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Ultrafast Shock Compression of an Oxygen-Balanced Mixture of Nitromethane and Hydrogen Peroxide

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ABSTRACT: We apply ultrafast optical interferometry to measure the Hugoniot of an oxygen-balanced mixture of nitromethane and hydrogen peroxide (NM/HP) and compare with Hugoniot data for pure nitromethane (NM) and a 90% hydrogen peroxide/water mixture (HP), as well as theoretical predictions. We observe a 2.1% percent mean pairwise difference between the measured shockwave speed (at the measured piston speed) in unreacted NM/HP and the corresponding "universal" liquid Hugoniot, which is larger than the average standard deviation of our data, 1.4%. Unlike the Hugoniots of both HP and NM, in which measured shock speeds deviate to values greater than the unreacted Hugoniot for piston speeds larger than the respective reaction thresholds, in the NM/HP mixture we observe shock speed deviations to values lower than the unreacted Hugoniot well below the von Neumann pressure ($\approx$28 GPa). Although the trend should reverse for high enough piston speeds, the initial behavior is unexpected. Possible explanations range from mixing effects to a complex index of refraction in the reacted solution. If this is indeed a signature of chemical initiation, it would suggest that the process may not be kinetically limited (on a ~100 ps time scale) between the initiation threshold and the von Neumann pressure.
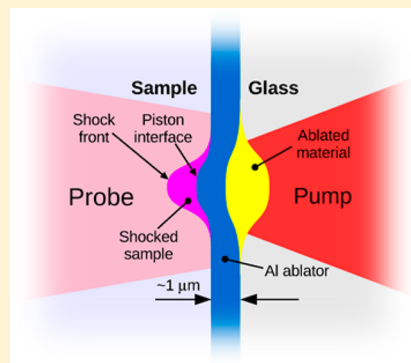
INTRODUCTION

The propagation of shockwaves in energetic liquids is accompanied by complex physical and chemical phenomena that remain of much interest both experimentally and theoretically[1−3] due to their fundamental and practical relevance. The transition from the shocked but unreacted state to one that has undergone exothermic chemistry is, for example, yet to be fully understood, although it determines important characteristics such as the failure diameter and shock front curvature in detonations.[4,5] Understanding the dynamic response of a shocked liquid prior to chemical bond breaking is a major component of modeling efforts aimed to better predict reactivity under high pressure and temperature conditions. Nitromethane is a prototypical energetic material and as a result its high pressure behavior has been often characterized using shock experiments;[6,7] more recently, molecular dynamics (MD) simulations have also been reported.[8−10] A comprehensive understanding of the shock physics and chemistry of most other energetic liquids, and particularly liquid mixtures, is, however, far less developed. Recently, the shock Hugoniots of nonideal and ideal fluid mixtures were experimentally measured and it was suggested that hydrogen bonding networks affect nonideal mixture response: nonideal mixture shock velocities shifted away from so-called universal liquid Hugoniot predictions.[11] Because most equation-of-state developments[6,7] and simulations[9,10] rely heavily on high pressure experimental data, it is important to understand how other fluids behave under similar shock conditions and to what extent such deviations are indicators of "non-universal" behavior.

Here we report new ultrafast shockwave measurements on an oxygen balanced mixture of nitromethane and hydrogen peroxide (NM/HP), two representative energetic liquids[4,12] with zero and positive oxygen balance, respectively, and compare the results with unreacted shock Hugoniot data for a 90% hydrogen peroxide/water (HP) mixture.[1] We also compare the NM/HP data with the empirical liquid Hugoniot proposed by Woolfolk et al.,[13] equation-of-state predictions based on intermolecular interactions,[14] and unreacted nitromethane (NM) Hugoniot data from gas gun measurements and our own ultrafast measurements. We propose an alternative liquid Hugoniot empirical form that yields the correct behavior both as $u_p/c_0 \rightarrow 0$ and asymptotically as $u_p/c_0 \rightarrow \infty$. For the NM/HP mixture we observe a likely reduction in volume above a piston velocity threshold of 1.7 km s^{-1} and discuss possible explanations of this effect.

