Video Article

Reaction Kinetics and Combustion Dynamics of $I_4O_9$ and Aluminum Mixtures

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Abstract

Tetraiodine nonoxide ($I_4O_9$) has been synthesized using a dry approach that combines elemental oxygen and iodine without the introduction of hydrated species. The synthesis approach inhibits the topochemical effect promoting rapid hydration when exposed to the relative humidity of ambient air. This stable, amorphous, nano-particle material was analyzed using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) and showed an exothermic energy release at low temperature ($i.e.,\sim 180~°C$) for the transformation of $I_4O_9$ into $I_2O_5$. This additional exothermic energy release contributes to an increase in overall reactivity of $I_2O_5$ when dry mixed with nano-aluminum (Al) powder, resulting in a minimum of 150% increase in flame speed compared to Al + $I_2O_5$. This study shows that as an oxidizer, $I_4O_9$ has more reactive potential than other forms of iodine(V) oxide when combined with Al, especially if $I_4O_9$ can be passivated to inhibit absorption of water from its surrounding environment.

Video Link

The video component of this article can be found at http://www.jove.com/video/54661/

Introduction

There are many iodine oxide compounds ($e.g.,\text{HIO}_3,\text{H}_2\text{IO}_3,\text{I}_2\text{O}_5,\text{I}_2\text{O}_3$) but the one most commonly studied for reaction with aluminum (Al) is diiodide pentoxide, $I_2O_5$. There are reasons for favoring $I_2O_5$ for combustion with Al: (1) $I_2O_5$ has an oxidation state of five which makes it a strong oxidizer for combustion applications; (2) $I_2O_5$ is semi-stable, depending on atmospheric conditions, and easily handled in powder form; and (3) $I_2O_5$ is relatively easy to produce and readily available.

Other forms of iodine oxide that have been studied are $\text{HIO}_3,\text{H}_2\text{IO}_3$, and $I_2O_3$. When heated to low temperatures ($i.e.,\sim 180~°C$), $I_2O_5$ thermally decomposes into $I_2O_3$ as shown in Equation 1 and the decomposition reaction is exothermic.

\[(1)\quad 5I_2O_3\rightarrow 9I_2O_2+I_2\]

If $I_2O_3$ could be used in place of $I_2O_5$, the total energy liberated from reaction could increase due to the exothermic decomposition of $I_2O_3$ at temperatures below the Al ignition and reaction temperatures ($i.e.,<660~°C$) and below the dissociation temperature of $I_2O_3$ ($i.e.,\sim 350~°C$). Also, $I_2O_3$ generates 8 wt.% more $I_2$ gas when compared to $I_2O_5$ that could be used to neutralize biological agents. However, $I_2O_3$ has a higher molecular weight when compared to $I_2O_5$ and it is unknown if more energy is released per mass or per volume when using $I_2O_3$ compared to $I_2O_5$. Using $I_2O_3$ could provide a way to transport large quantities of solid iodine and upon ignition, release gaseous iodine. But, $I_2O_3$ powder is usually unstable. In fact, Wikjord et al. showed that over very short times $I_2O_3$ decomposed into $I_2O_5$ even with limited exposure to the atmosphere. This instability limits the usefulness of $I_2O_3$ as an oxidizer in combustion applications.

Iodic acids, such as $\text{HIO}_3$ and $\text{H}_2\text{IO}_3$, form when $I_2O_3$ is exposed to water either from the relative humidity (RH) of the atmosphere or from immersion in a fluid. For combustion applications, $I_2O_3$ is usually preferred over the hydrated iodic acids because evaporation of water upon combustion absorbs energy and reduces the overall heat produced. Despite the endothermic nature of this phase change, Smith et al. showed rapid evaporation of water during combustion of Al with $I_2O_3$ comprised partially of iodic acids produced significant gas generation that increased convective energy transport and produced higher flame speeds than Al + $I_2O_3$ alone. Specifically, mixtures with higher concentrations of iodic acids had up to 300% higher flame speeds than mixtures with lower concentrations of iodic acids.

The rate of absorption from atmospheric water is dependent on RH. There is a RH threshold where absorption begins and dependent on the hydration state. Little et al. showed a RH threshold of 70% for $\text{HIO}_3$ and a RH threshold of 40% for $\text{H}_2\text{IO}_3$. From this, it is assumed that the RH threshold increases with increasing hydration states. Because of its deliquescent properties, most studies that use $I_2O_3$ as an oxidizer are actually using $I_2O_3$ with significant concentrations of iodic acid. However, the initial concentrations of the samples can be controlled by...
heating the samples above 210 °C until all of the hydrated species have dehydrated. This follows the hydration and dehydration mechanism of I₂O₅ shown in Selte et al.¹ in Equation (2).

