

Experimental Investigation of Gasless Detonation in Metal–Sulfur Compositions

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Samples of zinc–sulfur and manganese–sulfur mixtures are shocked using an explosive pentolite charge to investigate if a shock-initiated reaction is able to support continued shock wave propagation. Samples of two different nominal densities (62 and 86% of theoretical maximum density) are prepared as weakly confined cylinders 50 mm in diameter and are instrumented along their length (≤ 280 mm) with sensitive piezoelectric pins. Experimental results showed that the shock wave transmitted into the sample by the explosive rapidly decays to an acoustic wave in all four sample types. Furthermore, in denser samples, the part of the sample farthest from the explosive is recovered intact and unreacted, which clearly indicates that the wave is unable to trigger reactions after 100 mm of travel along the sample. Thus, it is concluded that insufficient reaction energy is transmitted forward to the shock wave to prevent its decay as it travels along the sample.

Key words: gasless detonation, shock wave, zinc–sulfur mixture, manganese–sulfur mixture.

INTRODUCTION

In the early 1990s, Boslough [1] and Bennett and Horie [2] presented methods to estimate the product Hugoniot curve for a shock wave (SW) in reactive powder mixtures, such as thermites and SHS-compositions. They found that, in some cases, even when the products were expected to be non-gaseous, the product Hugoniot curve lies above the initial unreacted powder state on the pressure-specific volume (p - v) plane. This was found to happen if the initial mixture porosity was not too large, if exothermicity of the reaction was sufficiently large, and if the volumetric expansion of the products was not too small. For these cases, a classical Chapman–Jouguet detonation solution (see [3]) to the one-dimensional conservation laws of mass, momentum, and energy exists.

The existence of a detonation solution stimulated some researchers to experimentally investigate the ques-

tion of whether such a gasless detonation can be observed. Merzhanov et al. [4] correctly pointed out that experimental difficulties stem from the fact that the minimum charge diameter that could permit reactions to occur before lateral expansions reduce pressure and temperature³ cannot be estimated without the knowledge of the reaction kinetics. Furthermore, the shock pressure and duration required to initiate reactions also depend on the kinetics. Merzhanov et al. [4] conducted preliminary experiments with charges of compacted Ti/C/Al/paraffin (48/12/90/12 ratio in wt.%) 50 mm in diameter and 200 mm long, which were initiated with a TNT charge. Shock deceleration followed by acceleration from 1.6 to 2.5 km/sec was observed. In those tests, paraffin acted as a source of gas; hence, al-

³Note that an upper limit for the reaction time could be provided by assuming a mass-diffusion-controlled reaction. Using a simple calculation as in [5], reaction times greater than 10^{-2} sec were obtained for powders with particle sizes of the order of 10^{-6} m. If the sound speed in the material is of the order of 10^3 m/sec, then simple “dimensional considerations” suggest that the critical diameter necessary to observe propagation would be much greater than a meter.

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though what they observed was not entirely gasless, the authors [4] believed that their results could be regarded as preliminary evidence of gasless detonation.

A few years later, Jiang et al. [6] measured the reaction front trajectory using ionization probes in high-density (low-porosity) manganese–sulfur (Mn + S) mixtures (samples 25 mm in diameter and 100 mm long) initiated by nitromethane charges sensitized with 15% of diethylenetriamine. The Mn + S mixture appeared a promising candidate due to its large heat of reaction (for the $\text{Mn} + \text{S} \rightarrow \text{MnS}$ reaction, $\Delta H = -2.46$ kJ/g) and gasless products at moderate pressures. In one experiment, Jiang et al. [6] observed what they interpreted as a re-acceleration of the reaction front in the solid Mn + S mixture from 1.8 to 2.2 km/sec after 40 mm of travel. Lee et al. [7] repeated similar experiments with a larger diameter (50 mm) and a stronger explosive initiating charge (C-4). The shock wave was tracked with piezoelectric pins. The results [7] did not show any shock acceleration; instead, the shock decayed from over 4 to 1.36 km/sec in 50 mm of travel.

However, Gur'ev et al. [8] believe that shock acceleration should eventually be observed in the Mn + S system, while Batsanov and Gordopolov [9] believe that Mn + S may not be a good candidate for gasless detonation. Indeed, Batsanov and Gordopolov [9] suggest that MnS experiences an irreversible phase transition at high pressures, which prevents the product density from being lower than that of the starting mixture. This contraction could offset the volumetric dilation caused by the chemical energy release and prevent energy from being “fed” to the shock wave. Finally, Bolkhovitinov and Batsanov [10] estimated the theoretical detonation velocity⁴ in the Mn + S mixture to be about 2.77 km/sec, which they compared to the reaction front velocity of Jiang et al. [6].

