorate (AP) and a metal inorganic framework (MIF) illustrated in Figure 2. Ammonium perchlorate (NH₄ClO₄) powder was provided by the Naval Air Warfare Center, Weapons Division, China Lake, CA, USA. Three MIFs were synthesized. The first was crystalline aluminum iodate hexahydrate (AIH), the second was amorphous AIH (a-AIH), and the third was partially amorphous AIH (pa-AIH). Individual AIH powders and AIH powder combined with AP powder were examined. The precursor materials are tabulated in Table S1, Supporting Information.

Crystalline aluminum iodate hexahydrate iodic acid (AIH, $[Al(H_2O)_6]$ (IO₃)₃(HIO₃)₂) powder was synthesized using methods detailed previously.^[21] The synthesis of amorphous aluminum iodate hexahydrate (a-AIH) is like that of AIH; however, the third and fourth steps were slightly modified for reduced time in solution and hexane replaced acetonitrile as the crashing agent. The details of a-AIH synthesis are provided here because they have not been previously reported.

The first synthesis step is to create an aqueous iodic acid solution by adding I_2O_5 powder to water at a 1:1 weight ratio. In these experiments, 600 mg of I_2O_5 powder was dissolved in 6 mL of water. A magnetic stirrer was set to 1000 rpm to facilitate dissolution. In about 10 min the I_2O_5 powder dissolved, and the solution became clear.

In the second step, aluminum hydroxide $(Al(OH)_3)$ was added to the aqueous acid solution (HIO_3) at a 10:1 HIO₃ to $Al(OH)_3$ weight ratio. In these experiments, 6000 mg of $Al(OH)_3$ was added to the aqueous HIO₃ solution from the first step. Once

the Al(OH)_3 was added, the solution was heated to $60\,^\circ\text{C}$ with a magnetic stirrer set to $1100\,\text{rpm}$ and mixed for two hours.

In the third step, the heat was removed, and hexane was added at a 1:1 volumetric ratio. Hexane is not soluble in water; hence, it forms a biphasic solution with water, different from the monophasic nature of acetonitrile–water solutions used to synthesize crystalline AIH^[25,26]. Using hexane results in a differential separation of ions in a-AIH synthesis when compared with AIH^[27].

In the fourth step, time in solution is critical to the formation of amorphous and partially amorphous phases (i.e., a-AIH or pa-AIH, respectively). When the stirring speed was held at a constant rate and the solution was mixed for 4 h, fully amorphous AIH was synthesized, that is, a-AIH. For partially amorphous AIH (i.e., pa-AIH), the solution was mixed for greater than 4 h after the heat was removed. At the appropriate time, the solution was filtered through a Buchner funnel to collect the solid particles. This experiment yielded 500 mg of amorphous AIH (a-AIH) powder.

2.2. Materials Characterization

All powders were characterized using scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS), with data shown in Figure S1–S4, Supporting Information. Microscopy using SEM was performed with a Zeiss Crossbeam 540 FIB–SEM and spectroscopy was performed with an Oxford EDS.

Powder X-ray diffraction (XRD) was performed using a Miniflex II powder diffractometer with Bragg–Brentano beam geometry. The diffractometer used a Cu K α X-ray source ($\lambda = 1.5418$ Å, current = 15 mA, voltage = 30 kV) and was operated in continuous θ –2 θ mode with a step size of 0.02° and a collection time of 1°–3° min⁻¹ in the range 3°–70°. Samples were finely ground and placed on a zero-background holder and diffraction data captured with a position-sensitive D/teX Ultra 1D silicon strip detector. Whole pattern fitting was done with MDI Jade-X v9.1 using the ICDD PDF 4+ database to identify crystal-line species.

Fourier-transform infrared spectroscopy (FTIR) data for the AIH powders were collected using a Bruker Optics VERTEX Fourier-transform infrared spectrometer (FTIR) with a diamond crystal attenuated total reflectance (ATR) accessory.