(2a) Hydration: 3I₂O₅+3H₂O→2HI₂O₂+2H₂O→6HIO₃

(2b) Dehydration: 6HIO₃→2HI₂O₂+2H₂O→3I₂O₅+3H₂O

The first step in dehydration happens at 110 °C when HIO₂ dehydrates into HI₂O₂. The second step of dehydration happens at 210 °C when HI₂O₂ dehydrates into I₂O₅. Because the initial concentration of commercially available I₂O₅ is composed mostly of iodic acids, the absorption characteristics of pure I₂O₅ have not been studied thoroughly. It is assumed that the RH threshold and absorption rates are dependent on physical properties (i.e., particle size, crystal structure) along with initial hydration state and that an iodine oxide that is amorphous may have a lower RH threshold and increased hydration rates. Isolating iodine oxides from atmospheric water is needed to control the initial state of iodine oxide compounds. One method of isolating I₂O₅ from the atmosphere is blocking water absorption with coatings. For example, Little et al. was able to reduce the absorption rate and total amount of hydrated iodine oxides by sputter coating samples with Au/Pd². Feng et al.³ passivated the surface of I₂O₅ particles with an Fe₂O₃ coating which prevented water absorption over long durations of exposure to ambient atmosphere. A similar approach could be applied to help stabilize I₂O₅.

Another way to improve the stability of I₂O₅ may be new approaches for its synthesis. If the material could be synthesized in a way that prevents introduction of hydrated species, then the topochemical effect that catalyzes water absorption could be inhibited thereby stabilizing the oxidizer. The I₂O₅ examined here was synthesized using a ‘dry’ process that does not introduce hydrated species and enables analysis of a more stable form of I₂O₅ powder. Our objective is to analyze the fundamental kinetics associated with I₂O₅ decomposition and reaction with Al as well as the basic energy propagation behavior of the Al + I₂O₅ reaction. Reaction kinetics are analyzed using thermal equilibrium diagnostics including differential scanning calorimetry and thermal gravimetric analysis (DSC-TGA). Energy propagation is analyzed using high speed imaging of reaction propagation through a powder mixture upon ignition in a transparent tube. Development of synthesis methods to produce I₂O₅ and methods to stabilize I₂O₅ have been slow in comparison to other forms of iodine oxide. A goal of this study is to show that the energy and gas liberated from reactions involving I₂O₅ are greater than reactions involving other iodine oxides. In this way, future research on synthesis and characterization of I₂O₅ may be beneficial for many applications.

NOTE: Six different oxidizers were investigated for the purpose of characterizing the kinetics of I₂O₅ in comparison to other iodine oxides. Each oxidizer is described below. The fuel used for all mixtures was constant: Al powder with 80 nm average spherical particle diameter. Mixture preparation is described following discussion of each oxidizer.

### Protocol

**1. Preparation of Iodine(V) Oxides**

**NOTE:** Nano-aluminum/oxidizer mixtures are highly volatile and can exhibit explosive behavior. These mixtures are susceptible to unintended ignition by electrostatic discharge, friction, impact, and other forms of accidental ignition. All equipment should be grounded to decrease the likelihood of accidental spark ignition. Quantities should be minimized and protective equipment should be used when handling these materials. More information on safety and handling procedures can be found in Maienschein et al.¹³

1. **Preparation commercial I₂O₅**
   
   1. Crush 10 g of I₂O₅ crystals with a mortar and pestle until a consistent powder is created.
   
   2. After the crystals are in a powder form, evenly spread the 10 g of powder in a ceramic crucible suitable for heating up to 250 °C.
   
   3. Place entire crucible in an oven and heat to 250 °C at 10°C/min and hold at 250 °C for 5 min.

2. **Preparation of amorphous I₂O₅**
   
   1. Place 3 g of the crushed and dehydrated commercial I₂O₅ in a glass beaker with a magnetic stirrer and add 3 g of distilled water. To ensure the sample is completely dissolved, add a 1:1 ratio of water to commercial I₂O₅ and mix for 20 min. Dissolution of I₂O₅ in water forms an aqueous phase of IO₅⁻.
   
