

Evaluation of the Deuterium Isotope Effect in the Detonation of Aluminum Containing Explosives

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This paper is dedicated to Michael A. Hiskey. This work would not have been possible without his advice and mentorship as well as his synthesis of materials used.

Abstract: During or shortly after a detonation in condensed explosives, the reaction rates and the physical mechanism controlling aluminum reaction is poorly understood. We utilize the kinetic isotope effect to probe Al reactions in detonation product gases in aluminized, protonated and deuterated high explosives using high-fidelity detonation velocity and cylinder wall expansion velocity measurements. By observation of the profile of cylinder wall velocity

versus time, we are able to determine the timing of aluminum contribution to energy release in product gases and observe the presence or absence of rate changes isotopic substitution. By comparison of the Al oxidation with lithium fluoride (LiF), data indicate that Al oxidation occurs on an extremely fast time scale, with post-detonation kinetic isotope effects observed in carbon containing formulations.

Keywords: aluminum • isotope effect • hydrazine • detonation • deuterium

1 Introduction

Shortly after the detonation in organic explosives, there exists a highly oxidizing environment in which electropositive metals such as aluminum will react. Because this reaction energy is much higher than oxidation reactions of H and C, Al has long been added to CHNO explosives to enhance the overall energy output. When considering most CHNO explosives, the oxidizing species are predominantly H₂O and CO₂. While it has been practice to formulate metals such as Al in explosives for nearly 100 years, little is understood of the kinetics and mechanism of Al reaction with product gases at the temperatures and pressures in a detonation reaction zone (in the sonic plane), or the post-detonation expansion zone (sub-sonic flow regime). This lack of understanding is due to a number of reasons; detailed experiments such as these are costly and difficult to set-up, and most experiments are performed with explosives that form a complex mixture of oxidizing gases, thus only a global understanding of Al reactions in a mixture of gases is achieved. In previous work, in order to limit the variables of different reactive gases in the post-detonation environment, we have prepared explosives that are free of either hydrogen or carbon, so that the predominate oxidizing species formed would be either CO₂ or H₂O, respectively [1]. These materials have been formulated with Al in order to better understand the post-detonation reaction chemistry between Al and CO₂ vs. H₂O. Lithium fluoride (LiF) was prepared in identical formulations as an inert surrogate for Al, given its similarities in density, 2.64 g cm⁻³ (Al = 2.70 g cm⁻³),

melting point 875 °C (Al = 660 °C), molecular weight, 25.9 g mol⁻¹ (Al = 27 g mol⁻¹) and shock Hugoniot, U_s/U_p = 7.509/1.696 mm μs⁻¹ (Al = U_s/U_p = 7.489/1.606 mm μs⁻¹) [2]. In this body of work two explosive materials, hydrazinium mononitrate/hydrazine (HzMN/Hz) eutectic and PBX 9501, were prepared in both protonated and deuterium-substituted forms; further differentiation of these materials was achieved by addition of aluminum or LiF at 15 wt%. In previous work involving the combustion of nanoparticulate Al with liquid water, a pronounced primary kinetic isotope effect was observed; thus it was concluded that this would be a powerful technique to probe Al reactions in detonations [3]. The HzMN/Hz eutectic (Figure 1 top) is carbon-free, which allowed us to compare Al reactions with only H₂O or D₂O as the major oxidizing product gas, without interference from CO₂, which is formed in classic CHNO explosives. The PBX 9501 formulations produced with Al or LiF allow for observation of Al oxidation of mixed H₂O or D₂O with CO₂. Because we obtained only deuterated Estane polymer, the formulation of the deuterated PBX 9501-like material did not contain the energetic plasticizer BDNPA/F, but rather 3.5% Estane (the remainder being 15% Al and 81.5% HMX-d₈ (Figure 1 bottom)). This formulation was thus calculated to be iso-energetic with the aluminized PBX 9501 for-

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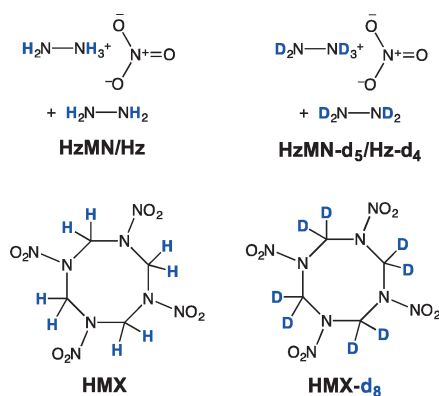


Figure 1. HzMN/Hz and HzMN-d₅/Hz-d₄ (top) along with HMX and HMX-d₈ (bottom).

mulation containing 2.5% Estane and 2.5% BDNPA/F, which was considered a better compromise compared to addition of non-deuterated BDNPA/F.

