

BURN RATE MEASUREMENTS OF HMX, TATB, DHT, DAAF, AND BTATz

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In this paper we present new burn rate results for several energetic materials. The burn rates of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), HMX and estane-based binder (PBX 9501), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), and TATB and Kelf binder (PBX 9502), are reported and compared with existing data. Burn rate data of these common explosives complement and extend existing data sets. Burn rate data of three novel high-nitrogen materials are presented in this work. Specifically, the high-nitrogen monopropellants considered are 3,6-dihydrazino-*s*-tetrazine (DHT), 4,4'-diamino-3,3'-azoxyfurazan (DAAF), and 3,6-bis(1*H*-1,2,3,4-tetrazol-5-amino)-*s*-tetrazine (BTATz). High-nitrogen compounds may be key to meeting the advanced performance objectives of next-generation solid propellants. High-nitrogen solids offer the possibility of high performance, reduced emissions, and lower plume signature (low temperature and no HCl) than current propellant systems. The theoretical specific impulse is comparable to HMX. In contrast to HMX, however, high-nitrogen materials tend to be insensitive to impact. Because high-nitrogen energetic materials have intrinsically large positive heats of formation and produce low-molecular-weight reaction products, they may be suitable for consideration in high-performance propellant applications. BTATz appears particularly interesting because of its rapid burn rate, relatively low-pressure exponent, and high heat of formation. The effect of a small amount of binder is investigated for all but one of these materials.

Introduction

Traditional energetic materials consist of a hydrocarbon backbone with attachments of nitro groups. The oxygen-carrying nitro groups produce much of the chemical energy that drives deflagration or detonation waves in these materials as a result of the oxidation of the fuel-like backbone. Nitramines, nitrate esters, and nitroaromatics are examples of this. At Los Alamos National Laboratory, a recent effort has been devoted to developing a new class of energetic materials with large positive heats of formation as their principal source of chemical energy [1,2]. Because these compounds often contain a large percentage of nitrogen atoms, they are referred to as high-nitrogen fuels or explosives.

The calculated theoretical specific impulse for these high-nitrogen materials is in the same range as that of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), an ingredient of some propellants. In contrast to HMX, however, high-nitrogen materials tend to be insensitive to impact, comparable to the insensitive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) in some cases. Specifically, the drop heights of 4,4'-diamino-3,3'-azoxyfurazan (DAAF), 3,6-dihydrazino-*s*-tetrazine (DHT), and 3,6-bis(1*H*-1,2,3,4-tetrazol-5-amino)-*s*-tetrazine (BTATz) were measured on our impact test to be greater than 320, 65, and 32 cm, respectively. For comparison, HMX

and pentaerythritol tetranitrate (PETN) have drop heights of 25 and 13 cm, respectively, on the same apparatus. Because high-nitrogen energetic materials have intrinsically large positive heats of formation and produce low-molecular-weight reaction products, they are particularly suitable for consideration in high-performance propellant applications. A large positive heat of formation is advantageous for enhancing the energy content of a high-nitrogen propellant matrix. This reduces the need for typical combustion-like reactions to provide the thermal energy (e.g., $C + O_2 \rightarrow CO_2 + \text{heat}$) for driving a propulsion engine. In addition, these materials have been observed to burn vigorously at 1 atm in air or in inert gases.

Burn rate data for the common plastic-bonded U.S. Department of Energy (DOE) explosives containing HMX and TATB (PBX 9501 and PBX 9502) is incomplete. In particular, there is no data for PBX 9502 in the archival literature and only high-pressure data for PBX 9501. In this work we present a few measurements of neat HMX and TATB to validate our burn rate facility through comparisons with previous work. The unique aspect of this paper is the burn rate study of the common DOE explosives PBX 9501 and PBX 9502 and three novel high-nitrogen materials as neat (pure) and with a small amount of binder, where possible. The results are compared with available data.