   2. Pour the IO₅⁻ solution into a beaker that is suitable for heating. To ensure enough amorphous I₂O₅ is produced, use three times the mass of IO₅⁻ solution than the mass needed of amorphous I₂O₅. For example, if one gram of amorphous I₂O₅ is needed, use 3 g of IO₅⁻ solution.
   
   3. Place the beaker with the IO₅⁻ solution into an oven and heat at 20 °C/min to 250 °C and hold for 10 min.
   
   4. Store the sample in a sealed container to limit exposure to atmospheric water from the environment.

3. **Preparation crystalline HIO₃**
   
   1. Repeat step 1.2.1 and place IO₃⁻ solution on a magnetic stirrer in a low humidity environment (below 50% RH) until all of the excess water has evaporated. Upon evaporation, the aqueous phase of IO₃⁻ will precipitate out as HIO₃¹⁷.
   
   2. Store the sample in a sealed container to limit exposure to atmospheric water from the environment.
   
   3. To ensure all excess water is evaporated, place a sample into a differential scanning calorimeter (DSC) and heat to 250 °C at 10 °C/min. **NOTE:** The weight loss at 110 °C will equal 5% and there will be no mass loss at 210 °C if the sample is pure HIO₃. Any additional mass loss is excess water, which means the sample needs more time to evaporate. Weight loss at 210 °C means the I₂O₅ has not completely dissolved and more water with agitation is needed to dissolve the sample.
2. Mixture Preparation

NOTE: The mixtures are prepared in two different ways: one using a carrier fluid to aid in intermixing and another without a carrier fluid but instead dry mixed. For processing using a carrier fluid, mixtures were prepared for only three oxidizers: I₂O₅, nano I₂O₅ and commercial I₂O₅.

1. **Preparation of mixtures in a carrier fluid**
   1. To prepare the samples mixed in a carrier fluid, mix 80 nm Al powder with each oxidizer for a total of two grams of Al and oxidizer mixture to an equivalence ratio of 1.0 in a beaker.
   2. Add 60 ml of isopropanol into the beaker and sonicate the solution with a sonic wand set at an output power of 4 watts programmed for 10 sec on and 10 sec off for a total of 2 min.
   3. Pour solution into a glass dish and allow the solution to evaporate in a fume hood at room temperature with a relative humidity of 20% for 24 hr, which will leave powder samples.
   NOTE: Before proceeding with step 2.1.4, assure razor blade is connected to an electrical ground with a conductive wire to avoid accidental ignition.
   4. Reclaim the powder with a grounded razor blade and sieve the sample to break up agglomerates directly into a container that can be sealed to limit sample exposure to atmospheric water.

2. **Preparation of dry mixed samples**
   1. Sieve and mix two grams of Al and oxidizer mixture with a spatula into a sample container to a fuel to oxygen equivalence ratio of 1.0. Seal the sample container to limit sample exposure to atmospheric water.
   2. Hold samples on a vibration table for 3 minute to aid intermixing. Refer to samples prepared in this way as dry mixed.

3. **Preparation of samples for thermal equilibrium analysis**

   NOTE: These samples react easily with atmospheric water. Relative humidity should be reduced below 30% and exposure to the atmosphere should be limited (i.e., store sample in sealed containers and use lids on DSC-TGA crucibles).
   1. Heat alumina crucibles (supplied with the DSC-TGA diagnostic) to 1,500 °C and hold for 30 min to remove any residue on the crucibles in the DSC-TGA.
   2. Weigh crucibles before the samples are placed in the crucible. This measurement is needed by the DSC-TGA.
   3. After the crucible is weighed, add 10 mg of each sample into a crucible. Place the crucible on the thermocouple in the DSC-TGA with an empty crucible in the reference holder on the DSC thermocouple.
   4. Heat the samples at 10 °C/min to 600 °C in an argon atmosphere.