EXPERIMENTAL DETAILS

The NM/HP sample was a mixture of 90% hydrogen peroxide (in water) and nitromethane with 48.2 (HP)/51.8 (NM) weight fractions. NM and HP are miscible at this concentration.[15] The experimental apparatus is the same as used in previous work,[1,16,17] shown schematically in Figure 1. A chirped ~350 ps duration, ~25 nm full width at half-maximum (fwhm) spectral width, 800 nm wavelength pump pulse is focused by a 2 cm focal length lens to ~25 μm fwhm intensity and drives a shock wave through a ~1 μm thick Al ablator on a glass coverslip into the sample, which is liquid in all cases.
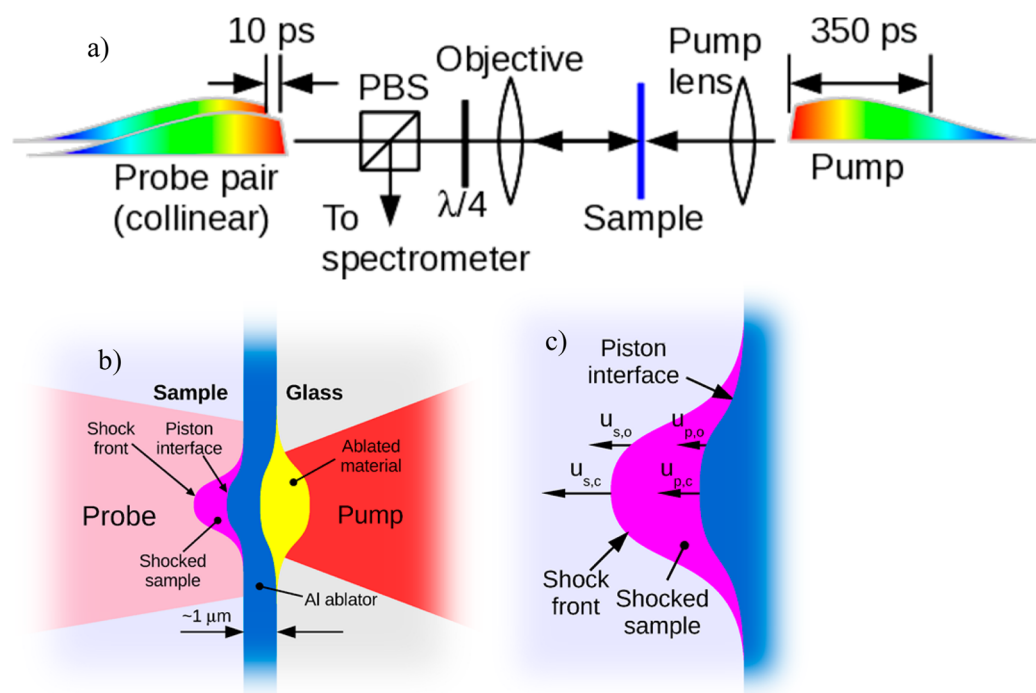
Figure 1. Scheme for shock loading the NM/HP mixture. (a) The experimental layout. PBS stands for polarizing beam splitter, and $\lambda/4$ is a quarter waveplate set to rotate the polarization 90° in the double pass. (b) A schematic cross section of the experiment at the sample. (c) The spatially resolved shock breakout, with the speed of the shock front (u_s) and the piston interface (u_p) at the center of the profile ($u_{s \text{ or } p,c}$) and off-center ($u_{s \text{ or } p,o}$). Each position in the profile corresponds to a row of pixels (each of which gives an independent time trace) in the detector CCD. The horizontal length scale is greatly expanded for clarity; in the actual experiment, off-axis components of velocities are neligible.