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TABLE 1
Energetic materials considered and equilibrium calculations for rocket motor

Compound	$\rho_{\max}$ (g/cm ³)	ρ_{tested} (g/cm ³)	ΔH_f (kJ/mol)	T_{ch}^a (K)	T_{ex}^a (K)	I_{so}^a (s)
3,6-Dihydrazino- <i>s</i> -tetrazine (DHT) C ₂ H ₆ N ₈	1.61	1.55	+ 535	2267	987	235
4,4'-Diamino-3,3'-azoxyfurazan (DAAF) C ₄ H ₄ N ₈ O ₃	1.75	1.70	+ 443	2669	1106	234
3,6-bis(1H-1,2,3,4-Tetrazol-5-ylamino)- <i>s</i> -tetrazine (BTATz) C ₄ H ₄ N ₁₄	1.74	N/A	+ 883	2560	1192	219
1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) C ₆ H ₆ N ₆ O ₆	1.94	1.80	− 145	1679	986	200
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) C ₄ H ₈ N ₈ O ₈	1.91	1.78	+ 75	3404	1543	266

Calculated assuming a Becker-Kistiakowsky-Wilson equation of state using the Cheetah 2.0 code at a specified 68.03 atm constant chamber pressure (1 atm exit pressure). Other equations of state and product libraries were found to produce very similar results. T_{ch} is the chamber temperature. The theoretical maximum density is $\rho_{\max}$, while the pressed density tested in the burn experiments is ρ_{tested} .

Experimental

Materials Studied

The energetic materials used in this work were HMX, PBX 9501, TATB, PBX 9502, DHT, DAAF, and BTATz. In Table 1, we list the densities of the neat materials considered (maximum theoretical densities and pressed densities of the neat material obtained) and specifics of the formulations considered. Pressed pellets 1 cm in diameter were used. Four 1 cm length pellets were used when break wires were employed. In most tests, a single pellet was sufficient to obtain a quantifiable video record. The densities of PBX 9501, PBX 9502, DHT/3% estane, DAAF/3% chlorotrifluoroethylene/vinylidene fluoride copolymer 3:1 (Kelf), and BTATz/Kelf used were 1.78, 1.86, 1.59, 1.67, and 1.60 g/cm³, respectively.

Equilibrium calculation results are also given in Table 1. Standard equilibrium calculations were performed for these materials. A typical rocket motor problem was considered, with a chamber pressure (constant pressure) of 68 atm and 1 atm exit pressure. The high-nitrogen materials have calculated specific impulse values greater than 200 s and very low exit temperatures, T_{ex} . The calculated specific impulse of composite formulations is of interest also since these materials will be formulated ultimately into propellants. For a composite propellant with 70% ammonium perchlorate (AP), 16% aluminum, and 14% hydroxyl-terminated polybutadiene (HTPB), the calculated specific impulse is 265 s with an exit temperature of 1987 K for the same pressure conditions considered in Table 1. Replacing the aluminum with DHT yields a specific impulse of 234 s and an exit temperature of only 1014 K. Since emission radiated by a rocket's exhaust is strongly dependent on temperature, the exhaust of a high-nitrogen propellant would produce a significantly lower IR signature. An AP/binder composite also has a much

higher predicted exit temperature (1359 K for 86% AP, 14% HTPB). Of course, other oxidizers could also be considered. In particular, oxidizers such as ammonium nitrate (AN) or ammonium dinitroamide (ADN) would be interesting to consider (no HCl in products). The combination of these energetic fuels with an oxidizer also may prove useful to eliminate undesirable secondary burn downstream of the nozzle and may help achieve complete combustion.

Another option is to formulate a propellant *without* oxidizer at all. A specific impulse for a mixture of 90% DHT and 10% HTPB is calculated to be 224 s, with an exhaust temperature of only 934 K. The primary gas-phase products are N₂ and H₂. Both N₂ and H₂ are simple diatomic molecules with relatively low molecular weight and specific heat, which increases specific impulse. Additionally, these molecules are difficult to detect by standard remote sensing techniques and are benign environmentally. Clearly, based on these calculations, the use of these novel materials as propellants may provide unique advantages.

Burn Rate Apparatus

Standard techniques were used to measure the burn rate; specifically, fine-wire solder break wires and video imaging were employed. The pressure vessel (Fig. 1) was designed for extensive optical access (four windows). All burns were video taped at normal or high-speed rates. The burn rate was obtained by digital analysis of the video record and from the break-wire record, when wires were used. Pressure rise during burn was minimal (nearly constant pressure burns). Uncertainties for the burn rate and pressure were each estimated to be within 5%. The most significant source of error, and most difficult to quantify, is nonplanar burning. Some data were eliminated because of severe nonplanar burning, but all burning samples exhibit some degree of non-planarity.

