



Performance of iodine oxides/iodic acids as oxidizers in thermite systems



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ABSTRACT

Iodine oxides are of interest as biocidal components in energetic application such as thermites due to their high energy release and biocidal agent delivery. In this study, various iodine oxides/iodic acids, including I_2O_5 , HI_3O_8 and HIO_3 , were employed as oxidizers in thermite systems. Their decomposition behaviors were studied using a home-made time resolved temperature-jump/time-of-flight mass spectrometer (T-Jump/TOFMS), which identified a single step decomposition for all oxides at high heating rates ($\sim 10^5$ K/s). In addition, both nano-aluminum (nAl, ~ 80 nm) and nano-tantalum (nTa, < 50 nm) were adopted as the fuel in order to fully understand how iodine containing oxidizers react with the fuel during ignition. The ignition and reaction process of nAl-based and nTa-based thermites were characterized with T-Jump/TOFMS, and their combustion properties were evaluated in a constant-volume combustion cell and compared to a traditional thermite system (nAl/CuO). The ignition temperatures of nAl-based thermites using these oxidizers were all very close to the melting point of aluminum (~ 660 °C), which suggests that the mobility of the aluminum core dominates the ignition/reaction and the gaseous oxygen released from the decomposition of the oxidizer does not participate in the ignition until the molten aluminum is available. Unlike nAl-based thermites, the ignition temperatures of nTa-based thermites are lower than the oxygen release temperatures from the corresponding bare oxidizers. All nTa-based thermites ignited prior to the release of gas phase oxygen. In this case, a condensed phase reaction mechanism is proposed to dominate the ignition process. Moreover, combustion cell tests results show that nAl/a- HI_3O_8 has the highest pressurization rate and peak pressure and shortest burn time, and since it also has an iodine content of $\sim 75\%$ as high as I_2O_5 on a per mass basis, this material may be a very promising candidate in biocidal application.

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1. Introduction

High efficiency neutralization of biological warfare agents has become a major research focus within the United States, in addition to many other countries, due to the increased threat of bioterrorism [1–7]. Preliminary laboratory studies have suggested that an ideal neutralization process should contain not only a high thermal but also long-lasting biocidal agent release [8–14]. The main problem with conventional energetic materials is low neutralization efficiency since a thermal neutralization mechanism is dominant in this case [8]. Therefore, it has been proposed that simultaneously delivering a rapid thermal pulse with a remnant

biocidal agent would prolong the exposure time and improve the inactivation process [15]. Halogens-based energetic materials show the most promise because of their excellent biocidal properties [16] when compared to silver-containing energetic materials [17–19]. To incorporate halogens in energetic materials, one can either directly add halogens into the system or assemble halogens into the oxidizers [16,20]. Wang et al. incorporated iodine molecules into Al/CuO thermite systems and found that the Al/CuO/ I_2 thermite reaction rate was significantly decreased with increasing the iodine content [21]. Guerrero et al. also showed that mechanical incorporation of iodine into aluminum severely decreases the reaction rate of Al/metal oxides mixtures and even resulted in failed ignition of Al- I_2 /Fe $_2$ O $_3$ [22]. In addition, Dreizin et al. employed mechanically alloyed aluminum–iodine composites as a replacement of aluminum as a fuel additive in energetic formulations and the ignition and combustion tests of those fuels in air indicated that higher iodine concentration lowers ignition tem-

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peratures but did not affect the combustion temperatures substantially [14]. They also found improvements in terms of pressurization rate and maximum pressure at constant volume with 15 wt.% and 20 wt.% of I_2 [14]. Furthermore, an effective inactivation of aerosolized spores were achieved using Al/ I_2 and Al/B/ I_2 composites with 15–20 wt.% of iodine [16].

Another approach is to use iodine-containing oxy-compounds that can release HI or I_2 when used as an oxidizer [23]. Iodine-containing oxy-compounds can be broken down into two main categories: metal iodates and iodine oxides/iodic acids. The metal iodates, $AgIO_3$ [8,24], $Bi(IO_3)_3$ [25], $Cu(IO_3)_2$ [15], $Fe(IO_3)_3$ [15] etc., have been previously investigated. One issue with employing metal iodates in thermites is that part of the produced I_2 vapor (all for $AgIO_3$) may react with the product metal particles to form corresponding metal iodides, which lowers the effective iodine content in the metal iodate-based thermite systems. Unfortunately, there are only a limited number of iodine oxides/iodic acids which are relatively stable and obtainable. These include I_2O_5 , I_4O_9 , HI_3O_8 , HIO_3 , H_5IO_6 , etc. [26–28]. Among these compounds, I_2O_5 (~76% iodine mass fraction) is the most studied in thermite systems [29–33]. In these studies, aluminum particles with different sizes were chosen as the fuel due to its high reaction enthalpy, thermal conductivity and availability. With reported propagation velocities of up to ~2000 m/s for loose ball-milled nAl and nano-scaled I_2O_5 (~10 nm) [32], I_2O_5 shows its high potential in aluminum-based thermites as an extremely aggressive oxidizer. Constant volume combustion tests also show nAl/micro- I_2O_5 outperforms traditional aluminum-based thermites such as Al/CuO and Al/ Fe_2O_3 [33]. A pre-ignition reaction was proposed as the ignition trigger in which ionic I_2O_5 fragments diffused into the alumina passivation shell of aluminum and to create some reactive complexes exothermically [31,34]. However this mechanism is far from clear as Smith et al. reported that a pre-ignition reaction was not found for aluminum/nano crystalline I_2O_5 reaction in contrast to nano amorphous I_2O_5 case [35].