Meanwhile, a pair of chirped probe pulses incident from the opposite side measure a time-dependent phase shift (effectively an ultrafast analog to the velocity interferometry system for any reflector (VISAR)[18] system used in longer time scale experiments) which, via methods described previously,[1,16] give the shock speed, the piston speed (ie. the speed of Al/sample interface), and the index of refraction between the shock front and the piston interface. On the probe side, the piston interface is imaged onto the slit of an imaging spectrometer with a 0.28 NA microscope objective, with 10× total magnification between the sample and the detector, and the ultimate spatial resolution is ~2 μm. From knowledge of the particle speed just behind the shock front and the shockwave speed, the pressure and density of the shockwave compressed state can be derived from the Rankine–Hugoniot equations, which connect the initial and final thermodynamic states of the material using conservation of mass and momentum. We note that our experiment measures the piston speed, not the particle speed just behind shock front, but it has been shown in previous work[1] that, assuming the particle speed is the same as the measured piston speed, the measured shockwave speed will correspond to the known Hugoniot to better than 2% accuracy.[1,17] Here, we measure the Hugoniot of a previously uncharacterized sample (HP/NM) and assume an accuracy of better than 2% in the measurement for the unreacted species. Generally, as discussed below, the standard deviation of our data is less than 2%.

For quantitative comparisons between our data and Hugoniots from theory or fits to previous data, we evaluate a mean pairwise difference (MPD) given by

$$\text{MPD} = \left\langle \frac{u_s}{H(u_p)} - 1 \right\rangle \tag{1}$$

where H, a continuous function, is a theoretical Hugoniot or a fit to previous data, u_s is the measured shockwave speed, u_p is the corresponding measured piston speed, and the average is taken over measured data points. Mean pairwise differences larger than the standard deviation of the data are statistically significant.

This technique obtains a full spatial profile[16,17] of the shock breakout (Figure 1c) where the aspect ratio of the experiment is sufficient to assume near 1D compression over the central portion of the profile.[17,19] Because the piston speed varies with spatial position, it is possible (analogous to previous work with UDE[20]) to obtain several points along the Hugoniot simultaneously with a single shot, rather than only one point per shot (typically at the center of the spatial profile) as in most previous work.[1,17,21] Here (for NM/HP), we measure shock parameters at several points along the spatial profile from each of multiple shots at a given pump energy, for three pump energies. This increases the amount of data that may be obtained per shot and allows averaging of Hugoniot points which reduces noise and enables statistical characterization of the measurement. This also enables direct confirmation of the assumption of 1D compression, where shock parameters should only depend on the local intensity of the pump[22] not (explicitly) the pump energy—when the 1D approximation is valid, the shock and piston speeds are correlated regardless of the total pump energy.

To calculate the universal liquid Hugoniot[13] (for a comparison to the measured Hugoniot data), the sound speed was measured in NM/HP under ambient conditions.

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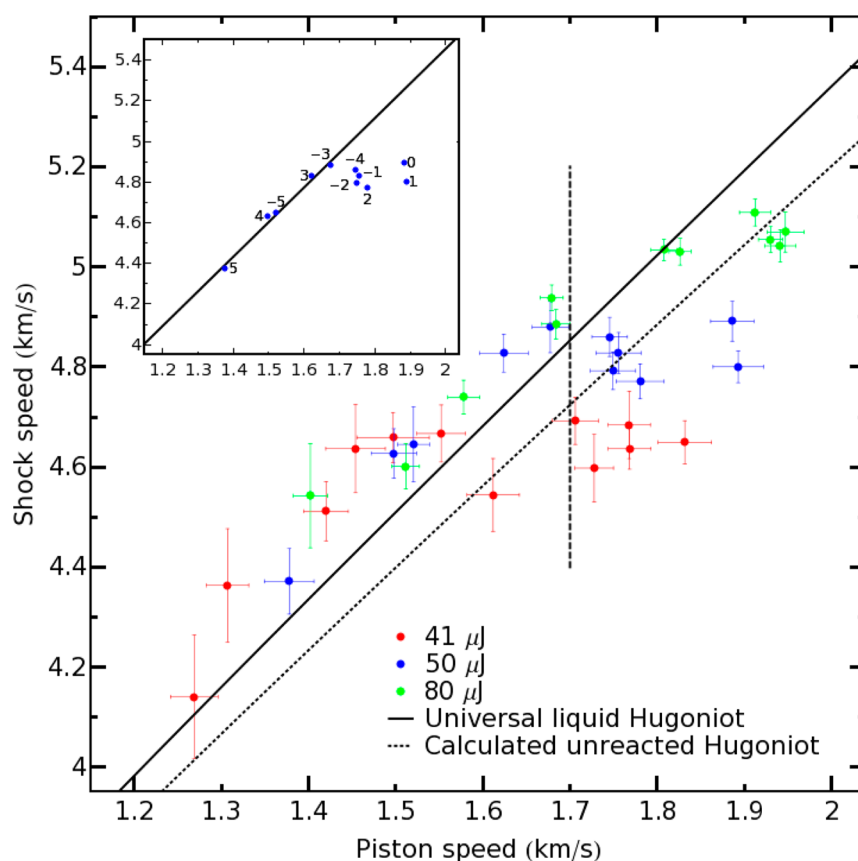dx.doi.org/10.1021/jp502891p | *J. Phys. Chem. A* 2014, 118, 6148–6153