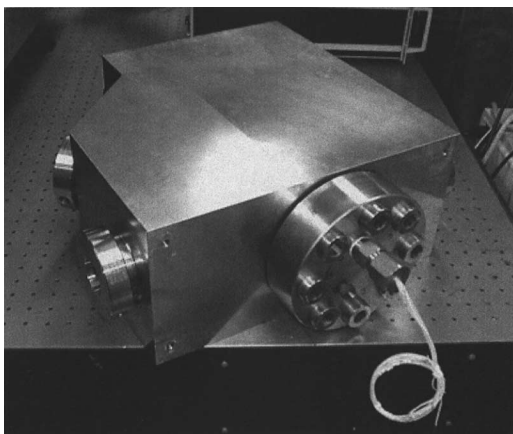


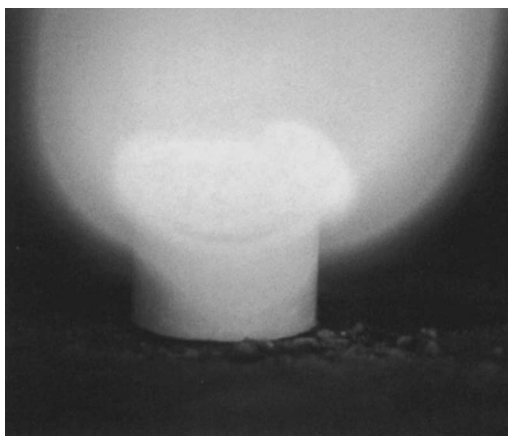
FIG. 1. Pressure vessel. Vessel can be oriented horizontally (shown in horizontal orientation) or vertically. There are four windows and a lid for access. The maximum pressure is 200 atm with windows in place. It has been tested to 340 atm with steel inserts.

Results

Burn Rates of HMX and TATB Explosives

Some data are available in the literature for the burn rate of neat HMX and TATB [3–5] over a fairly extensive pressure range. The temperature dependence of the burn rate was also reported by Parr and coworkers [6] for HMX. However, similar temperature sensitivity data does not yet exist for any of the other materials considered here. Although there is no burn rate data for PBX 9502, there is burn rate data of PBX 9501 available at elevated pressures, obtained by Maienschein and Chandler [7].

In Fig. 2, the HMX and PBX 9501 data obtained in this work are plotted with previous data. As shown, the HMX data compare well with previous data (generally within the estimated 5% data uncertainty). These data were obtained to verify the techniques and equipment used. The PBX 9501 data also merge with previous data and extend the measured range to lower pressures. For the purposes of these comparisons, data sets from experiments of Maienschein and Chandler [7] that showed erratic accelerated (anomalous) burn rates were eliminated and are not shown on this plot. A fit of LX-04 (another HMX-based explosive), also from the paper by Maienschein and Chandler [7], and modeling results of HMX [8] also appear in this figure for comparison. The fit of PBX 9501 includes both new data presented here and the data of Maienschein and Chandler [7]. The effect of the estane-based binder appears to retard the burn rate, which is the expected effect. The addition of binder to HMX drops the adiabatic flame temperature, because the addition of



(a)

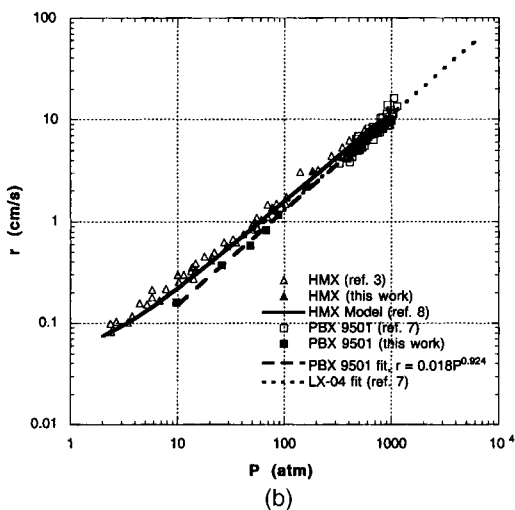


FIG. 2. Burn rate data of HMX and PBX 9501. HMX data from Refs. [4,5]; PBX 9501 data from Maienschein and Chandler [7] and a fit of LX-04 data from Maienschein and Chandler [7] are plotted for comparison. Calculated burn rates are shown using the model of Ward et al. [8]. The picture is of PBX 9501 burning at 1 atm.

fuel makes the stoichiometry even more fuel rich and does not add energetically to the material. The effect appears to diminish at higher pressures. However, approximately a 10% difference still occurs between HMX and PBX 9501 at the highest pressures considered, although it is difficult to see this difference on the log plot.