2 Results and Discussion

Table 1 summarizes detonation velocities and wall velocities for each shot. Data was collected for 12.7 mm diameter copper confined detonations of hydrazinium mononitrate (91.86 wt%) mixed with hydrazine (8.14 wt%) (HzMN/Hz) or deuterated hydrazinium mononitrate (91.86 wt%) mixed with deuterated hydrazine (8.14 wt%) (HzMN-d₅/Hz-d₄). Aluminum was added to the mixtures at the 15 wt% level for both protonated (HzMN/Hz-Al) (78.37/6.63/15.00) and deuterated samples (HzMN-d₅/Hz-d₄-Al) (78.24/6.78/14.98). Additionally, lithium fluoride was used as an inert surrogate (HzMN/Hz-LiF) for comparison. Similarly, for PBX 9501, Al or LiF were added at the 15 wt% level (HMX/estane/BDNPA-F/Al or LiF 80/2.5/2.5/15) samples as well, with both proto-

nated (PBX 9501-Al) and deuterated (PBX 9501-like-HMX-d₈-Al) HMX. The cylinder setup has been described in detail elsewhere [4]. As we have observed in our previous aluminized tests, the presence of Al in HzMN-Hz-Al slows the detonation velocity of HzMN-Hz (8.218 mm/μs compared with 8.722 mm/μs). As expected, the substitution of explosive content for Al decreases the detonation velocity, and the Dv of HzMn-Hz-Al and HzMn-Hz-LiF are within error of one another. Although the shorting pin wire detonation velocity measurement failed for PBX9501-LiF, the two point time of arrival from PDV jump-off matches the predicted velocity (Table 1), and previous work by our group has shown that detonation velocities are similar between HMX-Al and HMX-LiF formulations [4].

For non-aluminized HzMN/Hz, and its deuterated counterpart, a detonation velocity ratio of 1.098 was observed. Similarly, the ratio of HzMN/Hz-Al to HzMN-d₅/Hz-d₄-Al is 1.090. The ratio of detonation velocities for PBX 9501-Al versus PBX 9501-HMX-d₈-Al is slightly smaller, at 1.057. An effect that may lead to the decrease in the detonation velocity that must be considered is that the deuterated materials may be close to their critical diameter. In both the HzMN/Hz and the HMX-based formulations, the critical diameters are not known, but we do have an indication that we are far from the critical diameter, particularly in the case of HMX-based formulations due to their inherently low critical diameters; for instance, PBX 9501 is known to have a critical diameter of 1.5 mm [5]. Less is known of the critical diameter of the HzMN/Hz mixture, but Petel et al., measured less optimal mixtures of HzMN/Hz to have a failure diameter in the range of 3 mm [6]. If a similar difference exists in failure diameters as observed by Engelke et al. in the case of nitromethane, a 2–3x increase will be observed upon deuteration [7]. Because we are well above the protonated failure diameter of less optimal mixtures, and we have copper confinement of the cylinder shot, a diameter effect is not likely the explanation for the reduced detonation velocities observed. A portion of this difference can be attributed to the relative mass of hydrogen difference between PBX 9501 and HzMN/Hz. Additionally, by replacing 15 wt% of the explosive with either Al or LiF reduced the detonation velocity; for both explosives, the detonation velocity of the Al-added and LiF-added formulations are within error of one another. This illustrates qualitatively that the chemical reaction zone is being lengthened by addition of non-explosive components.

The wall velocities are summarized in Figure 2 and Table 1, and show remarkably similar behavior among the protonated and deuterated materials, indicating that the overall energy output of the H and D explosives are very similar. It is worth noting that although the mass ratio of each material in deuterated and protonated forms is identical, the molar ratio will necessarily vary (HzMN/Hz molar ratio is 79.2/20.8, and HzMN-d₅/Hz-d₄ is 80.3/19.7). However, this small deviation (~1%) does not make a significant impact on the overall energy release, as shown by the similar