2.3. Reactive Characterization

Thermal equilibrium experiments were conducted in a NETZSCH STA 449 F3 Jupiter, a simultaneous DSC and thermalgravimetric analyzer (TGA). Temperature and sensitivity calibrations were conducted with standard materials including indium, tin, bismuth, zinc, aluminum, silver, and gold. Melting temperatures were within 1°C of reference values. Enthalpies measured with sensitivity calibration were within 1.5% of reference values. The TGA mass calibration was performed using calcium oxalate and within 1% of reference values.

All experiments were performed at 10 °C min⁻¹ heating rate in an inert argon environment flowing at 100 mL min⁻¹. Mixtures of AP and AIH powders used a mass ratio of 70:30 AP:AIH prepared by mixing individual powders in a Retsch Cryomill for 20 min at 25 Hz. Experiments were performed in



triplicate to confirm repeatability of the data. Experiments used 2 mg powder in open alumina crucibles and programmed from room temperature up to 520 °C. Further tests of AIH powders were performed to identify stages of AIH decomposition. When studying AIH powders alone, 2 mg of powder was examined from room temperature up to 700 °C in open alumina crucibles. The experiments with pure AIH powders provided a baseline for comparison of thermal and mass change behavior with the AP + AIH mixtures. Additionally, partial decomposition experiments of mixtures up to 300 and 340 °C were performed using 6–9 mg powder and condensed-phase product residue was further analyzed using SEM/EDS.

3. Results and Discussion

3.1. Material Characterization

Ammonium perchlorate particles have a rounded morphology with nominal diameters in the range $150-400 \,\mu\text{m}$ with an average size of $270 \,\mu\text{m}$ (see **Figure 3**a,b). The image in Figure 3c shows crystalline AIH particles, with a nominal size in the range of $10-20 \,\mu\text{m}$. Figure 3d–f shows a-AIH particles with porous,

corrugated surfaces and nominal size range $10\text{--}100\,\mu\text{m}.$ Note that AIH is a discretely separate powder from AP powder.

When mixtures of AP + AIH and AP + a-AIH were combined in mass ratio of 70:30, the smaller AIH and a-AIH particles coat larger AP particles, as shown in **Figure 4**. The images of mixtures at varied resolution and corresponding spectroscopy maps of chlorine in AP and iodine in a-AIH/AIH are shown in Figure 4 for AP + a-AIH and AP + AIH, respectively. Overall, a-AIH and AIH particles coat AP particles, thereby facilitating their interaction during decomposition.

Figure 5 shows diffraction patterns for AIH, a-AIH, and pa-AIH and the gradual shift from amorphous to crystalline. The diffraction pattern for AP is shown in Figure 5 indicating high purity for crystalline materials.

Results from the elemental maps of the surface spectroscopy analysis are shown in **Table 1**. The Al:I:O mass ratios for a-AIH are 24.1 \pm 0.9 (Al): 35.4 \pm 2.9 (I): 40.6 \pm 2 (O) (average \pm standard deviation). For AIH, the Al:I:O mass ratios are 4 \pm 1.5 (Al): 81.8 \pm 5.5 (I): 14.3 \pm 4.1 (O). Crystalline AIH data compares reasonably well with the Al:I:O mass ratios from the chemical formula ([Al(H₂O)₆](IO₃)₃(HIO₃)₂), that is, 2.7 (Al): 63.6 (I): 33.7 (O). Thus, AIH has more iodine and less aluminum at its surface than a-AIH. Partially amorphous pa-AIH shows



Figure 3. SEM images of a,b) ammonium perchlorate, c) crystalline aluminum iodate hexahydrate (AIH), and d-f) amorphous AIH (a-AIH).



