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Evidence of a Kinetic Isotope Effect in Nanoaluminum and Water Combustion[**]

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***Abstract:** The normally innocuous combination of aluminum and water becomes violently reactive on the nanoscale. Research in the field of the combustion of nanoparticulate aluminum has important implications in the design of molecular aluminum clusters, hydrogen storage systems, as well as energetic formulations which could use extraterrestrial water for space propulsion. However, the mechanism that controls the reaction speed is poorly understood. While current models for micron-sized aluminum water combustion reactions place heavy emphasis on diffusional limitations, as reaction scales become commensurate with diffusion lengths (approaching the nanoscale) reaction rates have long been suspected to depend on chemical kinetics, but have never been definitely measured. The combustion analysis of nanoparticulate aluminum with H_2O or D_2O is presented. Different reaction rates resulting from the kinetic isotope effect are observed. The current study presents the first-ever observed kinetic isotope effect in a metal combustion reaction and verifies that chemical reaction kinetics play a major role in determining the global burning rate.*

The study of the mechanism of combustion dates back to the foundation of the scientific method itself, yet even with systems as seemingly mundane as a burning candle, insights are still being made.[1] However, with the introduction of more complex systems, such as combustion in nanoparticulate metals, this problem becomes even more confusing. Relatively recently, nanoaluminum (nAl) has been suggested for a myriad applications in advanced energetic materials such as superthermites, hydrogen generators, and propellants which utilize extraterrestrial water for interstellar travel. Nanoaluminum can be considered a core–shell nanoparticle with a center of elemental aluminum and a 2–5 nm shell of amorphous Al_2O_3, which prevents further oxidization of the very reactive aluminum. Because of the highly reactive nature of nAl, its combustion with balanced amounts of liquid or solid water has recently been observed.[2] The ability for aluminum/water mixtures to sustain self-propagating combustion allows for the direct determination of reaction rates and, as this work demonstrates, the application of the kinetic isotope effect (KIE) as a simple yet effective method to interrogate the reaction mechanistically (Figure 1). The better understanding of nanoparticulate aluminum reactivity will also augment the understanding of aluminum reactivity on the microscale, and also that of near atomic level $Al_{7\text{-}18}^-$ clusters, whose reactivity with water has also been recently studied.[3]

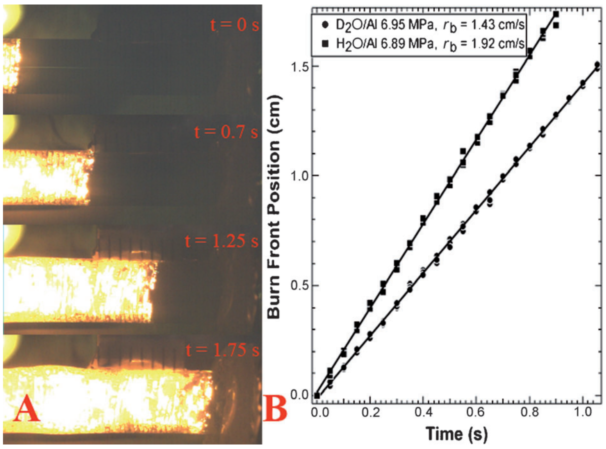

Figure 1. a) Burning-rate sequence of 80 nm aluminum + D_2O at 6.9 MPa. b) The determined rate from flame front position versus time of 80 nm aluminum with both H_2O and D_2O.

The kinetic isotope effect (KIE) has long been applied to the study of chemical kinetics and is a powerful tool for the determination of reaction mechanisms, and has also been applied to mechanistic studies on the combustion reaction of organic energetic materials.[4] In one study, the explosive octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) was synthesized with either H or D, and rates of combustion were determined at various pressures.[4d] The observation of a ratio of k_H/k_D of greater than 1.35 is the accepted experimental minimum for a high-temperature kinetic isotope effect, while greater than 1.41 is the theoretical minimum.[4b] A primary KIE was observed, thus giving

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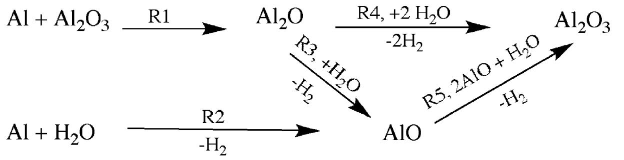
evidence of the rate-limiting step in decomposition, but also importantly, the role of kinetic control in the combustion rate was verified. A similar approach was taken in this work, and it is the first reported application of the KIE in the study of metal combustion, and also likely the highest-temperature isotope effect study recorded.