Recently, Smith et al. reported that a minimum of 150% increase in flame speed was found for Al/amorphous I_4O_9 compared with Al/ I_2O_5 indicating I_4O_9 has more reactive potential than I_2O_5 as an oxidizer when combined with aluminum [36]. Other iodine-containing oxy-compounds have received comparatively much less attention due to their relatively lower iodine content and availability. Nevertheless, their iodine content is still much higher than metal iodates or per-iodates on a per mass basis. This is particularly so for HI_3O_8 , which has an iodine content of ~75% and very close to the 76% for I_2O_5 . Currently no comparative study examining how the aforementioned iodine oxides/iodic acids perform as oxidizers in thermites system is available. Moreover, we have recently reported that iodine oxides/iodic acids with different particles' sizes can be prepared via either aerosol spray pyrolysis (ASP) or thermal treatment [37,38], making a variety of these materials readily available.

Most of the focus on reactive studies of oxidizers has focused on Aluminum as the fuel. Aluminum has a passivating alumina shell that stabilized the material at ambient conditions. However once the aluminum core reaches near the melting temperature, it can diffuse through the oxide shell and interact with any available oxidizer leading to ignition [39]. To explore the fuel melting aspect of ignition, we also explore in the paper tantalum as a fuel because it has a melting point of ~3000 °C, and thus would not be melted at the point of ignition.

In this paper, we examine the performance of various iodine oxides/iodic acids (I_2O_5 , HI_3O_8 and HIO_3) as oxidizers in nAl-based and nTa-based thermites system. Iodine-containing oxides/acids were prepared via an ASP method following procedures in our previous work [37]. Time-resolved temperature-jump time-of-flight mass spectrometer (T-Jump/TOFMS) was used to study the ignition

and decomposition of nAl-based and nTa-based thermites. A high-speed camera simultaneously captured optical emission from the ignition/reaction of the thermites allowing for the ignition time, and corresponding ignition temperature. In addition, constant volume combustion cell tests were performed on aluminum-based thermites.

2. Experimental

2.1. Materials

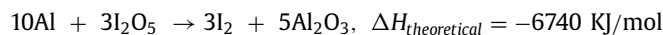
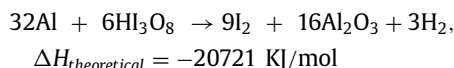
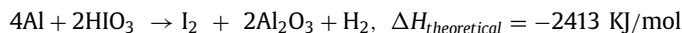
The aluminum nanopowders (nAl) (Alex, ~80 nm) were purchased from Novacentrix. The active Al was 81% by mass, determined by TGA. Nano-tantalum powders (nTa, <50 nm) were purchased from Global Advanced Metals, with 70% of the mass. Iodic acid (c- HIO_3) (99.5 wt %), iodine pantoxyde (c- I_2O_5), CuO nanoparticles (n-CuO, <50 nm) and micro-sized CuO powders (m-CuO) purchased from Sigma-Aldrich were directly used as received ("c" represents commercial product; "n" and "m" represents nano-scaled and micro-scaled sizes, respectively). All other chemicals were of analytical grade and were used as purchased without further treatment.

2.2. Preparation of iodine oxides/iodic acids particles

Small-sized (<1 μ m) particles of oxides includes δ - HIO_3 , a- HI_3O_8 and a- I_2O_5 were synthesized via aerosol spray pyrolysis (ASP). Here, "a" represents ASP and " δ " refers to HIO_3 with a delta phase. Detailed information on the ASP synthesis method has been previously described [37]. Briefly, 100 mL iodic acid solution (10 mg/mL) was aerosolized (~1 μ m in diameter) with a home-made pressure atomizer (~35 psi pressure air) and passed through a silica-gel diffusion drier to remove water. The dry particles are then passed through a tube furnace for chemical conversion. The furnace temperature was set at ~230 and ~375 °C to obtain either δ - HIO_3 or a- I_2O_5 , respectively with a residence time of about 1 s. For both δ - HIO_3 and a- I_2O_5 , silica-gels were regenerated at 50 °C. We find that δ - HIO_3 can be obtained within a large range of temperature from 210 to 250 °C. In addition, a- HI_3O_8 was obtained with a tube furnace temperature ~250 °C with a silica-gel regeneration temperature of ~80 °C. The final product was collected on a Millipore membrane filter (0.4 μ m pore). HI_3O_8 was also prepared via thermal treatment of commercial HIO_3 at ~180 °C and labeled as t- HI_3O_8 . The final product was characterized by scanning electron microscopy (SEM, Hitachi, SU-70 FEG-SEM) and powder X-ray diffraction (XRD, Bruker D8 Advance using Cu K α radiation).

2.3. Preparation of thermites

Physically mixed stoichiometric mixtures of nAl and nTa with δ - HIO_3 , c- HIO_3 , a- HI_3O_8 , t- HI_3O_8 , a- I_2O_5 , c- I_2O_5 , and CuO were based on the following equations. The mixtures were sonicated in dry hexane for 30 min, and left uncapped at room temperature in a low-pressure desiccator to evaporate the solvent. All of the samples employed in this work were stored in a sealed desiccator for future use. Below we list the stoichiometric relations used to prepare the mixture ratios and the associated enthalpy of reactions.



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