Table 1. Detonation and wall velocity of HzMN-Hz and PBX 9501 formulations

Formulation	Density ^[a] (% TMD)	D _v (mm/μs)	Wall velocity (m/s) ^[b]	D _{vH} /D _{vD}
HzMN/Hz	1.523 (95.37)	8.722 ± 0.004	1501/1665	1.098
HzMN-d ₅ /Hz-d ₄	1.670 (98.57)	7.941 ± 0.018	1479/1615	
HzMN/Hz-Al	1.627 (95.48)	8.218 ± 0.084	1468/1657	1.090
HzMN-d ₅ /Hz-d ₄ -Al	1.725 (96.10)	7.540 ± 0.031	1446/1651	
HzMN/Hz-LiF	1.624 (95.45)	8.151 ± 0.012	1354/1481	
PBX 9501	1.833 (98.62)	8.795 ± 0.008	1730/1815	
PBX 9501-Al	1.893 (97.45)	8.464 ± 0.023	1689/1825	1.057
HMX-d ₈ -Al	1.960 (97.66)	8.004 ± 0.011	1585/1762	
PBX 9501-LiF	1.892 (97.60)	~8.50 ^[c]	1575/1682	

[a] g cm⁻³ [b] (at 5 μs)/(HzMN formulations at 20 μs; PBX 9501 formulations at 13 μs) [c] approximate value determined from PDV probe positions.

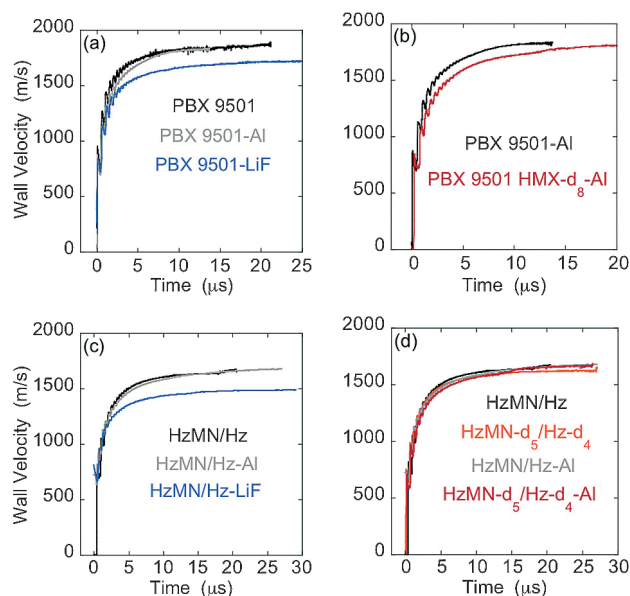


Figure 2. Wall velocities for HzMN/Hz formulations with and without Al addition, as well as with and without D-substitution. Almost no change is observed with D-substitution, and additionally, energy from fast Al reactions make up removal of 15 wt% explosive in formulation.

wall velocity behavior. In contrast to the detonation velocities, the wall velocity of HzMN-d₅/Hz-d₄-Al is almost identical to HzMN/Hz-Al, and is greater than the LiF wall velocity; since LiF is truly inert, it is unsurprising that the aluminized HE wall velocity is greater than the LiF-substituted formulation. This lack of change in wall velocity between H and D (Figure 2d) as well as the dramatic change between Al and LiF points to all Al reactions with H₂O/D₂O occurring in the chemical reaction zone (CRZ) of the detonation. The Al contribution compared to LiF occurs on an extremely fast time scale, and is realized within 1–2 μs of expansion, as observed in Figure 3, which provides an expanded view of 0–10 μs expansion seen in Figure 2a and c.

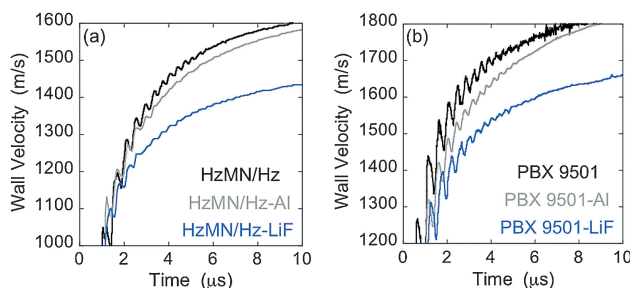


Figure 3. Expanded view of first 10 μs of cylinder wall expansion showing Al reaction contribution to wall expansion within 1–2 μs relative to LiF.