The burn data of TATB and PBX 9502 appear in Fig. 3. The only data found in the literature involving TATB were from Boggs and coworkers [3]. Only three data points were obtained in this work for TATB because they agree well with these previous measurements. A line representing the HMX burn

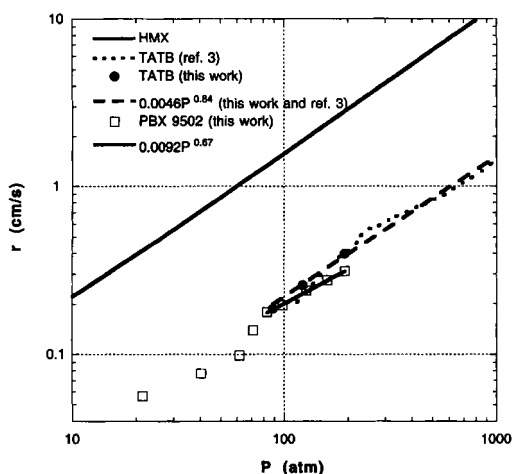


FIG. 3. Burn rate data of TATB and PBX 9502. TATB data from Boggs [4,5]; PBX 9502 data and a fit of HMX data plotted for comparison. The lowest pressure TATB data point was obtained from a sample that self-extinguished in the middle of a pellet. This was slightly below the pressure where Boggs and coworkers were able to obtain steady self-deflagration for TATB.

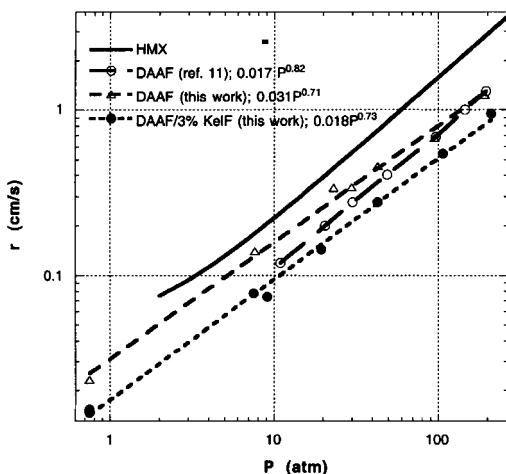


FIG. 4. Burn rate data of DAAF and DAAF/3% KelF. DAAF data from Sinditskii et al. [11]; a fit of HMX data is plotted for comparison.

rate is shown for comparison. The pressure exponent is similar to that of HMX; specifically, the average pressure exponent for HMX in this pressure range is about 0.85 compared with 0.84 for TATB. However, the burn rate is about an order of magnitude slower for the TATB and corresponding PBX. The burn rate is far too slow to be considered for most propellant applications. Further, significant residue

remains after the burn and may indicate incomplete combustion. The only data found in the archival literature involving TATB were from Boggs and coworkers [3]. Actual data points were not reported in the previous work, but the reported line was digitized and is reproduced in Fig. 3. A fit is shown in the figure using both new and previously reported [3] TATB results. Some data exists for PBX 9502 in reports and conference proceedings [9,10]. Most of the data reported comes from a self-pressurizing bomb and is inferred from the pressure trace. This may introduce some additional uncertainty. For comparison, Holy [10] reported a fit of $0.0072P^{0.768}$ compared with our fit of $0.0092P^{0.67}$, which is measurably different.

In the sample configuration and apparatus used by Boggs and coworkers, sustained self-deflagration was achieved only above 1500 psi (102 atm). For TATB pellets, we also observed that TATB would not sustain self-deflagration below a similar pressure level for similar conditions. The lowest pressure data point we report occurred near 1300 psi (88 atm). However, the burning self-extinguished part way into the pellet for this test. A steady rate could be obtained before it self-extinguished, and it appears to fit on the same line.

Data for PBX 9502 also appears in Fig. 3. The binder, in this case KelF, also retarded the burn rate, although sustained self-deflagration extended to lower pressures than is attainable in pure TATB. Interestingly, the relative effect of the binder appears to increase with pressure; that is, the pressure exponent of PBX 9502 is lower than that of TATB (0.67 for PBX 9502 compared with 0.84 for TATB). The opposite trend was observed with the addition of the estane-based binder into HMX. There was a slight increase in the pressure exponent in the PBX (0.92 for PBX 9501 compared with 0.85 for HMX). A possible explanation for this may lie in the details of how the chemistry interacts between the binders used and the energetic materials. The lowest burn obtained in this study was 316 psi (21.5 atm). Below this pressure, self-extinguishment occurred.