Early models of the combustion process of micron-sized aluminum were introduced both by Glassman and Law, and later expanded upon by Brooks and Beckstead.[5] These models are analogous to hydrocarbon droplet combustion in that endothermic surface reactions of the particle are driven by the heat input of exothermic reactions in the gas-phase flame. Aluminum, like any metal that can support combustion, has a boiling point which is much lower than that of its final oxide.[5c] Volatilization of aluminum occurs, leading to gas-phase reactions, to create aluminum suboxides which condense to the final oxide state of Al_2O_3. In this process, when considering relatively large microaluminum particles, mass and heat transport are the rate-limiting processes. Vaporization of the metal and reaction kinetics with oxidizers are so fast, comparably, that they have been assumed to be instantaneous.[5a,b]

Scheme 1 illustrates possible pathways to the final aluminum oxide via reaction with water. Because microaluminum contains negligible Al_2O_3 relative to active elemental aluminum, little attention has been given to reactions of aluminum and Al_2O_3 with one another. In fast-heating conditions prior to exposure to an oxidizer gas, Al and Al_2O_3 can react to produce the gaseous suboxide Al_2O (R1 in Scheme 1). With nAl this could be one of the primary first steps in combustion, as it can contain 20–53 % Al_2O_3 as the passivating shell. This reaction is well known, with rates having been determined by aluminum sublimation into Al_2O_3 at about 1400–1900 K.[6] Al_2O was also observed from rapid heating (T-Jump/TOFMS) of nAl in an inert environment,[7] although the mechanism in R1 was not identified in this work. In shock-tube studies with various oxidizer gases, AlO is the primary intermediate species observed by absorption spectroscopy, and Al_2O is not observed.[8] This result suggests that R5 is relatively slow compared to either R2 or R3, and AlO can reform at combustion temperatures because of dissociation of Al_2O_3.[6] Detailed steps of R2 are described experimentally by McClean et al.,[9] and theoretically by Sharipov et al.[10]



Scheme 1. Possible pathways of for conversion of aluminum into a suboxide vapor state and final liquid or solid oxide state.

While historic work has made the assumption that the rates of the aluminum combustion reaction at larger particle sizes (ca. 1 μm and above) are solely diffusion limited, recent work by Bazyn et al. has indicated that there may be a transition away from strictly diffusion control for particles of less than 10 μm.[5b,8b,11] Without a direct means to observe the relative contributions from diffusion versus kinetic control, predictive models for the vapor-phase combustion of metals assume infinitely fast kinetics relative to diffusion. However, as demonstrated in this work by the KIE, during the combustion of nAl, size scales are sufficiently small that the diffusion of reactants are no longer rate-limiting, and differences in reaction kinetics play a significant part in global reaction rates.

The process of nAl combustion is a complex mixture of chemical and physical processes, with differing theories of how the combustion occurs. Three proposed mechanisms are a) solid diffusion of oxygen or aluminum through alumina in the shrinking-core model, b) the melt-dispersion mechanism (MDM) in which explosive spallation of aluminum occurs because of mechanical stresses imposed on the alumina shell by expanding liquid aluminum, or c) a vapor-phase reaction of aluminum species with surrounding oxidizers, as is suggested by this study.[8b,12] Further consideration may also be necessary regarding melting behavior at the nanoscale. Recently, it has been shown that nanostructured Fe_3O_4 melts at temperatures more than 800 °C lower than the bulk oxide.[13] While water is required for KIE studies of aluminum oxidation, implications of the physical reaction mechanism can be expanded to gas-phase reactions with other oxidizers. Observation of a KIE implies a vapor-phase reaction in nAl combustion, as diffusional control of reaction rates would eliminate any notably observable kinetic effects. The MDM is unlikely, as the generation of explosive pressures within the nAl particle is thought to be rate-limiting, and thus would be independent of kinetics. The MDM also ignores Al/Al_2O_3 reactions which form gaseous suboxides so that a coherent alumina shell is intact to fulfill the model.

Aluminum particles with diameters of 38, 80, and 110 nm were mixed with either H_2O or D_2O at an equivalence ratio of one (oxygen balanced to form all Al_2O_3 and H_2) and burning rates were determined. A full profile of burning rate versus pressure of mixtures with 38 and 80 nm aluminum was determined, and replicates at selected pressures were performed for 110 nm aluminum. Figure 1 a shows an image sequence from high-speed video recording of the burning-rate determination of 80 nm aluminum with D_2O at 6.9 MPa.

Burning rates were determined with a least squares fit of the burning front position, measured from frames of high-speed video footage, as a function of time. One example of a determined rate at about 6.9 MPa is shown in Figure 1 b. Individual rates (r_b) are plotted versus pressure (p) and fit to $r_b = ap^n$ as shown in Figure 2, where, a is the pre-exponential factor and n is the pressure exponent. From these results, the 80 nm Al/H_2O or D_2O burning rates were calculated at specific pressures and the ratios $r_b(H)/r_b(D)$ are given in Table 1. This methodology allowed the smoothing out of minor inconsistencies in ratio determination resulting from scatter in the data. Pressures of 1.000, 2.760, and 6.895 MPa were selected for ratio determination, and as seen in Table 1 result in a ratio between 1.38 and 1.39.