The PDV record of PBX 9501-Al in Figure 2b shows much different behavior than HzMN/Hz-Al material in Figure 2d. The difference in wall expansion velocities can be explained in the more complex reaction chemistry when carbon is added to the product distribution with fast Al reactions: H₂O and CO₂. It has been observed that the apparent kinetics of Al reaction are faster with CO₂ compared to H₂O [1,8], so gaseous CO₂ reacts with Al first in CRZ forming a large amount of elemental carbon, followed by the equilibrium reaction; C + H₂O → H₂ + CO. This is apparent in our observation of the thermal equilibrium calculations of product distribution gases (Cheetah 8.0), summarized in Figure 4. Full wall velocity can only be realized when the condensed phase carbon turns to gas, effectively doubling the molar gas content relative to the H₂O contribution alone. This is interesting evidence that much or all of the Al must be reacting in the CRZ of the detonation, otherwise it is unlikely that such an effect could be observed.

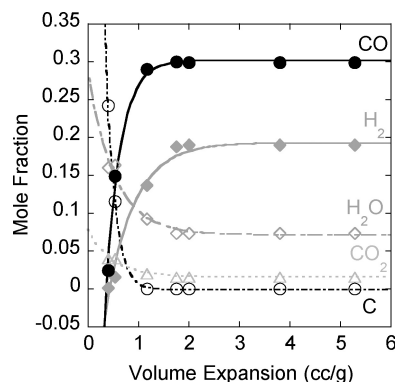


Figure 4. Mole fractions of calculated gaseous products versus volume expansion, relevant to PBX 9501-Al reactivity during detonation (C + H₂O → H₂ + CO) using the thermochemical code Cheetah.

Cheetah v8.0 [9] was used to determine basic properties of the protonated materials, and the major gaseous products are shown in Table 2. Notably, the calculated detonation velocity of the aluminized HzMN/Hz formulation is lower than those modeled as containing inert Al or LiF, due to the formation of solid Al₂O₃ products in the presence of reactive aluminum leading to a mole decrement of gas in the CRZ. The predicted mole of gas per mole of explosive is 2.353 mol for active Al and 2.526 mol of LiF (2.599 mol if inert Al is modeled). The calculations indicate a greater decrease in detonation velocity for HzMN/Hz-Al relative to HzMN/Hz-LiF than what is experimentally observed in this system. Previous experiments indicate that this is due to the fact that fully oxidized Al is held at a high-temperature for sufficiently long periods as to not allow Al condensation, which mitigates a detonation velocity decrease. At small diameters without confinement, Al₂O₃ condenses instantaneously from the perspective of the CRZ and a larger decrease in detonation velocity is observed [1].

Table 2. Thermal equilibrium calculated parameters using Cheetah 7.0/8.0

Formulation	Calculated D_v (mm/ μ s)	Total E of Detonation (kJ/cc)	Major products
HzMN/Hz	8.556	6.996	H ₂ O, N ₂ , H [*] , OH [*] , NH ₃ , H ₂
HzMN/Hz-Al	7.981	10.99	H ₂ O, N ₂ , H [*] , OH [*] , NH ₃ , H ₂ , Al ₂ O ₃
HzMN/Hz-LiF	8.229	6.665	H ₂ O, N ₂ , H [*] , OH [*] , NH ₃ , LiF
PBX 9501	8.800	10.20	N ₂ , H ₂ O, CO ₂ , OH [*] , H [*] , NH ₃ , CO, C
PBX 9501-Al	8.063	13.11	N ₂ , H ₂ O, CO, CO ₂ , NH ₃ , CH ₄ , H [*] , OH [*] , C, Al ₂ O ₃
PBX 9501-LiF	8.317	8.996	N ₂ , H ₂ O, CO ₂ , OH [*] , H [*] , NH ₃ , CO, C, LiF