Figure 2. Hugoniot data for the NM/HP mixture, the universal liquid Hugoniot, and the Hugoniot calculated using thermochemical techniques. The vertical dashed line is at 1.7 km/s piston speed, which is near the initiation threshold for HP and NM (see main text). The inset shows the data taken with 50 μJ pump energy (without error bars). Each point is labeled by CCD pixel row, where each pixel row corresponds to a spatial position on the sample along a 1D cut through the pump profile. Pixel 0 is the center of the profile. A fit to data below 1.7 km/s piston speed is shown as a guide.

RESULTS AND DISCUSSION

For the NM/HP mixture, we measured shock and piston speeds at three different pulse energies, 41, 50, and 80 μJ. For each pump energy, we obtained between 40 and 50 shots. Shock and piston speed pairs were determined for approximately 10 positions near the spatial center of the pump pulse for all shots, and all shots of a given energy and position were averaged to obtain the u_s–u_p data shown in Figure 2. Error bars are plus or minus one standard deviation of the data from the mean for data at a given pump energy and spatial position. For pure NM, we obtained center of profile Hugoniot data under conditions similar to those for HP data obtained previously.[1] The MPD between our NM data and a linear fit to previously measured unreacted NM shock Hugoniot data[24] for $u_p > 1.2$ km/s (i.e., where the noise is low) is 0.6%, which is within the standard deviation of the previously measured NM data from its linear fit, 1.6%.

The inset to Figure 2 shows NM/HP data for 50 μJ pump energy where points along a spatial 1D cut through the pump profile are labeled by the corresponding position in CCD pixels

at the detector. The spacing of CCD pixels scales to 2 μm/pixel at the sample. Consistent with the spatial profile of the pump, the piston speed in the inset to Figure 2 starts from a minimum on one side of the spatial profile (at pixel −5), reaches a maximum at the center of the pump profile (near pixel 0), and then decreases to another minimum on the other side of the profile (at pixel 5). A similar progression is observed in data at all pump energies.

To calculate the ULH, the sound speed in the NM/HP mixture was measured under ambient conditions using ISLS as described in the Experimental Details. Based on an average of three measurements, the sound speed was 1582.0 km/s ± 1.6 m/s. The acoustic frequency for the measurements was 0.94 GHz; we did not attempt to measure acoustic dispersion as a function of frequency and so cannot be absolutely certain that we measured the fully relaxed sound speed. If a glass-like hydrogen bonding network persists in this mixture, then it is conceivable that the sound speed would be approximately 4–8% lower than our measured value.[23]

For points below 1.7 km/s piston speed, shock speeds are larger than the unreacted universal liquid Hugoniot[13] by an MPD of 2.1%, assuming the measured sound speed (at ambient conditions) of 1.582 km/s, and also larger than a thermochemical calculation of the mixture Hugoniot by an MPD of 5.1%. The latter estimate is based on thermodynamic modeling[14] using isotropic exponential-6 potentials augmented by dipole–dipole interactions, calibrated to available experimental data for the individual mixture components.[1,6,7,14,25]