4. **Energy Propagation**

   1. **Preparation of flame tubes**
      1. Use quartz tubes with an inside diameter of 3 mm and length of 7 cm to contain the powder mixture.
      2. Put tape on one end so powder cannot escape from the tube.
      3. Place each 7 cm tube with one end taped on a scale and zero the scale. This will allow the measurement of just the mass of powder.
      4. Using a spatula with a small end, insert the powders samples into the tube. For each of the mixtures, make three tubes filled with each mixture for repeatability testing.
      5. Using a rod that has a diameter smaller than 3 mm, compact the powder inside the tube for the samples with low bulk densities (i.e., Al + I₂O₅ and Al + amorphous I₂O₅) until the volume of the sample does not change. This procedure is necessary to maintain consistent bulk densities between multiple experiments. This may require 200 mg of powder mixture.
      6. For all other mixtures, which have higher densities, do not compact the powder using external force. Keep the bulk density constant between samples with similar bulk densities. The amount of powder in the tubes will vary depending on bulk density of the powder. This may require up to 500 mg of powder mixture.
      7. Measure the mass of powder mixture in each tube using the balance that was tared for each tube; add mass until the density of the powder is within 5% of the other samples in each group. Make sure each tube is completely filled.

   2. **Preparation of hot wire ignite**
      1. To prepare the hot wire, use a nickel-chromium (i.e., nichrome) wire cut into sections 10 cm long.
      2. Make a "v" shape in the middle of the wire and place the wire so the "v" shape is inside the tube.
      3. Tape this end of the tube so the wire is stationary and no powder can escape the tube.

   3. **Preparation of high speed camera**
      1. Place the high speed camera outside the combustion chamber perpendicular to the direction of flame propagation and focus the camera on the tube through a viewing port in the combustion chamber.
      NOTE: The primary function of the combustion chamber is to protect personnel and equipment from the reacting material and should be ventilated through a fume hood.
      2. Adjust placement and lens of the camera so the lowest resolution (i.e., highest frame rate) can be used.
      3. To allow distance calibration, place a ruler with mm and cm increments in the field of view and take a snapshot with the high speed camera prior to recording flame speeds.
      4. As the flame front is significantly brighter than ambient light and the camera will over-saturate when exposed to the light generated by the reaction, lower the exposure time in the camera settings or add neutral density filters to the lens of the camera to reduce the
amount of light received by the camera sensors. Lower the amount of light received by the camera until the propagation front of the reaction can be seen clearly. Here, set up neutral density filters allowing only 5% of the light to pass, and an exposure time of 1 µsec.

5. Attach a voltage generator to the ends of the wire. The combustion chamber should have insulated leads through the chamber which will allow the chamber to be sealed and allow remote heating of the wire.

6. After the chamber is sealed, set the voltage generator to 10 volts and simultaneously begin the camera recording. When the voltage is applied, the reaction should start almost immediately.

7. Export the video into a software program that will track the position of the flame front as a function of time in each individual frame.

8. Export the distance and time step information into a spreadsheet and plot a linear trend line with R² values. For slower reactions, time is needed for the reaction to reach a steady state. The curve before the steady state will be an exponentially increasing curve. Remove the data that are not in steady state until the R² value is greater than 0.95. The slope of the line is the flame speed.

**Representative Results**

Figure 1a shows the endothermic and exothermic behavior of the initial states for all six oxidizers examined from DSC analysis and Figure 1b shows the corresponding mass loss from TGA analysis. It is noted that all oxidizers when heated beyond the dissociation temperature of I₂O₅ (350 °C) lose 100% mass but the I₂O₅ sample releases I₂ gas instead of water liberated by dehydration of hydrated species at temperatures below the dissociation temperature of I₂O₅. The abundance of I₂ gas released from the I₂O₅ samples is specified in Figure 1b at over 7 wt.%. Figure 1a shows that the only iodine compounds that produce exothermic behavior is I₂O₅ and I₂O₃, formed by decomposition of I₂O₅, and the exotherm corresponds to an onset temperature of about 180 °C for decomposition into I₂O₃. Figure 1b also shows that the iodine compound with the greatest overall iodine gas generation is I₂O₅.

There are no endotherms for commercial and amorphous I₂O₅ samples between 110 °C and 210 °C. This shows that these samples are purely I₂O₅ with no iodic acids. The nano I₂O₅ and I₂O₃ have endotherms with onset temperature at 150 °C. This shows those samples contain I₂O₅₉. The nano I₂O₅ is thermally treated I₂O₅. The small exotherm at 150 °C shows that there is some residual I₂O₃ in the nano I₂O₅ sample. Using the TGA data from Figure 1b, the residual I₂O₅ in the sample is less than 15 wt. %. The I₂O₃ dehydrate has a single endotherm starting at 130 °C and indicates this sample is crystalline HIO₃. The commercial HIO₃ sample has two distinct endotherms starting at 160 °C and 210 °C. An endotherm with an onset temperature of 160 °C is outside of the range of HIO₃ dehydration in the CRC handbook. However, TGA results show a mass loss of 2.47 wt. % over this range indicating it is the dehydration of a hydrated species.