(a)

(c)





Figure 4. SEM images of mixtures: a) AP + a-AIH, b) AP + AIH, c) AP + a-AIH, d) spectroscopy mapping of chlorine (magenta coloring) indicating AP particles, e) spectroscopy mapping of iodine (yellow coloring) indicating a-AIH particles coating AP particles, f) AP + AIH, g) spectroscopy mapping of chlorine (magenta coloring) indicating AP particles, and h) spectroscopy mapping of iodine (yellow coloring) indicating AP particles.



Figure 5. Diffraction patterns of ammonium perchlorate (AP) XRD pattern PDF#04-013-7376, crystalline AIH (AIH): XRD pattern PDF#04-009-2066, partially amorphous AIH (pa-AIH), and amorphous AIH (a-AIH).

average Al and I content intermediate between crystalline and fully amorphous a-AIH; however, there is wide variation in these values.

Fourier-transform infrared spectroscopy (FTIR) data for the AIH powders are shown in **Figure 6**. The a-AIH powder shows a strong, broad peak at $3800-3200 \text{ cm}^{-1}$ associated with O–H stretching of H₂O molecules. The FTIR peak for pa-AIH is

Table 1. The composition of crystalline AIH (AIH), amorphous AIH (a-AIH), and partially amorphous AIH (pa-AIH) MIF determined from EDS measurements (average \pm standard deviation) of Al, I, and O and compared with formula ratios of Al:I:O.

	Al	I	0
a-AIH (EDS)	$\textbf{24.1}\pm\textbf{0.9}$	35.4 ± 2.9	40.6 ± 2
pa-AIH (EDS)	$\textbf{10.3} \pm \textbf{9.48}$	$\textbf{44.53} \pm \textbf{31.45}$	$\textbf{45.2} \pm \textbf{22.06}$
AIH (EDS)	4 ± 1.5	$\textbf{81.8} \pm \textbf{5.5}$	14.3 ± 4.1
AIH (Formula)	2.7	63.6	33.7

redshifted toward 3200–2700 cm⁻¹, a weaker O–H stretching group, and AIH shows a dominant peak in this wavenumber range. These redshifts in pa-AIH and AIH are due to the intermolecular H-bonds with HIO₃/IO₃. Studies explain^[28,29] that the 3550–3200 cm⁻¹ peak is indicative of higher surface area associated with increased porosity relative to the weaker O–H stretching for pa-AIH and AIH. Greater surface area for a-AIH is consistent with SEM images in Figure 3. It is noted that traditional Brunauer Emmett Teller (BET) measurements require dehydration of the AIH samples. The dehydration process affects the structure and porosity of AIH such that BET measurements are not representative of the material properties in this study. Alternatively, FTIR data in Figure 6 provide a





Figure 6. FTIR of AIH (red curve), a-AIH (blue curve), and pa-AIH (green curve). The a-AIH powder shows strong, broad O–H stretching, whereas AIH does not. The peak wavenumber regime $3800-3200 \text{ cm}^{-1}$ is indicative of greater surface area for a-AIH compared to AIH. The pa-AIH powder shows an FTIR signal intermediate between crystalline AIH and a-AIH.

qualitative indication of relative porosity variations between materials.

Figure 6 when combined with the higher surface Al concentration in a-AIH (Table 1) and increased surface porosity evident in SEM images (Figure 3) provides evidence that a-AIH has a relatively high surface area and an Al-rich surface to increase the potential for reactions with AP compared to crystalline AIH.

3.2. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)

Figure 7a,b shows heat flow (DSC) and mass loss (TGA) for AP and AP + a-AIH. Also shown in Figure 7c is the mass decomposition rate and peak mass loss rate (PMR) from differential thermogravimetric (DTG) analysis of the TGA data. Key results from Figure 7 are summarized in **Table 2**. The standard deviations are reasonable given the heterogeneity of mixtures and the complex cascade of reactions occurring in AP decomposition.