The most recent attempt to obtain gasless detonation in a metal–sulfur mixture was published by Gur'ev et al. [11]. They measured the entrance and exit times of shock waves transmitted through zinc–sulfur (Zn + S) powder mixtures (particle size 3–5 μm) with densities of 59.4–71.6% of the theoretical maximum density (TMD) in cylindrical samples 16.5 mm in diameter and between 40 and 200 mm in length that were initiated by a

⁴The theoretical model of Bolkhovitinov and Batsanov consists in obtaining a substitute for the ratio of specific heats γ in the Chapman–Jouguet detonation solution for ideal gases $D^2 = 2Q(\gamma - 1)$ in the form $\gamma = 2b - 1$, where b is the tangent of the slope of the linear fit to the Hugoniot curve of the reaction product in the “shock velocity–material velocity” plane. Their method does not account for the initial density of the unreacted mixture. In their model, the same detonation velocity will result whether the starting mixture is fully non-porous or extremely porous.

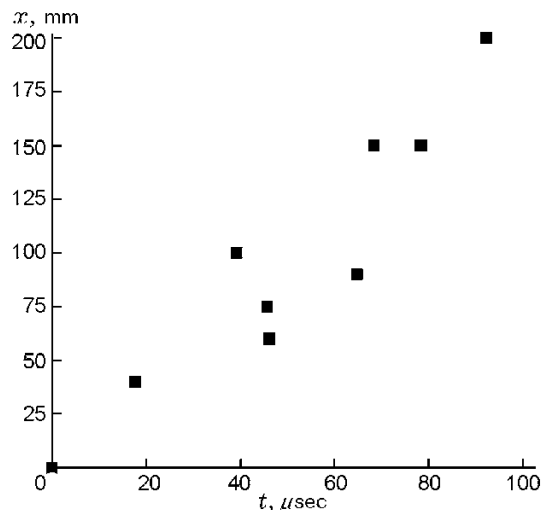


Fig. 1. Shock velocities data [11] reconstructed as an x - t diagram.

TNT/RDX charge (35 mm high and 40 mm in diameter). By comparing the average shock velocities in samples of different lengths, they concluded that the shock initially decelerated to 1.3 km/sec in samples shorter than 60 mm but then accelerated from 1.4 km/sec to values oscillating near 2.2 km/sec in charges longer than 100 mm. The shock acceleration was “regarded as experimental evidence for the occurrence of solid-state detonation in the system under study” [11]. Note that the exothermicity of the reaction between Zn and S is similar to that between Mn and S (for the $\text{Zn} + \text{S} \rightarrow \text{ZnS}$ reaction, $\Delta H = -2.09$ kJ/g).

However, if the average velocities reported in [11] are used to reconstruct a position–time x - t diagram of the measured wave trajectories in the samples, it is difficult to see any systematic acceleration or deceleration of the wave (Fig. 1). The scatter in those data [11] may be a result of large variations in the starting densities of the samples or, perhaps, spurious signals from the contact gauges used, rather than due to an accelerating and oscillating shock front. Nevertheless, subsequent papers [9, 10, 12] have attempted to correlate the observed shock velocity (2.2 km/sec) [11] with predicted detonation velocities (2.56 km/sec for the Zn + S mixture [10]), as well as to explain the oscillatory behavior of the shock velocity [9]. Lastly, Batsanov [12] estimated the sound speed of the powder Zn + S mixture to be in the range from 0.53 to 0.77 km/sec, which led him to conclude that the measured 2.2 km/sec wave was supersonic.

Though the focus of this paper is on sulfur-based compositions, similar attempts to observe gasless detonation have been performed in other gasless or low-gas

production compositions such as Zn + Te [8] and aluminum + Teflon [13, 14]. While some of these experimental investigations have reported what appears to be a steady or amplifying shock wave due to chemical energy release from these compositions, the existence of a self-sustained wave propagating at supersonic speeds for a large number of effective charge diameters has not been definitively established.

Thus, the evidence concerning gasless detonation in metal–sulfur systems (as well as in the other systems mentioned above) is not unambiguous and depends mainly on a few cases of apparent shock or reaction front acceleration or on apparent steady shock velocities.