DAAF and DAAF/KelF Burn Rates

Sinditskii et al. [11] measured the burn rate of DAAF; however, they did not specify the density of the pressed samples. Furthermore, there was no mention of a binder material used, if one was used. Nevertheless, we show data of Sinditskii et al., as well as the HMX curve for comparison (Fig. 4). Suitable neat DAAF pellets could be generally obtained. Some pellets, however, cracked and were discarded, and in one case a burning anomaly was observed. The data of Sinditskii et al. lies between our two data sets but has a different pressure exponent. DAAF burns significantly slower than HMX and has a similar pressure exponent. The effect of the binder



(a)

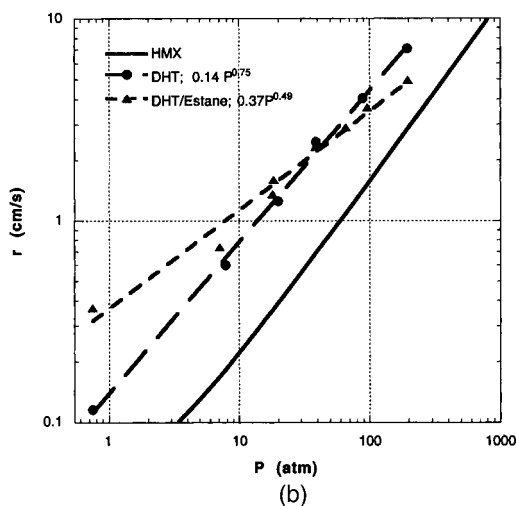


FIG. 5. Burn rate data of DHT and DHT/3% estane. A fit of HMX data is plotted for comparison. The picture is of DHT near 1 atm in air. There is very little gas-phase luminosity (compare PBX 9501 in Fig. 2 at 1 atm).

(KelF) is a simple retarding effect that maintains essentially the same pressure sensitivity. As mentioned above, a significant feature of DAAF is that it is very insensitive.

DHT and DHT/Estane Burn Rates

The data obtained in this work for DHT is shown in Fig. 5. The burn rate appears to be faster at lower pressures with the estane-based binder and slower at higher pressures. The burn rate is substantially faster than that of HMX, as shown. The neat material

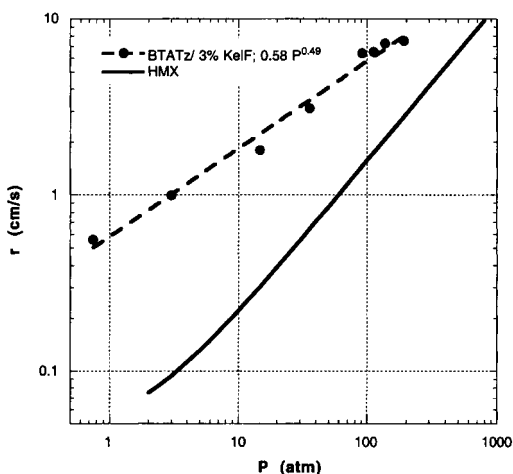


FIG. 6. Burn rate data of BTATz/3% KelF. A fit of HMX data is plotted for comparison.

is nearly as pressure sensitive, but the binder-containing material has a significantly lower pressure exponent than HMX. Also shown in Fig. 5 is a picture of burning DHT. There is very little luminosity in the gas phase. The visual appearance of burning DHT is very different from that of more typical propellants such as HMX, as can be seen by a comparison of the image in Fig. 2 and that in Fig. 5, taken at the same exposure. The primary reason for this is probably that there is much less carbon in DHT and the temperatures are much lower compared with HMX or other propellants. The lower temperatures are nearly compensated by the lower-molecular-weight products, such as H_2 , to yield respectable specific impulse values.

BTATz/Estane Burn Rates

Adequate pellets could not be formed from neat BTATz. Consequently, the burn rate was measured for only the binder-containing material (Fig. 6). As shown, the burn rate is much higher than that of HMX and, over the range considered, has a much lower pressure exponent (near 0.49). This would make it an attractive propellant prospect. A low-pressure exponent implies that this material may be less prone to combustion instabilities. Temperature sensitivity is another factor that influences oscillatory combustion and should be measured also. It is also of interest to determine the flame structure (species and temperature profiles). Presumably, the burn rate would be somewhat higher for neat BTATz.

Summary

The burn rates of several high-nitrogen monopropellants were measured. The burn rates of HMX,

PBX 9501, TATB, and PBX 9502 were also reported. Burn rate data of these materials complements and extends existing data sets. The effect of binder is investigated for most of these materials. Future work includes formulating these materials with an oxidizer and additional binder. Direct measurements of the specific impulse and determination of the flame structure would be useful to determine if complete combustion has been achieved. Temperature sensitivity should also be measured.

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