Figure 2a shows the heat flow behavior from DSC analysis of four Al and iodine oxide mixtures. The Al + I₂O₅ dry mixture has an exotherm at 180 °C indicating the oxidizer is still I₂O₅ with an increased onset temperature. The Al + I₂O₃ and Al + nano I₂O₅ samples are almost identical. Both of these mixtures were processed using isopropanol as the carrier fluid to aid intermixing and identical thermal behavior seen in Figure 2a indicating that mixing powders in isopropanol transformed I₂O₅ into I₂O₃.

Figure 2b shows I₂O₅, I₂O₃ exposed to 20% RH for 4 hours, and nano I₂O₅ exposed to 20% RH for 4 hours. After 4 hours exposure to 20% RH, I₂O₅ is identical to nano I₂O₅ and there are endotherms at 110 °C and 210 °C showing the samples are partially composed of HIO₃ and H₂I₂O₅. This may be explained by the I₂O₅ "dry" synthesis method which is then heated and transformed into I₂O₅. The crystal structure of I₂O₅ is not known, but because hydration is observed (Figure 2b bottom two curves with endotherms shaded), the low density of the powder (i.e., fluffy, highly porous nature), and the lack of a reported crystalline structure, an amorphous structure is assumed. Nano I₂O₅ is formed by thermal decomposition of amorphous I₂O₅, according to Eq. (1) such that I₂ is released from amorphous I₂O₅ leaving amorphous I₂O₃. Crystal structure formation of iodine(V) oxides is catalyzed by water. Since the synthesis method is dry, there is no water to catalyze crystal formation. The first step required for absorption of water is to raise the relative humidity to disrupt the bonds between molecules. Without this crystal structure (that wants to release the weakly bonded water) the dynamic equilibrium is shifted so I₂O₅ will absorb any available water. As soon as water is absorbed by I₂O₅, formation of HIO₃ molecules begin. HIO₃ has a hydrogen that attracts oxygen in amorphous I₂O₃ and creates an H₂O₅ crystal structure. Water is still the catalyst in crystal structure formation. The synthesis method of I₂O₃ and I₂O₅ which form an amorphous structure instead of a crystalline structure is the reason water absorption is seen at lower RH (i.e., 20%) than what was required to start absorption in previous studies (i.e., 70-80% RH)¹⁷. In summary, the iodine compounds' amorphous structure may promote absorption of hydrated species and formation of ionic acids.

In Figure 2a the main endotherms around 500 °C are all similar. In the Al + I₂O₅ dry mix, the exotherm at about 180 °C indicates phase transition from I₂O₅ to I₂O₃. Also, all mixtures have a pre-ignition reaction (PIR) between 300 - 400 °C, but Al + I₂O₅ and Al + nano I₂O₅ have a PIR with lower onset temperature and greater magnitude but also show unique endotherms followed by exotherms at 210 °C. These samples were processed in isopropanol and the behavior at 210 °C indicates these samples are partially HI₂O₃. The exotherm may be reaction between HI₂O₃ and I₂O₅ because HI₂O₃ is dissociating at nearly the same temperature as I₂O₅ decomposition. These reactions may help promote greater exothermicity in the PIR and catalyze earlier onset of the PIR. Osborne and Pantoya²⁵ first showed an exothermic reaction preceding the main exothermic reaction in Al combustion and coined this a PIR. Their analysis indicated the PIR reaction was between the alumina shell surrounding an aluminum core particle with fluoride from decomposing fluropolymer²⁶²⁷. Farley et al.²⁶ then extended observations of the PIR to aluminum-alumina core-shell particles reacting with iodine based oxidizers. The Al + commercial I₂O₃ sample has an endotherm at 210 °C indicating HI₂O₃ presence and a mild PIR exotherm with delayed onset temperature. Mulamba et al.²⁸ also showed that the PIR onset temperature is concentration dependent.