In all cases the D-Substituted materials showed a decrease in D_v . While at first approach this may appear to be due to a kinetic isotope effect, basic detonation theory teaches us that detonation reactions are controlled by chemical thermodynamics and density of the explosives. To determine if the lower experimental detonation velocities of the deuterated materials is due to simple thermodynamic properties of the materials, we sought to find simple relationships between basic properties of explosives and their detonation behavior. The detonation performance of ideal explosives is generally predicted well using simple properties such as heat of formation, density, and product gas formation. Specifically, Kamlet and Jacobs have shown remarkable agreement among detonation velocities for different explosives using the simple relation $D_v = A \cdot [NM^{1/2}Q^{1/2}]/(1 + B \cdot \rho_0)$, where A ($=1.01$) and B ($=1.30$) are empirically determined values, N is the moles of gaseous products per gram of explosive, M is the average weight of detonation product gas, ρ_0 is the initial explosive density, and Q is the heat of formation of the explosive (cal/g) [11]. The values for D_v for HzMN-z, HzMN-d₅/Hz-d₄, HMX-Al and HMX-d₈-Al were calculated using the Kamlet-Jacobs equation, assuming that the heat of formation values for the deuterated materials were equivalent to the established values for the protonated materials. In order to make this assumption, we evaluated the heat of formation values for the major detonation products shown in Table 2. Table 3 summarizes $\Delta H_{f,rxn}$ for the major products containing H/D, and shows that the heats of formation are very similar for some of the major product gases in H or D-substituted form, with the $\Delta\Delta H_{f,H/D}$ being ~ 1 – 2% in agreement. With our calculated values, we observe no decrement in D_v from the Kamlet-Jacobs treatment, only a $\sim 5\%$ increase in velocity of the deuterated materials predicted from the higher overall density owing to presence of the heavier isotope in the molecule. Therefore, other effects must be responsible for the decrease in D_v .

Table 3. Heat of formation of common detonation products containing H/D

Reaction ^[a]	$\Delta H_{f,1}$ ^[b]	$\Delta H_{f,2}$ ^[c]	$\Delta H_{f,prod}$ ^[d]	ΔH_{rxn} ^[e]	$\Delta\Delta H_{f,H/D}$ ^[f] (%)
H [*] + OH [*] \rightarrow H ₂ O	218.0	37.36	−241.8	−497.16	2.21
D [*] + OD [*] \rightarrow D ₂ O	221.7	37.23	−249.2	−508.13	
NH [*] + 2H [*] \rightarrow NH ₃	376.56	2·218.0	−45.90	−858.46	2.19
ND [*] + 2D [*] \rightarrow ND ₃	375.31	2·221.7	−58.58	−877.29	
H [*] + H [*] \rightarrow H ₂	218.0	218.0	0	−436.0	1.70
D [*] + D [*] \rightarrow D ₂	221.7	221.7	0	−443.4	

[a] all units kJ/mol, Experimental values obtained from NIST website [10] [b] heat of formation of first reactant (ie. H^{*} in reaction H^{*} + OH^{*} \rightarrow H₂O) [c] heat of formation of second reactant (ie. OH^{*} in reaction H^{*} + OH^{*} \rightarrow H₂O) [d] heat of formation of product (ie. H₂O in reaction H^{*} + OH^{*} \rightarrow H₂O) [e] overall heat of formation for reaction ($\Delta H_{rxn} = \Delta H_{f,prod} - \Delta H_{f,1} - \Delta H_{f,2}$) [f] percent difference between protonated and deuterated $\Delta H_{rxn} = 100 \cdot [\Delta H_{rxn}(H) - \Delta H_{rxn}(D)] / \Delta H_{rxn}(H)$

Experiments by Chesick and Kistiakowsky show a 30% decrease in D_v for D₂ + O₂ + $\frac{1}{2}$ Xe gaseous mixtures compared to the corresponding H₂ mixture [12]. Hinshelwood et al. also observed a rate decrease with deuterium and oxygen compared to hydrogen with slow thermal reactions with oxygen at comparatively lower temperatures [13]. This effect was attributed quantitatively as the effect of the isotopic zero point energy change on the rate of elementary reactions involved. According to Chesick and Kistiakowsky, when extrapolated to the temperatures existing in the CRZ of the gas-phase detonation, the calculated value for D_v agrees well with the observed 30% decrease. They also point out that there is no evidence that the faster diffusion of H atoms from the main body of the CRZ to the shock front has a significant effect on the start of the reaction.

In another treatment of the detonation velocity decrement observed in deuterated nitromethane (DNM) compared to the protonated nitromethane (NM), Engelke and coworkers applied a correction factor to the known heat of detonation by a simple ratio of molecular weight of the H/D species [7]. Using classical ZND theory, they determined that by taking into account the heat of detonation per unit mass, or “mass effect” along with zero point energies of CH₃NO₂ versus CD₃NO₂, they were able to predict the slowed detonation velocity of the deuterated explosive to a high level of accuracy. In Table 4, we see that the mass effect on detonation velocity predicted by Engelke et al., dominates, accounting for -148 m/s difference out of the -182 m/s observed, leaving -34 m/s that was accounted for by the calculated change in zero-point energy (ZPE), as deduced by Chesick and Kistiakowsky [12].

