



Research paper

Oxidation and decomposition mechanisms of air sensitive aluminum clusters at high heating rates



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ABSTRACT

Molecular near zero oxidation state clusters of metals are of interest as fuel additives. In this work high heating rate decomposition of the Al(I) tetrameric cluster, $[\text{AlBr}(\text{NEt}_3)]_4$ ($\text{Et} = \text{C}_2\text{H}_5$), was studied at heating rates of up to 5×10^5 K/s using temperature-jump time-of-flight mass spectrometry (T-jump TOFMS). Gas phase Al and AlH_x species were rapidly released during decomposition of the cluster, at ~ 220 °C. The activation energy for decomposition was determined to be ~ 43 kJ/mol. Addition of an oxidizer, KIO_4 , increased Al, AlO, and HBr signal intensities, showing direct oxidation of the cluster with gas phase oxygen.

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1. Introduction

Metal fuels such as aluminum have been employed as additives for propellants and explosives due to their high volumetric energy densities. In a recent study, we demonstrated burn rate enhancements in a liquid hydrocarbons using a hydrocarbon soluble molecular aluminum cluster, with a near zero oxidation state, as an accelerator [1]. Specifically, there is a significant enhancement in droplet burn rate with small additions of a Al(I) tetrameric cluster, $[\text{AlBr}(\text{NEt}_3)]_4$ ($\text{Et} = \text{C}_2\text{H}_5$) [1]. While the combustion characteristics of aluminum cluster materials are largely unknown, the more well-studied nanosized metal particles show faster reaction kinetics and lower ignition temperatures relative to their micron-sized analogs [2]. However, with decreasing particle size, the contribution of the native oxide layer to the total mass of the particle significantly increases, thereby reducing the energy content of the particles [3,4]. In addition, the native oxide creates a barrier between the metallic fuel and any oxidizer that limits the reaction kinetics. Molecular aluminum compounds with sufficient ligand stabilization offer an intriguing alternative to nano-aluminum fuels in that oxide coatings may be circumvented giving rise to potentially new combustion mechanisms and enhanced oxidation kinetics [5,6]. However, until fundamental properties of these clus-

ters are studied, such as their compatibility with oxidizers in a composite, their utility as a fuel remains unclear.

Because the oxidation mechanisms of ligated Al clusters are unknown, their combustion characteristics are difficult to predict. For example, if combustion of the ligand shell precedes the combustion of the Al core, then any enhancement in combustion rate relative to Al NPs may be overshadowed. Simulations by Hooper and coworkers [7–9] suggest that oxidation of aluminum precedes that of the ligand shell in Cp^*_4Al_4 clusters but mechanistic experimental data on these processes are necessary to further develop these models. To study aluminum cluster oxidation, we require the ability to investigate air-sensitive compounds via thermally-activated chemistry on a time scale and with heating rates nominally associated with an ignition event encountered in combustion, as previous studies have demonstrated that reaction pathways can vary greatly between slow and fast heating [10–12]. In prior work, we have employed a temperature-jump time-of-flight mass spectrometer (T-jump TOFMS) to probe decomposition of nitrocellulose and RDX [13], the reaction mechanisms of nanothermite systems [14–17], and activation energies for oxygen release from metal oxides [18].

In this study, we build on our previous work on T-jump TOFMS with the incorporation of an air sensitive sample holder (ASSH) capable of heating samples at rates of up to 5×10^5 K/s [13]. The ASSH enables loading of air sensitive samples in a glove box and transfer to the TOFMS without ambient exposure. In this paper we study the high heating rate decomposition of $[\text{AlBr}(\text{NEt}_3)]_4$ in an oxygen-free environment as well as its oxidation with bismuth

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oxide (Bi_2O_3) and potassium periodate (KIO_4). These results also demonstrate that a molecular aluminum fuel ($[\text{AlBr}(\text{NET}_3)]_4$) can be in immediate physical contact with a strong oxidizer (KIO_4 or Bi_2O_3) and remain stable under an inert atmosphere.

2. Experimental

2.1. Materials

The tetrameric Al(I) cluster $[\text{AlBr}(\text{NET}_3)]_4$ was synthesized from an $\text{AlBr}\cdot\text{NET}_3$ starting material produced in a Schnöckel-type metal halide co-condensation reactor (MHCR) [19–21]. A rendering of the cluster's crystal structure is shown in Fig. 1.

Bismuth oxide (Bi_2O_3) nanopowder was purchased from Sigma Aldrich. Potassium periodate (KIO_4) nanoparticles were prepared by dissolving KIO_4 (Sigma Aldrich) in distilled water and then using a previously described aerosol based spray drying procedure [22]. Hexane was dried over sodium benzophenone ketyl and stored over activated 3Å molecular sieves.

2.2. Air sensitive sample holder

A custom-built air-sensitive sample holder (ASSH) was used with a previously described temperature-jump time-of-flight mass spectrometer (T-jump TOFMS) [13]. The ASSH uses a $\sim 25\ \mu\text{m}$ thick aluminum foil membrane to prevent oxygen exposure of the sample while transporting the holder to the TOFMS. The membrane is sealed using a gasket compressed by a threaded cap at the end of a stainless steel housing that surrounds the T-jump probe. A 3D printed collar (designed in SolidWorks and printed using a Stratasys Objet30 Pro) was fixed to the electrical feedthrough of the T-jump probe. This collar punctures the aluminum foil membrane when inserted into the TOFMS.