The motivation for the current study was to repeat experiments [11], with additional mixtures and densities. High-density (low-porosity) samples of Mn + S and Zn + S prepared using the same technique as in [6, 7], as well as low-density (high-porosity) Mn + S and Zn + S samples prepared as in [11] were shocked using a powerful explosive, and the shock trajectory was measured for distances of at least 200 mm using piezoelectric pins.

EXPERIMENTAL DETAILS

The experimental setup is illustrated in Fig. 2. Stoichiometric Mn + S and Zn + S mixtures [with metal particles of 1–5 μm and 100 mesh ($<149 \mu\text{m}$) sublimed sulfur] were prepared in 50.8 mm inside-diameter cardboard tubes. The high-density test samples were prepared as described in [15]. The metal and sulfur powders were well mixed in a roller mill and then heated until sulfur began to melt. This mixture of the metal powder suspended in melted sulfur was poured into the cardboard tube and left to solidify as it cooled. Using this method, samples with density in the range of 81 to 88% TMD were obtained. The low-density test samples were prepared by hand-compacting the well-mixed powder inside the cardboard tube. With this technique, sample densities of 59 to 66% TMD were produced. To ensure uniform density throughout the sample, the tube was filled in about 200 g increments, and compaction was performed using a plastic rod after each increment. All samples were filled from the bottom to guarantee that the top surface was flat and uniform.

Piezoelectric shock pins (Dynasen CA-1135) were installed at various locations along the samples, as is shown in Fig. 2. For the low-density powder tests, the shock pins were inserted simply by pushing them into the sample. For the high-density tests, the shock pins were glued into positions before the samples were cast. The shock pins were installed so that their tips con-

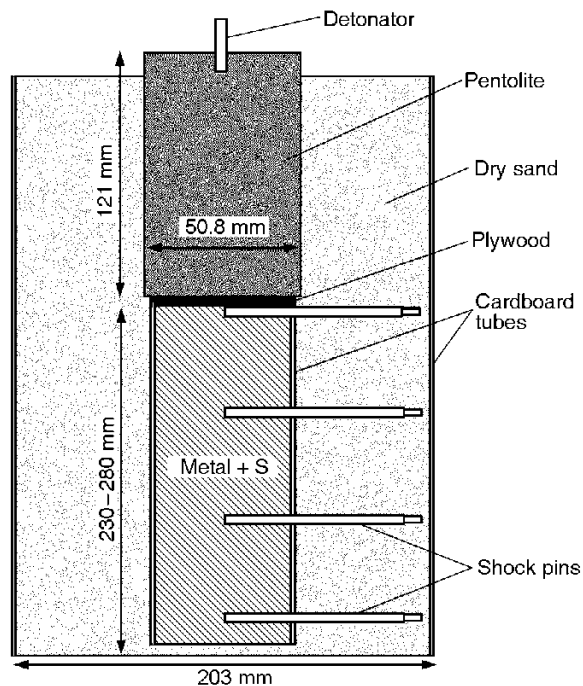


Fig. 2. Experimental setup.

taining the piezoelectric crystals would be at the sample center, so as to measure the earliest appearance of the curved shock front at every given axial location. When inserted as shown, the shock pins produced a negative voltage signal when the shock reaches their location. Since the piezoelectric crystal of the shock pin was shocked on its side, a slight decrease in sensitivity (by approximately a half) and a reversal of signal polarity occurred, as compared to a shock pin loaded on its tip (see, e.g., [16]). In laboratory tests, the response of shock pins loaded sideways was found to be as fast as that of shock pins loaded on their tip in PMMA at pressures below 6.5 GPa. Considering the fact that those sensors are extremely sensitive (gentle tapping the tip with a finger produces a measurable signal), placing them sideways caused no significant loss in sensitivity and/or response time for the work performed here. A 460-g charge of pentolite (50/50 TNT/PETN; Dynonobel D45) 50.8 mm in diameter and 121 mm long was placed on the test sample. A thin (3 mm) layer of plywood separated the test sample from the charge to prevent direct contact between the pentolite detonation products and the metal–sulfur sample. An electric detonator was used to detonate the pentolite charge. A fiber optic cable was inserted into the top of the pentolite charge and a photodiode monitored the onset of detonation. This photodiode signal was used to trigger all instrumentation (all data shown in the next section

is referenced to this triggering time). To reduce the rate of the shock pressure decrease due to side unloading, a cardboard tube 203 mm in diameter was placed around the explosive and the sample, and the empty space between the sample and the cardboard tube was filled with sand. Because of the low speed of sound in sand (see, e.g., [17]), no precursor waves could affect the shock propagation in the samples or disturb the sensors prior to the arrival of the shock front in the test sample. Finally, the sand surrounding the explosive charge helped contain the detonation products, which prevented them from damaging the coaxial cables used to bring the shock pin signals to the recording oscilloscopes (Lecroy Wavesurfer 424).