In order to test the treatment by Engelke and coworkers in this system, the mass and ZPE decrements to D_{CJ} were calculated using equation (2) from Engelke [7], and as described therein. The ZPEs of the reactants were calculated with PBE/cc-pVTZ [14,15] using the MOLPRO quantum chemistry package [16]. This combination of functional and basis set was chosen, as it gives quite good agreement the

Table 4. Detonation change predicted from deuterium mass effect (M.E.) and change in ZPE^[a]

Formulation	ΔD_v (m/s) Measured ^[b]	M.E. ΔD_v Predicted ^[c] (m/s)	ΔD_v from ΔZPE (m/s) ^[d]	Total residual difference ^[e]
NM/DNM ^a	−182	−148	−37	+3
HzMN-Hz/HzMN-d ₅ /Hz-d ₄	−781	−271.3	−91.2	−418.5
HzMN-Hz-Al/ HzMN-d ₅ /Hz-d ₄ -Al	−678	−159.3	−79.6	−439.1
PBX9501-Al/HMX-d ₈ -Al	−460	−35.2	−37.7	−387.1

[a] Using treatment from ref. [7] [b] measured difference in H/D detonation velocities [c] predicted difference in detonation velocities due to M.E. of all gaseous detonation products [d] predicted difference in detonation velocities due to ZPE of all gaseous detonation products [e] difference between ΔD_v from combined M.E. and ZPE effects and measured ΔD_v (m/s)

ZPE of hydrazine with respect to experiment. As summarized in Table 5, the PBE/cc-PVTZ ZPE is 11355 cm^{−1} as compared to the experimental value of 11205 cm^{−1} [10]. The ZPEs of the detonated states were calculated from the compositions provided by CHEETAH at the CJ conditions [9]. The ZPEs of the products (as shown in Table 2) were taken from NIST [10] and the mass and ZPE decrements are reported in Table 4.

Table 5. Zero point energies (ZPE) for HzMN/Hz detonation products

Product ^[a]	ZPE ^[b]	Calc. ZPE ^[c]
H ₂ O	4504	
D ₂ O	3318.5	
OH•	1868.9	
OD•	1360.1	
NH ₃	7214.5	
ND ₃	5339	
H ₂	2200.6	
D ₂	1557.8	
CH ₄	9480	
CD ₄	7029	
N ₂ H ₄	11204.9	11355.26
N ₂ D ₄		8479.04
N ₂ H ₅ ⁺		14493.25
N ₂ D ₅ ⁺		10782.28

[a] in cm^{−1} [b] Experimental values obtained from NIST website [10] [c] Calculated using PBE/cc-pVTZ in this work.

In the evaluation of our systems, it is clear from Table 4 that for HzMN-Hz/DzMN-Dz and HzMN-Hz-Al/DzMN-Dz-Al, the mass and ZPE decrements calculated as described above leave a large amount of ΔD_{CJ} unaccounted for. A greater decrement was observed between H and D deto-

nation velocities in our system relative to Engelke, et al., as well as a smaller change in the H mass relative to the overall molecular weight, so the mass effect treatment did not account for nearly the same amount of D_v reduction. There is a notable approximation made in the calculation procedure; the equilibrium product species at the CJ state of the normal and deuterated compounds are assumed to be the same. In other words, the direct effect that the deuterated compounds' heats of formation and ZPEs have on the equilibrium composition is decoupled from the EOS. It is unclear how large this effect is, but in future work we plan to calculate a full HE-EOS using our thermochemical code to quantify it.

3 Conclusions

Dramatic reductions in detonation velocities for deuterated HzMN/Hz and PBX 9501, relative to protonated forms, were observed for both aluminized and non-aluminized formulations. Through much consideration must be made regarding sources for this isotope-induced velocity decrement, it appears that 1) Al reaction with H₂O/D₂O species in the HzMN/Hz or HzMN-d₅/Hz-d₄ occurs promptly within the chemical reaction zone; 2) cylinder wall velocities for PBX 9501-like aluminized formulations with HMX-d₈ versus protonated HMX indicate a marked change in wall velocity vs time, attributed to a kinetic isotope effect in carbon-water equilibrium reactions showing a slowing rate in deuterated species, although final values converge before cylinder break-up. The HzMN/Hz system, devoid of carbon, illustrates a unique example of a large reduction in detonation velocity associated with D-substitution, while the cylinder wall expansion profile was basically unaffected; which is attributed to a lack in equilibrium reactions affected by kinetic isotope effects. This observation leads back to observation 1, that Al reaction occurs promptly within the chemical reaction zone of the detonation.