Table 1 shows measured flame speed results for Al mix with the indicated oxidizer as a dry mixture and also mixed using isopropanol as the processing carrier fluid. Only the first three samples were tested after being mixed in isopropanol and the Al + commercial HIO₃ dry mix either did not ignite or did not sustain reaction long enough to obtain measureable results. The percent uncertainty is determined based on repeatatability of up to three separate experiments for each mixture. Bulk density is determined as a function of mixture powder mass and volume of the tube.
When interpreting reactivity with flame speed measurements, there are many factors that influence results such as homogeneity of the mixture, particle size, and bulk density. Mixture homogeneity can be optimized using a carrier fluid to aid intermixing of the reactants. The I$_2$O$_5$ examined in this study is more stable than previously studied I$_2$O$_3$ samples and did not appear to decompose into I$_2$O$_3$ or form hydrated species seen in Wikjord et al. (as seen in Figure 1a with only an exotherm corresponding to I$_2$O$_3$ decomposition). However, the only way to observe the combustion performance of Al + I$_2$O$_5$ is by dry mixing with as little exposure to the atmosphere as possible in order to maintain the integrity of I$_2$O$_5$. Additionally, the flame speed measurements of Al with the oxidizers in different states allowed us to narrow the effects that cause variance in flame speed results and reveal differences attributed specifically to particular iodine compounds. These comparisons will be discussed below. Overall Table 1 shows that I$_2$O$_5$ significantly improves reactivity when compared with other iodine compounds.

Mixing in a carrier fluid provides improved distribution of fuel and oxidizer particles that increases mixture homogeneity and reactivity. This is seen in the difference in flame speeds in Table 1 for the dry and isopropanol mixed Al + nano I$_2$O$_5$ and Al + commercial I$_2$O$_5$ samples where the flame speeds increased by 1.07 and 3.34 times, respectively. Mixture homogeneity implicit from the measured flame speed is only slightly improved for the Al + nano I$_2$O$_5$ mixture, whereas the Al + micron scale commercial I$_2$O$_5$ exhibits a three times increase in flame speed when the carrier fluid aids intermixing. Clearly particle size and carrier fluid contribute to measured flame speed. The homogeneity effects can also be seen by the uncertainty between flame speeds. The samples that are mixed in isopropanol and the samples with smaller particles have less uncertainty in measured flame speeds. This small uncertainty is also seen in all of the amorphous samples, which suggests that an amorphous structure facilitates improved homogeneity in dry mixing. It is further noted that each sample was sieved before dry mixing to break up agglomerates and help eliminate uncertainty caused by poor homogeneity.

The HIO$_3$ molecules have a hydrogen end cap, which is electropositive, and an oxygen end cap, which is electronegative and causes an attraction between the ends of individual HIO$_3$ molecules. Because of this attraction, during sieving the HIO$_3$ particles instantly agglomerated before the Al can be mixed. This caused extremely poor homogeneity and is the reason Al + commercial HIO$_3$ samples could not sustain the reaction. The Al + HIO$_3$ dehydrate sample had water available to catalyze crystal structure formation (Figure 1a), which reduced, but did not eliminate this effect.

Energy propagation is dependent on the bulk density of the reactant mixture. The density will change based on the concentration of the reactants, so the bulk density of the mixture is usually reported as the percentage of the theoretical maximum density (TMD). The %TMD is calculated using a weighted average of the concentration and the densities of the reactants and accounts for the density of the actual sample according to its mass and volume occupied. In this way, bulk density in terms of %TMD represents the amount of solid space occupied by the volume (i.e., 60% TMD is equivalent to 40% air voids and 60% solids). Low %TMD usually result in higher flame speeds than high %TMD powders. The higher concentration of air voids with lower %TMD provide convective pathways to enhance flame speeds. For this reason, the flame speeds reported in Table 1 are not comparable as a function of mixture, because each was prepared at a discretely different bulk density.

Two conclusions can be drawn from Table 1: (1) I$_2$O$_5$ cannot be processed in isopropanol because it changes into I$_2$O$_3$ and thus alters its reactivity; and (2) I$_2$O$_3$ is more reactive than I$_2$O$_5$ because at higher and lower bulk densities (i.e., 11% TMD compared with 6 or 17% TMD), I$_2$O$_3$ demonstrates increased reactivity. This finding suggests that I$_2$O$_3$ would be advantageous for reactive applications if it could be passivated to improve stability.