In Figure 7a, after AP dissociation at about 250 °C (Stage 1 in Figure 1), decomposition begins exothermically (i.e., Stage 2 in Figure 1). The third stage of AP decomposition at about 363 °C



Figure 7. Average of triplicate measurements of pure AP and AP + a-AIH mixtures for a) DSC b) TGA, c) DTG. All experiments were performed at a heating rate of 10 °C min⁻¹ in argon flowing at 100 mL min⁻¹. All onset temperatures correspond to the beginning of the endotherm/exotherm or mass gain. All measurements are rounded to the nearest integer. PMR is peak mass loss rate, *** is p < 0.002 Welch t-test for PMR compared with pure AP at the same temperature.

Table 2. Key DSC, TGA, DTG results with average and standard deviation. Note that PMR is average peak mass loss rate (PMR) at corresponding temperature (p < 0.002 Welch *t*-test). NA is not applicable.

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Material	Total DSC Enthalpy [J g ⁻¹]	Decomp. Exotherm Enthalpy [J g ⁻¹]	Decomp. Endotherm Enthalpy [J g ⁻¹]	PMR and Temperature
AP	$+240\pm83$	-424 ± 87	$+664\pm14$	18% min ⁻¹ at 365 °C
AP+a-AIH	-1040 ± 121	-1040 ± 121	NA	17% min ⁻¹ at 401 °C

is endothermic, indicating that gaseous species escape without significant exothermic reaction, as expected. The multistage AP decomposition behavior is consistent with previous studies on AP in open crucibles and conceptually illustrated in Figure 1.^[2–6,8]

Most noteworthy is data for AP + a-AIH in Figure 7. Stage 3 flips from endothermic (for AP) to completely exothermic (for AP + a-AIH). The average exothermic enthalpy of AP + a-AIH is -1040, -616 J g^{-1} greater and 2.45 times the average stage 2 exotherm of AP at -424 J g^{-1} (Figure 7a). AP + a-AIH exothermic enthalpy is -1280 J g^{-1} greater than

the net enthalpy of AP decomposition, which is $+240 \text{ Jg}^{-1}$ net endothermic. Also, Figure 7b,c shows an increase in mass decomposition rate for AP + a-AIH compared to AP. The PMR for AP + a-AIH is 18% min⁻¹ at 365 °C, while at the same 365 °C temperature AP mass loss is only 9% min⁻¹. The PMR for AP is at an elevated temperature of 401 °C and is 17% min⁻¹.

When AIH replaced a-AIH, the AIH did not significantly influence AP decomposition (see Figure 8). Partially amorphous AIH (pa-AIH) reduced the onset temperature for AP PMR but is not as effective as a-AIH (see Figure 9).

The behavior associated with AIH (Figure 8 and 9) is instructive in identifying key mechanisms promoting AP decomposition. Specifically, AIH cannot trap gases generated by AP decomposition as effectively as the more porous a-AIH (Figure 3), thereby limiting a decreased temperature for the PMR (Figure 9a). Therefore, a porous surface morphology is important for promoting AP decomposition rate. Also, since a-AIH has less gasifiable iodine on the surface (Table 1), AP + a-AIH exothermicity (Figure 9b) may be incited by the heterogeneous reactions at the a-AIH surface that are less available in AIH and pa-AIH.



Figure 8. Average of triplicate measurements of a) DSC, b) TGA, and c) DTG of pure AP versus AP + AIH (70:30 mixture by mass). DSC shows that AP + AIH mixture does not become completely exothermic as occurs in AP + a-AIH. TGA and DTG show AP + AIH has a smaller effect on average mass change than AP + a-AIH. DTG shows that PMR of 17% min⁻¹ at 392 °C is not as much as that in AP + a-AIH–18% min⁻¹ at 365 °C, and the difference in peak DTG of AP + AIH versus AP–17% min⁻¹ at 401 °C is not statistically significant.