2.3. Sample preparation

Samples were prepared in a glovebox with 2 mg of combined solids suspended in 1 mL of dry hexane. Mixed samples containing the $[\text{AlBr}(\text{NET}_3)]_4$ cluster and Bi_2O_3 or KIO_4 (1:3 cluster to oxidizer ratio by mass) were sonicated for 10 min in a sealed, oxygen-free vial. Samples were loaded as a suspension in hexanes via autopipette onto 76 μm platinum (Pt) wires held by the ASSH within the glove box. The ASSH sample holder was then capped under inert atmosphere, removed from the glovebox, and transferred to the TOFMS.

2.4. Sample analysis

During standard operation, the roughing chamber of the TOFMS is pumped and purged with UHP nitrogen (N_2) gas prior to mount-

ing the ASSH. N_2 was chosen over argon due its lower background signal intensity. A positive pressure of N_2 is maintained in the roughing chamber during mounting of the ASSH, after which the aluminum foil membrane is punctured and the roughing chamber evacuated to ~ 0.5 torr. Once the roughing chamber is evacuated, the gate valve to the main chamber of the TOFMS is opened and the sample inserted. When the system is under vacuum, the platinum wires are resistively heated within the TOFMS (sampling rate = 10 kHz) with time resolved wire temperatures calculated using the Callendar-Van Dusen equation. A 600 MHz digital oscilloscope was used for data acquisition. To perform activation energy analysis, wire heating rates were varied between 1×10^5 and 5×10^5 K/s by increasing or decreasing the pulse width and/or driving voltage of the heating circuit. With the exception of the experiments used in determining the activation energy, a heating rate of $\sim 4 \times 10^5$ K/s was employed. All mass spectra signal intensities were normalized to the maximum signal intensity of $m/z = 86$ (the predominant fragment observed from electron impact ionization of NET_3) unless otherwise noted.

3. Results and discussion

3.1. Thermal decomposition of $[\text{AlBr}(\text{NET}_3)]_4$ during rapid heating

Analysis of the decomposition of $[\text{AlBr}(\text{NET}_3)]_4$ was performed on both oxidized and unoxidized samples. Analysis of the data was complicated by the fact that the mass of aluminum ion ($m/z = 27$) also corresponds to the mass of any ethyl fragments generated by the direct decomposition of triethylamine (NET_3). Unfortunately, the analogous trimethylamine and tripropylamine complexes of AlBr are not known, which precludes the resolution of the mass degeneracy by chemical substitution. When ionized using electron impact ionization, pure NET_3 has multiple mass envelopes between the m/z values of 27 and 101 with the highest relative signal intensity corresponding to the $m/z = 86$ fragment [23]. Since the peak at $m/z = 86$ is solely a result of NET_3 decomposition, we employed it as an internal reference standard to normalize the signal intensities. Fig. 2 shows the spectra at the time of the maximum absolute $m/z = 86$ signal intensity for the unoxidized $[\text{AlBr}(\text{NET}_3)]_4$ introduced via ASSH (Fig. 2a), and after exposure to the ambient atmosphere for ~ 3 h (Fig. 2b).

We find that peaks corresponding to m/z values of 27, 28, 29, and 30 have much higher signal intensities prior to oxidation (Fig. 2a). When exposed to oxygen, the NET_3 remains intact but the Al in the cluster oxidizes, resulting in decreased signal intensities in the 27–30 mass envelope seen in Fig. 2b. The spectrum of the oxidized cluster in Fig. 2b also shows an increased H_2O signal intensity and the presence of AlO and HBr species (discussion below). To highlight the differences in the decomposition of unoxidized and oxidized $[\text{AlBr}(\text{NET}_3)]_4$, a difference plot was generated using the normalized spectrum at the time of maximum $m/z = 86$ signal intensity for the oxidized sample and the unoxidized sample as seen in Fig. 2c. The difference spectrum removes all peaks associated with NET_3 decomposition and highlights the Al containing species in the anaerobic sample and the H_2O , AlO, and HBr in the oxidized signal. The increased normalized signal intensity of the $m/z = 27$ peak of the unoxidized sample affirms that reactive aluminum is present in the system and is being generated during decomposition of the cluster. During rapid decomposition under anaerobic conditions, the Al(I) tetrameric cluster will presumably react with hydrogen-containing fragments from the NET_3 . Thus, we conclude that signals in the 27–30 m/z range in the difference spectrum (Fig. 2c) correspond to Al, AlH, AlH₂, and AlH₃.

The observed Br and HBr in the oxidized sample is a result of hydrolysis of $[\text{AlBr}(\text{NET}_3)]_4$ [4]. In the presence of air, the aluminum

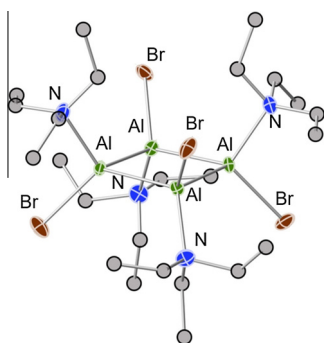


Fig. 1. X-ray crystal structure of $[\text{AlBr}(\text{NET}_3)]_4$ [21]. Thermal ellipsoids drawn at 50% probability level. Unlabeled grey spheres represent carbon; hydrogen atoms omitted for clarity.

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