The adiabatic speed of sound of the liquid mixture at ambient pressure and 294 K was measured using the impulsive stimulated light scattering (ISLS) technique,[23] where here, instead of containing the sample in a diamond anvil cell, a drop of the liquid sample was placed between two borosilicate microscope coverslips separated by a 120 μm thick Teflon gasket.
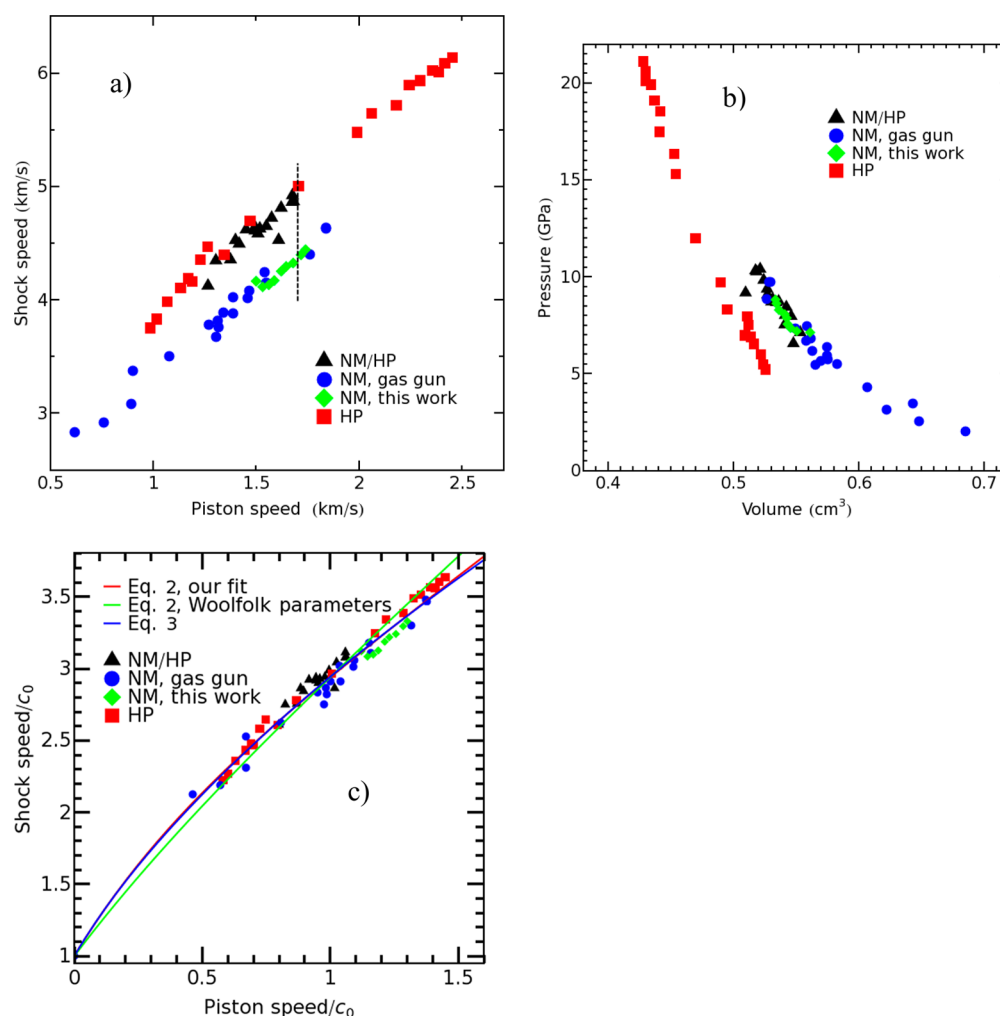
Figure 3. (a) Unreacted Hugoniot data for the NM/HP mixture, NM Hugoniot data from previous gas gun experiments, averaged ultrafast NM data, and averaged ultrafast HP Hugoniot data from previous work. The vertical dashed line is at 1.7 km/s piston speed, which is near the initiation threshold for HP and NM. (b) Thermodynamic states corresponding to shock data, with initial volumes of 0.79 cm^3 for NM/HP, 0.88 cm^3 for NM, and 0.71 cm^3 for HP. Thermochemical calculations give a temperature for the NM/HP mixture of 920 K at a piston speed of 1.7 km/s. (c) The same data as Figure 3a, but in the normalized form of Woolfolk et al.,[13] where the shock and piston speeds are normalized by the ambient condition sound speed (for a given sample). The three fits are the Woolfolk form of the ULH[13] (eq 2) with our fit for the parameters (red), the Woolfolk ULH using his parameters (green), and our form (from the text, blue). The blue and red curves very nearly overlap.