Figure 9. a) DTG and b) differential scanning calorimetry (DSC) graphs of ammonium perchlorate (AP) plus AIH in increasing amorphous nature 70:30 AP:a-AIH/pa-AIH/AIH. DTG shows that a-AIH has the greatest effect of increasing mass decomposition rate. All experiments are conducted in argon with a heating rate of 10 °C min⁻¹.

To further identify the mechanism influencing AP decomposition, DSC–TGA experiments were performed on pure a-AIH and AIH powders. Results are shown in **Figure 10**.

Crystalline AIH decomposes in four endothermic stages of gas generation according to the mechanism described by Reaction $(3-6)^{[20,23,24]}$ and shown in Figure 10.

$$[Al(H_2O)_6](IO_3)_3(HIO_3)_2(s) \rightarrow Al(IO_3)_3(HIO_3)_2(s) + 6H_2O(g)$$
(3)

$$Al(IO_3)_3(HIO_3)_2(s) \to Al(IO_3)_3(s) + I_2O_5(s) + H_2O(g)$$
 (4)

$$\begin{array}{l} 3 \mathrm{Al}(\mathrm{IO}_3)_3(\mathrm{s}) + \mathrm{I}_2 \mathrm{O}_5(\mathrm{s}) \to \mathrm{Al}(\mathrm{IO}_3)_3(\mathrm{s}) + \mathrm{I}_2(\mathrm{g}) \\ &+ 10 \mathrm{O}_2(\mathrm{g}) + \mathrm{Al}_2 \mathrm{O}_3(\mathrm{s}) \end{array} \tag{5}$$

$$Al(IO_3)_3(s) \rightarrow \frac{1}{2}Al_2O_3(s) + \frac{3}{2}I_2(g) + \frac{15}{4}O_2(g)$$
(6)

Notice that Reaction (3) and (4) correspond to 16 wt% loss and endothermic dehydration occurring below 250 °C in AIH (Figure 10). Then, Reaction (5) corresponds to 30 wt% endothermic loss beginning at 340 °C and ending at 424 °C and overlaps with the endothermic decomposition phase of AP, that is, from 363 to 420 °C and partially with the exothermic decomposition phase from 255 to 363 °C seen in Figure 7. Finally, Reaction (6) is the last mass loss step beginning at 466 °C.

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In AIH, decomposition Reaction (3) and (4) occur during Stages 1 and 2 of AP decomposition, and Reaction (5) coincides with Stage 3, in the range of 255–420 °C. From Reaction (3–5), \approx 46 wt% of AIH loss occurs during AP decomposition (i.e., <420 °C). In contrast, Figure 10 shows a-AIH exhibits a continuous mass loss up to 650 °C with a rapid mass loss beginning at about 420 °C. The less well-defined transition is a hallmark of amorphous structures. Only 9 wt% is lost between 255 and 420 °C, the temperature range corresponding to decomposition of AP. Overall, only 58 wt% loss occurs in a-AIH compared with \approx 100 wt% in AIH. Therefore, heterogeneous surface reactions with AP gaseous decomposition products may contribute to AP + a-AIH high exothermicity (Table 1 and Figure 10a).

Figure 11a,b shows a drop in I/Al ratios when AP + a-AIH is heated to 300 and 340 °C, indicating iodinated gas-phase species expose Al on the surface. Unlike I and O, Al will not gasify at temperatures below 700 °C. Interestingly, Figure 11c,d shows



Figure 10. Data from a) TGA and b) DSC of AIH and a-AIH powders. Experiments were performed at a heating rate of 10 °C min⁻¹ in 100% argon flowing at 100 mL min⁻¹. All onsets correspond to the beginning of mass gain and endotherms as defined in UNE-EN ISO 11357-1.