RESULTS AND DISCUSSION

Sample traces from the piezoelectric shock pins obtained in high-density samples are shown in Fig. 3 (signals from broken gauges were truncated to keep the figure clean). The very sharp signals like those at the bottom of Figs. 3a and 3b have been attenuated by a factor of 2–4 for displaying purposes. The vertical offset between different signals represents the nominal distance between the shock pins in inches. For instance, in Fig. 3a, the first shock pin was located in an immediate vicinity of the pentolite charge, while the others were located at 4" (101.6 mm), 8" (203.2 mm), and 11" (279.4 mm), respectively, from the pentolite charge.

At locations near the pentolite explosive, the shock wave caused a sharp signal spike typical for a piezoelectric crystal breaking under an intense shock. As the wave moved down the sample, the signals became much more continuous, which implies that the shock pin crystal was not destroyed. As these signals were less sharp, the error in determining the time of wave arrival is slightly greater for those signals than for sharper signals. The amplitude of the signals also decreased as the travel distance increased, which implies that the shock was decaying into an acoustic wave.

Sample traces from the piezoelectric shock pins obtained in low-density samples are shown in Fig. 4 (as in Fig. 3, the very sharp signals have been attenuated by a factor of 2–4 for displaying purposes). As with the high-density samples, the shock rapidly decayed into what appeared to be an acoustic wave of decreasing amplitude. The decay was such that the pressure decayed below the level of detection of the transducer at the farthest shock pin from the pentolite charge (279.4 mm or 11").

Figure 5 shows a summary of all wave arrival times for all tests performed with high-density samples. The wave velocity appears to decay rapidly (in less than

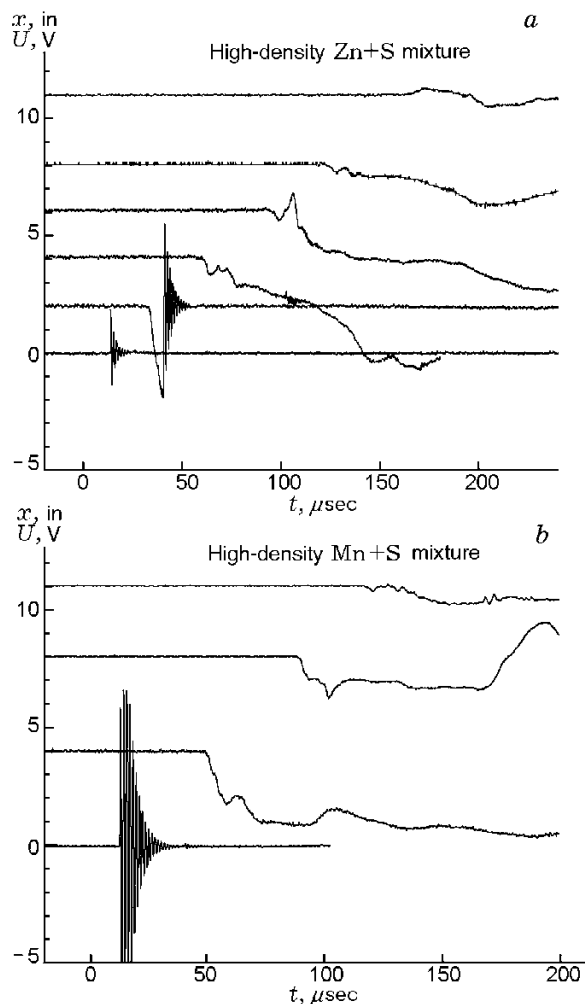


Fig. 3. Sample piezoelectric shock pin signals for tests on Zn + S with sample densities of 81–88% TMD (a) and Mn + S with sample densities of 85–88% TMD (b).

150 mm of travel) to a steady value of ≈ 2.5 km/sec for the Mn + S mixtures and 1.8 km/sec for the Zn + S mixtures (dot-and-dashed curves). No re-acceleration of the wave was observed at positions beyond 150 mm.