Through reactivity and thermal analysis, results show I$_2$O$_3$ can be more reactive than other forms of iodine(V) oxides when combined with aluminum (Al) powder. The I$_2$O$_3$ sample used here was synthesized using a ‘dry’ method that combines elemental oxygen and iodine such that hydrated species are not introduced at any point during synthesis. For this reason, the I$_2$O$_3$ sample is initially devoid of iodic acids and produces a large exotherm at a low temperature (i.e., 180 °C) corresponding to its decomposition into I$_2$O$_5$. The nano-scale I$_2$O$_3$ particles that are created by thermal decomposition of I$_2$O$_3$ are likely amorphous and produce flame speeds over 1,000 m/sec when combined with Al powder (Table 1). The Al + I$_2$O$_3$ reaction produces flame speeds over 1,500 m/sec. This is the first study to explore the potential of I$_2$O$_5$ as an alternative to I$_2$O$_3$ for energy generation technologies, especially motivated by high iodine gas generation.
Figure 1. DSC Analysis of Heat Flow / TGA Analysis of Mass Loss. 

a) Heat flow behavior from DSC analysis of six oxidizers and shows different states of iodine(V) oxides used in the range of iodic acid dehydration. 

b) Mass loss from corresponding TG analysis.
Figure 2. DSC Analysis of Heat flow. a) Heat flow behavior from DSC analysis for Al + I\(_4\)O\(_9\) dry mix and Al + I\(_4\)O\(_9\), Al + nano I\(_2\)O\(_5\) and Al + commercial I\(_2\)O\(_5\) mixed in isopropanol. Temperature range includes iodic acid dehydration and main reaction temperature range. b) I\(_4\)O\(_9\) initially and I\(_2\)O\(_5\) exposed to 20% RH for 4 hours. Also, the I\(_2\)O\(_5\) was exposed to 20% RH for 4 hours.

| Oxidizer    | Isopropanol Mixed Flame Speed (m/sec) | % Uncertainty | Dry Mix Flame Speed | % Uncertainty | Bulk Density Dry Mix (g/cm\(^3\)) | Dry Mix %TMD |
|-------------|--------------------------------------|---------------|---------------------|---------------|-----------------------------------|--------------|
| I\(_4\)O\(_9\) | 1,261*                               | 0.4           | 1,551               | 3             | 0.48                              | 11.7         |
| Nano I\(_2\)O\(_5\) | 1,146                               | 4.5           | 1,070               | 3.7           | 0.33                              | 8            |
| Commercial I\(_2\)O\(_5\) | 719                                | 5.5           | 215                 | 46.5          | 0.93                              | 22.6         |
| Amorphous I\(_2\)O\(_5\) | NM                                 | NM            | 1,085               | 0.3           | 0.73                              | 17.8         |
| HIO\(_3\) Dehydrate | NM                                 | NM            | 393                 | 12            | 0.8                               | 19.3         |
| Commercial HIO\(_3\) | NM                                 | NM            | 1                  | 1.11          | 27.1                              |              |

Table 1. Flame Speed Results. Flame speed results for Al + oxidizer indicated in first column. NM indicates not measurable. * Indicates I\(_4\)O\(_9\) was decomposed into I\(_2\)O\(_5\) during mixing.

Discussion

The I\(_2\)O\(_5\) powder studied here was synthesized using a "dry" approach to form I\(_2\)O\(_5\) by combining elemental iodine and oxygen. This sample is referred to as I\(_2\)O\(_5\). Nano-particle I\(_2\)O\(_5\) was also synthesized for this study. Specifically, a portion of I\(_4\)O\(_9\) was heated past the dissociation temperature of I\(_2\)O\(_5\) (i.e., 180 °C) but under the dissociation temperature of I\(_2\)O\(_5\) (400 °C). This process results in particles with a diameter between 200-400 nm. This sample is referred to as nano I\(_2\)O\(_5\). Particle size measurements were obtained by TEM which requires the sample to be in a vacuum. However, I\(_2\)O\(_5\) dissociates into I\(_2\)O\(_5\) in a vacuum, so dimensions of I\(_2\)O\(_5\) were not obtained directly. Because the nano I\(_2\)O\(_5\) particle diameters are between 200-400 nm and synthesized by heating the I\(_4\)O\(_9\) sample, it is assumed that I\(_2\)O\(_5\) has similar diameters.

A more common approach to synthesizing I\(_2\)O\(_5\) is by thermal dehydration of iodic acid to form I\(_2\)O\(_5\)\(^{1,2,8}\) and material made using this process is commercially available. The commercial I\(_2\)O\(_5\) is received as coarse crystals and can have different concentrations of iodic acids depending on storage and handling conditions. To ensure samples are pure I\(_2\)O\(_5\), the samples are dehydrated prior to use as explained in step 2.1.1.3. The diameter of the particles in this sample are between 1-5µm. This sample is referred to as commercial I\(_2\)O\(_5\).