Figure 11. a) SEM image of partially decomposed surface from an AP + a-AIH mixture at 340 °C in an open crucible. b) Graph showing trends of EDS measurements of I/AI ratios in AP + a-AIH from initial mixture to partially decomposed mixtures at 300 and 340 °C in open crucibles. Reduction in I/AI ratio indicates iodine-containing gas generation exposing increased AI at the solid surface. c) SEM image of partially decomposed surface from an AP + AIH mixture at 340 °C in an open crucible. d) Graph showing trends of EDS measurements of I/AI ratios in AP + AIH from initial mixture to partially decomposed surface from an AP + AIH mixture at 340 °C in an open crucible. d) Graph showing trends of EDS measurements of I/AI ratios in AP + AIH from initial mixture to partially decomposed mixtures at 300 and 340 °C in open crucibles. Reduction in I/AI ratio indicates iodine-containing gas generation exposing increased AI at the solid surface only at elevated temperatures. A statistically significant difference occurs between the starting mixture and mixture heated to 340 °C ***, *p* < 0.002 using a Welch *t*-test on both data sets in (b) and (d).

a drop in I/Al ratios only when AP + AIH is heated to 340 °C, consistent with early mass loss in AIH from dehydration, as described in Reaction (3) and (4). The comparison between Figure 11b,d suggests that a-AIH surface gasification leaves Al exposed at lower temperatures than AIH. Therefore, a-AIH with its increased surface Al and higher surface area incite surface exothermic reactions with AP to accelerate decomposition.

A 70:30 AP:a-AIH mass ratio was selected to provide enough surface aluminum to incite exothermicity coincident with AP decomposition. At 30 wt%, a-AIH has \approx 7 wt.% Al concentrated at the a-AIH surface. 7 wt% concentration aligns with burn rate modifier concentrations in other studies.^[2,8–12] At 5 wt% a-AIH with AP, **Figure 12** shows the a-AIH concentration is too low to have the desired effect on AP decomposition, further supporting that mechanisms driving AP decomposition include 1) enough surface area to scaffold and trap reactive gases and 2) \approx 7 wt% of surface AI to incite heterogeneous exothermic reactions during AP decomposition.

3.3. Thermodynamics Calculations

Thermodynamic calculations of reaction enthalpies between mixtures at standard conditions were calculated using data from



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Figure 12. DSC (dashed line) and DTG (solid line) of AP + 5% a-AIH showing that 5% a-AIH does not remove later endotherm from AP decomposition. The shift in PMR is very slight compared with AP average PMR of 17% min⁻¹ at 401 °C. Experiments were performed at a heating rate of 10 °C min⁻¹ in argon flowing at 100 mL min⁻¹. Values are rounded to the nearest integer.

NIST JANAF thermochemical tables.^[30] Reaction enthalpy was determined by the sum of the enthalpies of all product species subtracted by the sum of the enthalpies of reactant species at standard temperature and pressure conditions.

A contributor to exothermic reactions from trapped gases is described by Reaction (7), which is a combination of AP decomposition processes described in Reaction (1) and (2).

$$NH_4ClO_4 \rightarrow 0.5 N_2 + 2H_2O + 0.5 Cl_2 + O_2$$
(7)

Reaction (7) assumes that all heat released comes from the most exothermic possible reaction that is, formation of water from the oxidation of hydrogen and results in an exothermic reaction enthalpy of -2.35 kJ g⁻¹. This enthalpy is a theoretical maximum and compares reasonably well with the experimental average AP + a-AIH decomposition enthalpy of -1.04 kJ g^{-1} in Figure 7a. The difference between theoretical and measured enthalpies suggests that experimentally, the AP + a-AIH reaction involves some endothermic processes such as nitrogen oxide formation or escape of reactive gases such as NH₃ and HClO₄. Also, surface aluminum concentration in a-AIH is higher than in AIH. The \approx 80% decrease in I/Al concentration (Figure 11) coupled with slower gas generation from a-AIH decomposition in Figure 10 suggests that off-gassing in a-AIH exposes Al so that exothermic reaction with AP can occur. Since a-AIH has less surface iodine and more exothermic behavior than AIH, surface Al is a key mechanism for exothermic combustion in AP + a-AIH, also consistent with results shown in Figure 12.