If the shock Hugoniot curve for the inert Mn + S mixture with 100% TMD is computed by the additive method [18], it is found that the intercept of the linear fit to the Hugoniot curve in the $U-u$ plane is 2.5 km/sec (U and u are the shock and material velocities, respectively). This intercept is usually close to the sound speed in the material. The wave velocity of the decaying shock in our experiments was also close to this value. For the Zn + S mixtures, the sound speed estimated from the intercept is 2.16 km/sec. This value is slightly greater than 1.8 km/sec obtained in our Zn + S experiments, but our test mixtures had a density slightly lower

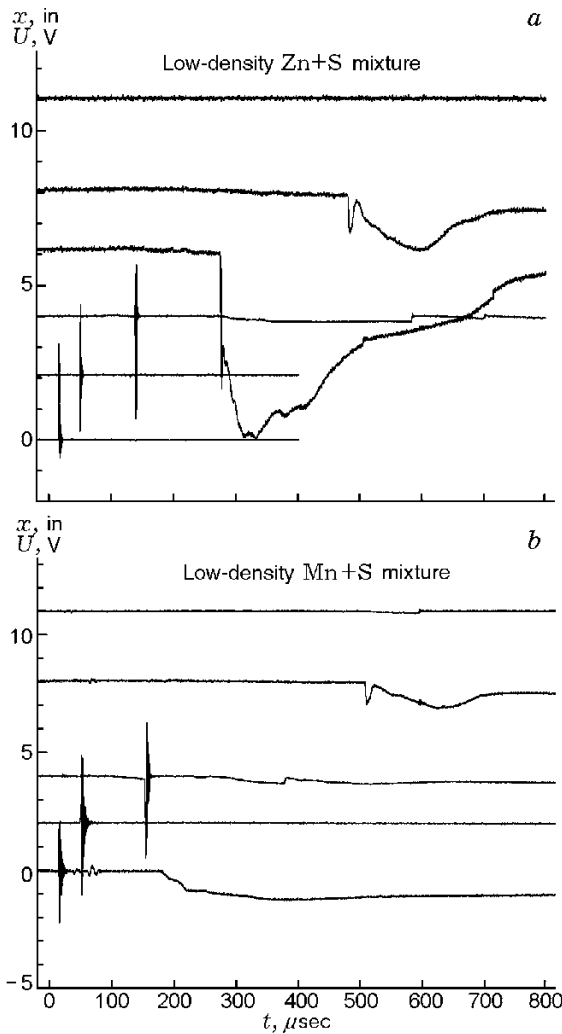


Fig. 4. Sample piezoelectric shock pin signals for tests on Zn + S with sample densities of 64–66% TMD (a) and Mn + S with sample densities of 59–61% TMD (b).

than 100% TMD. Overall, it appears that the wave in both mixtures decayed to an acoustic wave whose velocity was very close to that estimated theoretically. It is also interesting to note from Fig. 5 that one Zn + S sample had a lower density than the other two that were tested. This sample exhibited a faster decay and a lower final velocity, consistent with the expectation of a lower sound speed in a less dense mixture. These data also demonstrate that there could be large differences in the arrival times of waves in samples of different densities.

Figure 6 shows a summary of all wave arrival times for all tests performed with the low-density (high-porosity) samples. As is shown by the dot-and-dashed curve, the wave velocity appears to decay to a steady value of ≈ 0.22 km/sec for both powder types. As with

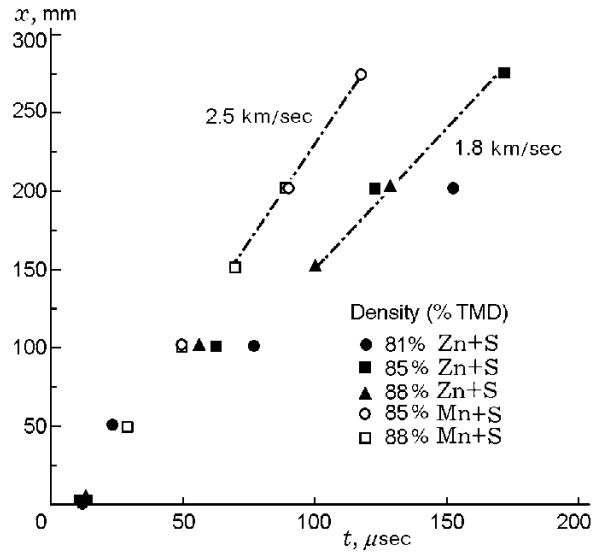


Fig. 5. Summary of SW arrival times at various locations for high-density samples.