The difference with the experiments may possibly be due to limitations of such modeling for relatively low temperature mixtures, particularly due to the use of isotropic short-range interactions and standard unlike-pair mixing rules for a fairly large molecule such as nitromethane.

Except for one point (at approximately 1.6 km/s piston speed and 4.5 km/s shock speed), all data below 1.7 km/s piston speed are consistent with a linear trend and, generally, the average piston speed increases with pump energy. The remaining data vary substantially with pump energy. Because 1.7 km/s is near the initiation thresholds of both NM (1.84 km/s[24]) and HP (1.7 km/s[26]), henceforth we will refer to data below this value as the unreacted Hugoniot of the NM/HP mixture. Further, above 1.7 km/s piston speed the data deviate significantly below the extrapolated unreacted Hugoniot, likely due to effects related to initiation, although the downward trend is puzzling given the expected exothermic reactivity (we should note, however, that the interpretation of our data rests on the assumption that the index of refraction behind the shock front is real, yet recent simulations[27] of shocked NM indicate

that the reacting sample may develop an imaginary index of refraction). Indeed, exothermic transitions are normally expected to exhibit the opposite behavior, as found, for example, in hydrogen peroxide;[1] nominally exothermic reactions within a ~300 ps time window have also been observed in pure nitromethane above about 2 km/s piston speed.[28] In contrast, downward trends have been previously associated with first-order phase transformations in shocked solids[29] and continuous shock-induced dissociation in fluids, e.g., molecular nitrogen.[30] Discontinuous dissociation, i.e., liquid–liquid phase transition, has also been suggested for molecular hydrogen[31] and likely occurs in shocked carbonyl disulfide (CS$_2$);[32] we note that all these are typically endothermic transitions. As opposed to longer time scale measurements that most often characterize only the final states, ultrafast measurements may also probe the kinetics of such transformations, which yields new insights but can also complicate the experimental analysis; further experimental development is desirable.

We also note that the observed deviation threshold varies with the laser drive energy and speculate that this variation is due to deviations from quasi-1D compression. Although the data explicitly confirm (over all pump energies) quasi-1D behavior for compression along the unreacted Hugoniot, the response of the sample may be sufficiently nonlinear (above a threshold piston speed) for the hydrodynamic response to diverge from quasi-1D, resulting in a variation of threshold hydrodynamic behavior with compressed volume (which is proportional to the pulse energy). Deviations from the unreacted Hugoniot are least severe for the highest pump energy, where we would expect the least departure from quasi-1D conditions.

Such deviations occur within the 350 ps time window of the experiment, in contrast to previous ultrafast HP data, which do not diverge from the corresponding unreacted Hugoniot for any piston speed between the initiation threshold (of 1.7 km/s piston speed)[26] and the von Neumann pressure for the steady detonation.[1] This suggests that the initiation mechanism in NM/HP may differ from that in HP, with the oxygen-balanced mixture possibly exhibiting faster initial kinetics.