To estimate the magnitude of the exothermic contribution, AII_3 is used as a proxy in the reaction enthalpy calculations to evaluate the theoretical potential for increased exothermicity of the AP + AIH mixtures. Excess AII_3 is considered to mimic localized effects of high-surface-area a-AIH that interacts with AP. Reaction (8) assumes that all oxygen in AP reacts completely with both hydrogen and aluminum to form H_2O and AI_2O_3 , respectively. Reaction (8) has potential for exothermic enthalpy of -8.42 kJ g⁻¹.





$$\begin{aligned} &\frac{4}{3} \mathrm{AlI}_3(\mathbf{s}) + \mathrm{NH}_4 \mathrm{ClO}_4(\mathbf{s}) \ \to \frac{1}{2} \ \mathrm{N}_2(\mathbf{g}) + \frac{1}{2} \mathrm{Cl}_2(\mathbf{g}) \\ &+ 2\mathrm{H}_2 \mathrm{O}\left(\mathbf{g}\right) + \frac{2}{3} \mathrm{Al}_2 \mathrm{O}_3(\mathbf{s}) + 2\mathrm{I}_2(\mathbf{g}) \end{aligned} \tag{8}$$

Since a-AIH is Al surface rich, Reaction (8) is more likely in AP + a-AIH, particularly in the later stages of AP decomposition (i.e., >300 °C as in Figure 11).

The potential to develop new burn rate enhancers after the lessons learnt in this study is important. An effective burn rate enhancer should be a material that is safe to handle, has a high surface area to trap decomposition gases and supports interface reactions, as well as produces gaseous species that support propellant combustion and releases gases in a timely fashion to expose discretely localized metal cations available to incite AP decomposition and exothermicity at temperatures coincident with AP decomposition. Results from this study provide a recipe for developing new materials strategically synthesized as MIFs, that will further develop solid oxidizers for propellant applications.

4. Concluding Remarks

Advancing propellant technology requires creative approaches to manipulating the decomposition behavior of ammonium perchlorate (AP). One approach introduces MIF based on an aluminum cation and iodine–oxygen–hydrogen inorganic linker. The MIF synthesized here is called aluminum iodate hexahydrate iodic acid, abbreviated AIH. Forms of AIH synthesized include crystalline AIH and a higher-surface-area amorphous phase called a-AIH. Both AIH and a-AIH powders were added to AP powder and analyzed for their potential as a burn rate enhancer.

Experiments were performed using thermal equilibrium diagnostics on pure materials including AP, a-AIH, and AIH, and their mixtures. Enhanced decomposition rate and exothermicity are seen in AP + a-AIH with an enthalpy of $-1040 \pm 121 \text{ J g}^{-1}$. The pure AP sample by comparison has a net endothermic enthalpy of $+240 \pm 83 \text{ J g}^{-1}$. Mass decomposition rate is also increased in AP + a-AIH with an average PMR advanced by 36 °C from 17% min⁻¹ at 401 °C in AP to 18% min⁻¹ at 365 °C in AP + a-AIH.

Isolating the mechanism of enhancement required additional tests on AP + AIH for comparison to AP + a-AIH. The a-AIH showed increased surface Al concentration and higher surface area compared to AIH. Crystalline AIH produced more gas species at lower temperatures (i.e., <300 °C) compared with a-AIH. Thus, heterogeneous reactions at the a-AIH surface, key among them being the exothermic reaction between AP decomposition gases and the Al-rich a-AIH surface, are main contributors to the high exothermicity of AP + a-AIH. Our results provide a guide for developing AP burn rate enhancers using an MIF that combines a high surface area, a metal cation-rich surface, and timely gas generation coinciding with AP decomposition to increase propellant decomposition rate.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

aluminum iodate hexahydrate, ammonium perchlorate, burn rate modifier, solid oxidizers, solid propellants

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