Experimental Section

Hydrazinium nitrate was prepared by addition of anhydrous hydrazine (Sigma Aldrich) to ammonium nitrate (Fisher Chemicals) on an equimolar basis. Hydrazine, being a much stronger base, will displace the ammonium ion as NH₃ gas, forming HzMN in a quantitative yield. An additional 7.8 wt% hydrazine (Hz) is added to the mixture to balance the explosive eutectic to form only H₂O as the oxidizer for Al reaction. This eutectic, or "ionic liquid" explosive was also formulated with 15 wt% Al or LiF to give an overall explosive formulation of 78.37 wt% HzMN, 6.63 wt% Hz and 15 wt% Al/LiF [1].

Deuterium substitution to HzMN-d₅ was achieved by dissolution of HzMN in a factor of 4 × D₂O (Cambridge Isotope Laboratories Inc., D 99.9%), and evaporated under reduced

pressure. This process was repeated with fresh D_2O three times. Hydrazine- d_4 was obtained by dissolving anhydrous hydrazine in a $25 \times$ excess of dry methanol- D (CH_3OD Cambridge Isotope Laboratories Inc., alcoholic D 99%), which was removed by distillation at 100 – $101^\circ C$. This process was repeated 3 times. Isotopic substitution was verified for the $HzMN-d_5/Hz-d_4$ samples used in cylinder shots by NMR spectroscopy, giving an approximate estimate of deuteration ($\pm 10\%$; Figure 5). $HzMN-Hz$ (32.5 mg; 0.00197 mol all H) and $HzMN-d_5/Hz-d_4$ (42.9 mg; 0.00236 mol all D) were prepared in separate NMR tubes with d -DMSO solvent and a standard (CH_3CN ; 5.17×10^{-4} mol all H). The $HzMN-Hz$ proton peak was integrated ($D1 = 5$ s) relative to the standard as a control (expected ratio 3.7; measured ratio 4.4), and $HzMN-d_5/Hz-d_4$ was integrated relative to the standard (expected ratio 4.6; measured ratio 0.34; 7.5% protonated and 92.5% deuterated). This level of deuteration is reasonable, given the level of error in this type of analysis, along with the fact that NH protons are exchangeable and necessary handling is required in air for charge setup.

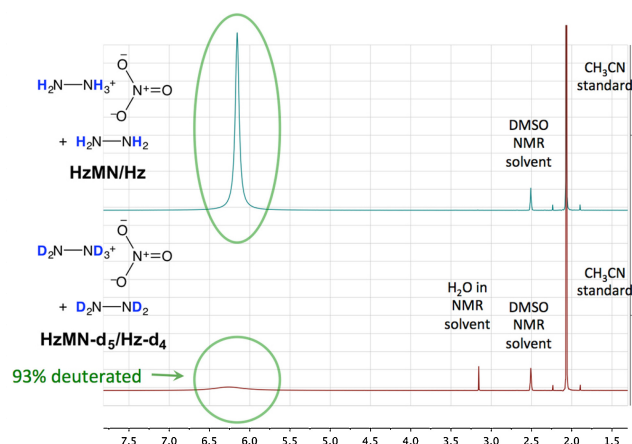


Figure 5. NMR spectroscopy showing proton peak for $HzMN-Hz$ and the lack of a proton peak for $HzMN-d_5/Hz-d_4$.

Isotopically pure deuterium labeled octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine ($HMX-d_8$) was obtained from the LANL explosives inventory as prepared by Mike Hiskey following the method of Coburn and Ott and used in the Al-Estane formulation.¹⁷ Deuterium labeled Estane polymer was also used from historical LANL MST-7 inventory, and was obtained courtesy of William Boncher. Formulation was achieved by dissolution of Estane polymer in ethyl acetate, a non-solvent for HMX, with addition HMX and $3.5 \mu m$, spherical H_2 aluminum powder from Valimet Corp., followed by subsequent evaporation of ethyl acetate with stirring.