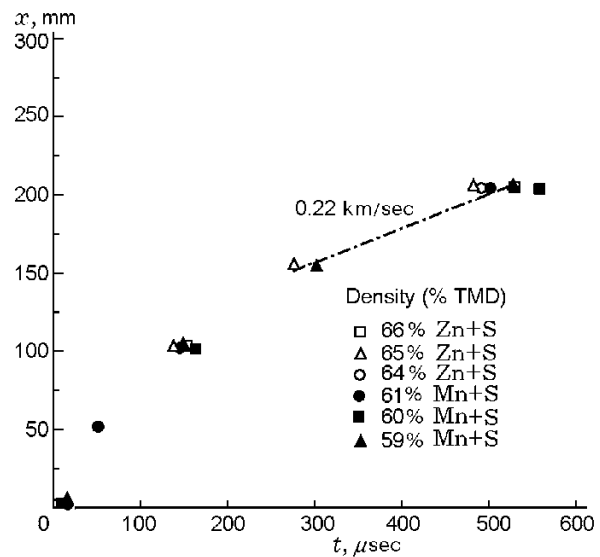


Fig. 6. Summary of SW arrival times at various locations for low-density samples.

the high-density samples, no re-acceleration was observed, in contradiction to the results [11]. As was mentioned in Introduction, Batsanov [12] estimated the sound speed in the Zn + S mixture with a density of 67% TMD to be in the range of 0.53 to 0.77 km/sec. Thus, the final wave velocity measured in this work is of the order of the theoretically estimated sound speed.

It is also useful to point out that a section 50 mm to 160 mm in length from the bottom of the test sample was recovered intact and completely unreacted for each high-density mixture tested. The last 50–90 mm of the

sample were recovered for the samples 230 mm long, while the last 80–160 mm were recovered for 280 mm long samples. The decayed shock, thus, became unable to trigger reactions. Unfortunately, for the low-density mixtures, the samples could not be recovered after the tests, because the cardboard and sand confinement failed to preserve them. It is, therefore, impossible to confidently determine whether any or all of the sample reacted in those tests.

In recovery tests performed using explosively shocked ampoules [15], the high-density Mn + S mixture was found to be easily initiated by relatively weak shocks (≈ 2 GPa). At the same time, it was also discovered that almost no exothermicity was observed via luminosity measurements in the first 100 μ sec following shock transmission into the same mixture [19]. Thus, these results suggest that reactions may be initiated locally by the shock wave in individual “hot spots” where density discontinuities exist, but the bulk of the reaction propagates as a classical thermo-diffusive flame. It is, therefore, postulated that the reactions in this test series may have been initiated locally near the pentolite explosive charge where the highest shock intensity is reached and propagate slowly by a diffusive mechanism. As strong lateral expansions stretched the sample, the liquid reacting parts were “blown off” the unreacted parts, thus, leaving an unreacted stump in the case of high-density samples or nothing at all in the case of low-density samples. Had a stronger confinement been used, it is likely that we would have recovered the reaction products ZnS or MnS, as Gur’ev et al. [11] reported.

CONCLUSIONS

In contrast to the results reported in [11], we did not observe shock acceleration in Zn + S (Mn + S did not exhibit shock acceleration either) in weakly confined samples 50.8 mm in diameter. Vice versa, a decaying shock that rapidly stabilized near the sound velocity in the material was observed. This decaying wave became too weak to ignite reactions near the base of the denser samples.

As the sample diameter in our experiments was three times that in the experiments performed in [8, 11], we should have been more likely to observe detonation in these tests (i.e., the likelihood that the sample diameter was greater than the hypothetical critical diameter required for detonation of the mixture was greater in our tests). Since we did not observe a detonation, our results provide no evidence for the new type of the fast reaction or the transport mechanism proposed in [11]. Rather, it is our opinion that known transport mech-

anisms can explain all of the results obtained in our study.

Investigating the existence of gasless detonation by performing tests similar to those in the present work requires using sufficiently long charges to unambiguously observe self-sustained propagation that is no longer influenced by the donor explosive. As the hypothetical critical diameter and initiating shock amplitude required for detonation of these compositions are unknown, tests should also be performed with increasingly large diameters and various sizes and strengths of donor explosives until detonation is observed. Thus, this type of experimentation is limited in usefulness until the time and length scales associated with detonation in the material of interest can be estimated. An alternative approach, which implies an attempt to measure the time of the onset of a significant exothermic reaction upon shock wave propagation through a sample, in order to determine if the time scale of a significant exothermic reaction is compatible with detonation propagation, may be a more productive strategy for laboratory-scale experimentation.

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