Ultrafast NM/HP data, NM data compiled from gas gun experiments,[24] ultrafast NM data, and ultrafast HP data from previous work[1] are shown in Figure 3. The ultrafast HP data were calculated by sorting previously published data[1] by piston speed, and taking an average of every subsequent 5 points in this sorted set. The original HP data set had 100 points distributed between 1 and 2.5 km/s piston speed. The averaged data set has 20 points total, with the averaged points well-centered in the larger set of unaveraged points. This procedure reduces the scatter per point and makes trends in the data easier to see. The ultrafast NM data were derived from the same averaging procedure applied to center of profile data acquired in the same way as the HP data of ref 1. Nine averaged points were derived from the original ultrafast NM data set comprising 45 shots.

Figure 3c shows the data plotted in the normalized form of Wookfolk et al.[13] The plot is consistent with the existence of an "universal" liquid Hugoniot (ULH), as proposed by Woolfolk et al., which posits that all liquid Hugoniot data should fall on the same curve when plotted as u_s/c_0 vs u_p/c_0, where c_0 is the speed of sound in the sample under ambient conditions. They suggested the functional form

$$\frac{u_s}{c_0} = 1 + a_0(1 - e^{-a_1 u_p/c_0}) + a_2\frac{u_p}{c_0} \tag{2}$$

for this "universal" curve, which has the correct limiting behavior at low piston speeds and trends to a linear dependence at high piston speeds, as usually assumed and often experimentally observed in shock physics; the Woolfolk et al. parameters for the form of eq 2 are $a_0 = 0.37$, $a_1 = 2$, and $a_2 = 1.62$. Although this relation is the most commonly cited, at least one other form for the high piston speed liquid Hugoniot was proposed by Voskoboinikov et al.,[33] without the exponential term. The Woolfolk et al. ULH matches well the HP and NM/HP data at higher piston speeds ($u_p/c_0 > 1$), with significant deviations occurring for lower values. Our fit to the data of Figure 3c using the form of eq 2 gives $a_0 = 0.670$, $a_1 = 2.43$, and $a_2 = 1.33$; such fits are sometimes used when the Woolfolk functional form, not the actual parameters, is assumed to be "universal".[7] It is worth noting that there is no fundamental basis for the above functional form (or the ULH idea). For example, we find that the relation

$$\frac{u_s}{c_0} = 1 + \frac{u_p/c_0}{\frac{u_p}{c_0} + b_0} - 2e^{-b_1 c_0/u_p} + \frac{4}{3}\frac{u_p}{c_0} \tag{3}$$

(shown in Figure 3c as a blue line), which actually yields the right asymptotic behavior for ($u_p/c_0 \to \infty$) (ideal gas limit), works equally well with $b_0 = 0.591$, $b_1 = 4.68$; of course, the exponential term can be easily neglected for the piston velocities of interest here.

Although unreacted data for all pump energies are consistent with a single Hugoniot for the NM/HP oxygen-balanced mixture, deviations of the data from the unreacted Hugoniot above the 1.7 km/s piston speed (1) depend significantly on the pump energy and (2) are substantially more scattered than unreacted data. No obvious mechanism explains this, but threshold reactivity effects may play a role above 1.7 km/s piston speed. Future experimental development may enable extending the data to higher piston speeds and longer time scales and thus help to elucidate these issues.

In conclusion, we have used ultrafast optical interferometry to measure the Hugoniot of an oxygen balanced nitromethane/hydrogen peroxide mixture and compared these data with Hugoniot data for pure nitromethane (NM) and a 90% hydrogen peroxide/water mixture (HP), as well as theoretical predictions. We observe a 2.1% percent mean pairwise difference between the measured shockwave speed (at the measured piston speed) in unreacted NM/HP and the corresponding "universal" liquid Hugoniot, which is larger than the average standard deviation of our data, 1.4%. For NM/HP, we observe deviations from the unreacted Hugoniot which may be related to mixing effects or an imaginary index of refraction. We also generally note that the low particle speed form of the "universal" liquid Hugoniot is not strongly constrained by empirical data—an alternate form which gives the correct behavior in the high particle speed limit fits the data as well as the conventional Woolfolk form. We emphasize that an empirical form such as the ULH (based on the Wookfolk parametrization or otherwise) cannot replace the direct measurement of Hugoniot data.

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Notes
The authors declare no competing financial interest.

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