The existence of the KIE alone implies a significant amount of kinetic control in the combustion reaction of nAl and H_2O, and to date has not been directly observed. The lack

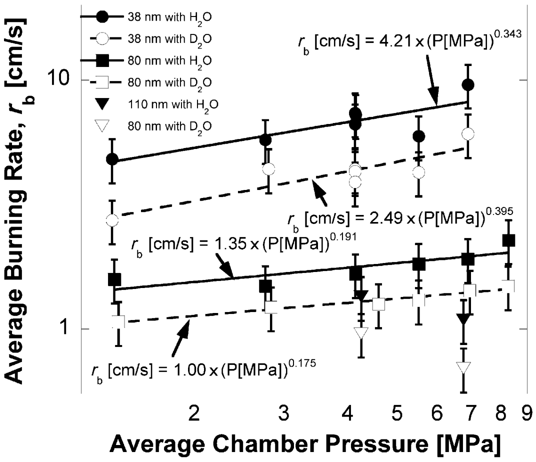


Figure 2. Average burning rate versus pressure for 38, 80, and 110 nm aluminum with either H_2O or D_2O.

Table 1: Burning rates [cm s^{-1}] obtained from curve fits for 80 nm Al with H_2O or D_2O and $r_b(H)/r_b(D)$.

Pressure [MPa]	r_b(H)	r_b(D)	$r_b(H)/r_b(D)$
1.000	1.354	0.9797	1.382 ± 0.131
2.760	1.644	1.185	1.387 ± 0.153
6.895	1.958	1.407	1.392 ± 0.050

of observable kinetic control has led to the proposal of solely diffusion-limited mechanisms. Recent work has concluded that the low-pressure dependence of the Al/H_2O reaction implies a diffusionally limited reaction.[14] However, the authors make note of evidence of the transition to a kinetic limitation as observed by Bazyn et al.[11b] The results presented in this study gives an indication that determining diffusion versus kinetic control by a pressure-dependence model utilizing micron-sized aluminum[15] is only partially useful when considering nAl. Significant kinetic control is particularly evident in the increase in $r_b(H)/r_b(D)$ to 1.6–1.7 in the 38 nm nAl combustion studies.

The determination of the rate-limiting step is challenging when using combustion studies alone, but a primary kinetic isotope effect of 1.4 (80 nm) to 1.6 (38 nm) is observed, where the high-temperature experimental minimum for a primary effect is 1.35.[4d] The effect becomes more pronounced as the particle size decreases. Fewer experiments were performed with the 110 nm because of limited quantities of material, but an effect of 1.4–1.6 was observed.

It can be deduced that the rate-limiting step in the reaction is the proton abstraction from oxygen and, not the reaction of Al with AlO, or the generation of an oxygen-free radical. The reaction mechanism of aluminum and H_2O has been previously studied, and the AlH_2O formation is predicted theoretically, and the HAlOH adduct is experimentally confirmed by matrix isolation studies.[16] The HAlOH* intermediate was observed by McClean et al. after reaction of aluminum atoms with H_2O formed from the photolysis of triethylaluminium.[9] The dissociation of HAlOH to H + AlOH is predicted by Sharipov to be fast, and the recombination reaction to AlO + H_2 is slow, so this is possibly the overall rate-determining step (RDS).[10] However in the reaction of Al_{12}^- clusters with H_2O, the RDS was calculated to be the cleavage of the O–H bond in the chemisorbed state of the cluster,[3b] and is also consistent with our results, yet different from the gas-phase studies.[9]

The change in rate indicates a primary KIE, with a value of $r_b(H)/r_b(D) \approx 1.6$ for 38 nm aluminum and ≈ 1.4 for 80 nm aluminum at a pressure range of 1–6.9 MPa. Furthermore, this observation indicates that in combustion nAl reacts in a vapor state, similar to mechanisms proposed for micron-sized aluminum.[8b,17]

At the interface of the particle and the atom, ambiguity arises in the determination of physical or kinetic control of chemical reactions. Here results from a simple yet illuminating experiment are presented and provide the first confirmed evidence of kinetically controlled combustion in nanoparticulate aluminum by the kinetic isotope effect, and is in contrast to a strictly diffusion-limited combustion controlled by physical processes. This observation is difficult to explain with the previously proposed solid-state diffusion or exploding particles models, as neither model takes into account the kinetic limitation of reactions. As chemical methodology is developed to produce aluminum particle sizes approaching that of molecular clusters, such as Al_{13}, these observations suggest a new combined model must be developed to include both diffusion and kinetic control of combustion reactions. This work provides the first demonstration of a kinetic isotope effect in a metal combustion reaction at the nanoscale, and opens a window to controlling processes which are otherwise difficult to observe.

Experimental Section

The burning rates of nAl-H_2O and nAl-D_2O mixtures were obtained at LANL using a 2 L stainless steel vessel (the volume is sufficiently large that the decomposition gases have little effect on the chamber pressure) and at PSU a 23 L constant volume optical pressure vessel, under pressurized N_2 or Ar environment. More detail on the experiment can be found in previous work.[2a,b] Samples were ignited with a 0.10 s, 60 W pulse from a 10.6 μm CO_2 laser from Coherent, or a resistively heated nichrome wire. Both chamber systems returned comparable results. Nanoaluminum was obtained from Technanogy or Novacentrix and D_2O was obtained from Cambridge Isotope Laboratories Inc., D 99.9 %. The nAl particles were mixed in small batches with deionized water or D_2O in a sealed plastic bag. An equivalence ratio of one was based upon the measured active aluminum content in the particle.

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