The amorphous I\(_2\)O\(_5\) sample is made from this saturated IO\(_3\) solution. When I\(_2\)O\(_5\) is mixed with water, a solution of IO\(_3\) is created. This is done in step 2.1.2 and these steps will leave a saturated IO\(_3\) solution. Water catalyzes the formation of crystals in iodic acids. To form amorphous I\(_2\)O\(_5\)
the temperature must be above the dehydration temperature of H$_2$O$_2$ and heated at a rate that will not allow a crystal structure to form, this is done in step 1.2. The concentration of I$_2$O$_5$ in solution will determine the amount of amorphous I$_2$O$_5$ created during dehydration. These samples should turn red after dehydration indicating the sample is an amorphous form of I$_2$O$_5$. This sample is referred to as amorphous I$_2$O$_5$. Also, XRD analysis (not included) was performed and confirmed the amorphous structure of the I$_2$O$_5$ and amorphous I$_2$O$_5$ samples.

When in solution, HIO$_3$ will release excess water and create a crystal structure. The time needed to evaporate the excess water is dependent on the size of the beaker, RH, and concentration of the IO$_3$ solution. In our lab at 20% RH mixing in the manner discussed above, 3-5 days were required to evaporate excess water from the samples. The solution will turn into a solid clear crystal. This process is shown in step 2.1.3 and the sample referred to as HIO$_3$ dehydrate. Iodic acid will be referred to as commercial HIO$_3$.

When exposed to solution or atmospheric water, iodine(V) oxide undergoes chemical reactions that change the composition of the final product. To mitigate this transformation, all six oxides are also mixed with Al without solution.

Thermal analysis using DSC-TGA was calibrated in an argon atmosphere using samples with known onset temperatures and mass losses. A flame tube apparatus known as a Bockmon Tube$^{20}$ is used to measure flame speeds. Flame speed experiments are sensitive to the bulk density of the mixture. Pantoya et al. showed that for nano-Al based thermite, increasing bulk density can suppress the Al reaction mechanism and reduced the role of convective energy transport thereby retarding flame speed$^{25}$. For this reason, experiments performed for different mixtures are usually designed to keep a constant bulk density. However, the physical and chemical properties of the oxidizers examined here vary dramatically such that it was not possible to obtain consistent bulk density with all six dry mixtures. Because of this, multiple iodine oxides with different physical and chemical properties are tested to provide a basis of comparison which includes differences in %TMD, crystal structure, and hydration states. After the powder has been placed inside the tubes and measured, hot wire is used to remotely ignite the mixture.

After the flame tubes are prepared with powder mixture, flame speeds are measured in a combustion chamber using a high-speed camera. The frame rate of the camera can be increased by lowering the resolution. Reducing the resolution to increase frame rate will produce less error than higher resolution at a slower frame rate. This is why, in step 4.2.2, the lowest resolution that can still image the entire flame tube is used, this will increase the maximum frames per second the camera can record without losing information. For our chamber, a resolution of 256 x 86 was used which allowed the camera to record at 300,000 fps.

Quantifying flame speeds in highly reactive mixtures is inherently difficult because of the large number of variables that can influence reactivity (i.e., mixture homogeneity, particle size, density, propagation direction, propagation velocity, etc.). By using a quartz tube with an inside diameter less than 4 mm in combination with a high speed camera with neutral density filters, the direction of propagation is controlled (i.e., 1-D) and the amount of light that is received by the camera can be reduced to a minimum threshold such that the leading edge of light emitted by the reaction can be seen and measured clearly. This measurement assumes that the progression of this low light level is at the same rate as the reaction front. For this reason, photodiodes may not be as accurate for tracking the reaction propagation because the high light intensity of emission may cause light to travel and saturate the sensors faster than the reaction. Also, the first 1-2 cm of tube length is considered an entrance region, or region of unsteady or accelerating propagation. Linear measurements of distance as a function of time must be taken beyond this entry region to determine steady state flame speed.

The DSC/TGA is a thermal equilibrium analysis that shows detailed reaction kinetics that cannot be observed in highly reactive materials (i.e., cannot be observed under non thermal equilibrium conditions). The combination of DSC/TGA analysis and flame speeds give specific information on differences in the reaction kinetics that may have implications for differences in the flame speed results. Because of this, the combination of these two measurement methods is a powerful tool for understanding and controlling highly reactive materials.

Disclosures

All authors have no competing financial interests or other conflicts of interest.

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