The cylinders were 127 mm (5 in) in length, with 12.7 mm ($1/2$ -in) ID and 15.2 mm OD, scaled down proportionally from the standard 1-in cylinder test configuration, where detonation and wall velocities are measured, Fig-

ure 2. For wall velocity measurements, PDV (Photonic Doppler Velocimetry) probe rail mounts were prepared with probe holes at nominally 5.5 degrees to angle the probe tips toward the detonator. In each Cu cylinder/test stand, a total of four PDV probes/fiber optic cables were connected to the probe rails. The probe head and laser spot locations were measured to an accuracy of ± 0.5 mm. The probe fibers were connected to a 4-channel PDV interferometry system which comprised the interferometer, one laser and either a 8 GHz, 20 G samples/s or a 20 GHz/50 G samples/s (Tektronix 6804B, or DPO72004). For the detonation velocity data, 44 gauge (0.05 mm diameter) formvar-coated Cu magnet wire was attached at 8 points along the tube, and measured with an optical height gauge (Mitutoyo) to ± 0.01 mm accuracy. The wires were held at a potential of -100 V using a Dynasen pin mixer and monitored with digitizing oscilloscopes (Tektronix TDS 540B) for the transient response of an RC circuit by shorting at the detonation front. The detonation velocity was obtained from a linear regression between the position of the magnet wire and the time of arrival of the detonation front, where initial times were normalized to zero. Charges were initiated with an SE-1 detonator and a 12.7 mm diameter \times 12.7 mm long cylindrical pellet of PBX-9407.

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References

- [1] B. C. Tappan, L. G. Hill, V. W. Manner, S. J. Pemberton, M. A. Lieber, C. Johnson, V. E. Sanders, Reactions of Powdered Aluminum with Explosives that Selectively Form Carbon Dioxide or Water as Oxidizers, *International Journal of Energetic Materials and Chemical Propulsion* **2016**, 15.
- [2] S. P. Marsh, *LASL Shock Hugoniot Data*, University of California Press: Berkeley and Los Angeles, California, **1980**.
- [3] B. C. Tappan, M. R. Dirmyer, G. A. Risha, Evidence of a Kinetic Isotope Effect in Nanoaluminum and Water Combustion, *Angew. Chem. Int. Ed.* **2014**, 53, 9218.
- [4] V. W. Manner, S. J. Pemberton, J. A. Gunderson, T. J. Herrera, J. M. Lloyd, P. J. Salazar, P. Rae, B. C. Tappan, The Role of Aluminum in the Detonation and Post-Detonation Expansion of Selected Cast HMX-Based Explosives, *Propellants Explos. Pyrotech.* **2012**, 37, 198.
- [5] R. Engelke, A. W. Campbell, The Diameter Effect in High-Density Heterogeneous Explosives, *6th International Detonation Symposium* **1976**, 642.
- [6] O. E. Petel, D. Mack, A. J. Higgins, R. Turcotte, S. K. Chan, Comparison of the Detonation Failure Mechanism in Homogeneous and Heterogeneous Explosives, *13th International Detonation Symposium*, Norfolk, VA, **2006**, p 2.

- [7] R. Engelke, S. A. Sheffield, H. L. Stacy, Campbell Effect of Deuteration on the Diameter-Effect Curve of Liquid Nitromethane. *J. Phys. Chem. A* **2006**, *110*, 7744.
- [8] T. Bazyn, H. Krier, N. Glumac, Oxidizer and pressure effects on the combustion of 10-micro m aluminum particles. *J. Propul. Power* **2005**, *21*, 577.
- [9] S. Bastea, L. E. Fried, W. M. Howard, I.-F. W. Kuo, P. C. Souer, P. Vitello, *Cheetah 8.0* Lawrence Livermore National Laboratory, **2015**.
- [10] NIST Computational Chemistry Comparison and Benchmark Database; NIST Standard Reference Database Number 101, Russell D. Johnson III Ed., 18, October **2016**.
- [11] M. J. Kamlet, S. J. Jacobs, Chemistry of detonations. I. Simple method for calculating detonation properties of carbon-hydrogen-nitrogen-oxygen explosives, *J. Chem. Phys.* **1968**, *48*, 23.
- [12] J. P. Chesick, G. B. Kistiakowsky, Gaseous detonations. X. Study of reaction zones, *J. Chem. Phys.* **1958**, *28*, 956.
- [13] C. N. Hinshelwood, A. T. Williamson, J. H. Wolfenden, Reaction between oxygen and the heavier isotope of hydrogen, *Nature (London, U.K.)* **1934**, *133*, 836.
- [14] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *77*, 3865.
- [15] T. H. Dunning, Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
- [16] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, MOLPRO, version 2015.1, a package of ab initio programs Cardiff, UK, **2015**.
- [17] M. D. Coburn, D. G. Ott, A convenient synthesis of nitrogen-15- and deuterium-labeled octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), *J. Labelled Compd. Radiopharm.* **1981**, *18*, 1423.

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