LA-UR-95- 2763

CONF-950846--34

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

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SUBMITTED TO: 1995 APS Topical Conference on "Shock Compression of Condensed Matter"
August 13-18, 1995 - Seattle, WA

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OBSERVATIONS OF SHOCK - INDUCED REACTION IN LIQUID BROMOFORM UP TO 11 GPa†

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Shock measurements on bromoform ($CHBr_3$) over the past 33 years at Los Alamos have led to speculation that this material undergoes a shock-induced reaction. Ramsay observed that it became opaque after a 1 to 2 μs induction time when shocked to pressures above 6 GPa (1). McQueen and Isaak observed that it is a strong light emitter above 25 GPa (2). Hugoniot data start to deviate from the anticipated liquid Hugoniot at pressures above 10 GPa. We have used electromagnetic particle velocity gauging to measure wave profiles in shocked liquid bromoform. At pressures below 9 GPa, there is no mechanical evidence of reaction. At a pressure slightly above 10 GPa, the observed wave profiles are similar to those observed in initiating liquid explosives such as nitromethane. Their characteristics are completely different from the two-wave structures observed in shocked liquids where the products are more dense than the reactants. As with explosives, a reaction producing products which are less dense than the reactants is indicated. BKW calculations also indicate that a detonation type reaction may be possible.

INTRODUCTION

Shock experiments on bromoform ($CHBr_3$) were done by Ramsay (1) at Los Alamos in the early 1960's. The objective of this work was to understand why some liquid explosives become opaque during shock-initiation. Nonexplosive liquids were also studied and bromoform was found to go opaque with an induction time of 1 to 2 μs when shocked above 6 GPa (1). Ramsay made Hugoniot measurements from 3 to 24 GPa, but from these no definitive reason for the material becoming opaque could be determined. He noted, however, that when compared with water, the Hugoniot had an odd shape in the shock-velocity vs. particle-velocity plane.

Experiments by McQueen and Isaak in the early 1980's showed that when bromoform is shocked to pressures above 25 GPa, the shock front emits radiation whose intensity varies with the shock pressure (2). In fact, light emission from shocked bromoform is used at Los Alamos as both a shock time-of-arrival detector and as an indicator of wave profile changes occurring in materials which are in contact with the bromoform. McQueen and Isaak's study did not lead to new information regarding a shock-induced reaction.

For some time we have been using the "universal" liquid Hugoniot developed by Woolfolk, Cowperthwaite, and Shaw (3) to estimate the Hugoniot for many liquids. Deviation from this Hugoniot often indicates the condition at which a shock-induced reaction might occur (4). When the Hugoniot data from Ramsay (1) and McQueen and Isaak (2) were plotted with the "universal" liquid Hugoniot for bromoform, deviations indicated that a reaction might be occurring at pressures as low as 10 GPa. Based on this, we have done further experiments to try to determine the shock pressure threshold and nature of the reaction.

EXPERIMENTAL DETAILS

Because bromoform has a relatively high density, 2.89 g/cm^3, pressures over 10 GPa could be obtained in single-shock experiments using our single-stage gas gun. Eight electromagnetic particle velocity gauging experiments of two different types have been completed in the pr ·re range of 3 to

† Work performed under the auspices of the U.S. Dept. of Energy.

10 Gpa. Parameters for these gas gun experiments are summarized in Table 1.

In the first type of experiments, called "Stirrup" experiments, magnetic "stirrup shaped" gauges at the front and back of the bromoform were used to measure the input and transmitted shock wave profiles. Stirrup experiments used a liquid cell 3 mm thick, 28.6 mm in inside diameter and 68.6 mm in outside diameter made from Kel-F plastic. A 3-mm-thick Kel-F front, and a 12-mm-thick Kel-F back plate completed the cell. The front, center ring, and back of the cell were epoxied and screwed together with nylon screws. Copper stirrup gauge elements, 5-μm thick on a 50-μm-thick Kapton substrate, were epoxied to the front and back cell pieces. The active gauge length was 9 mm, and the Kapton backing was in contact with the liquid. Five stirrup experiments were done.

The second type of experiment, called "MMG", for Multiple Magnetic Gauge experiment, consisted of a thin gauge package (with up to 10 particle velocity gauges in it) suspended at an angle in the liquid bromoform. This enabled the wave profile to be monitored at various depths in the liquid.

The MMG experiment is shown in an exploded view of Fig. 1. It consists of a two-piece PMMA body with an MMG package epoxied between the two pieces. The gauge package is on a plane at a 30 degree angle with the top of the cell. A Kel-F front completes a cell which is 40.6 mm inside diam. by 9 mm thick. The inside of the cell was lined with either Teflon or epoxy to keep the bromoform from dissolving or reacting with the PMMA. On some experiments a stirrup gauge was epoxied to the cell top as shown in Fig. 1. MMG cells were also epoxied and screwed together with nylon screws. Three of these experiments were completed.

Cells were filled just before the impact

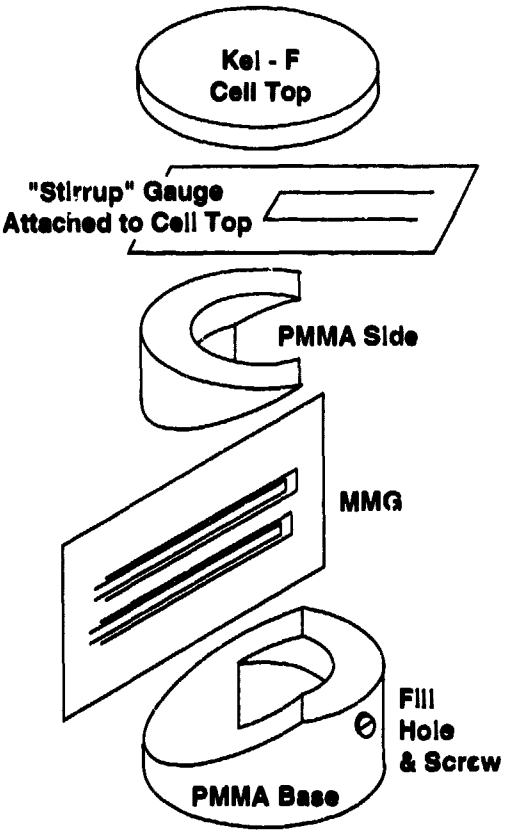

FIGURE 1. Exploded view of the MMG experiment showing the magnetic gauge and construction details.

experiment using Aldrich Chemical Co. bromoform (Aldrich #24,103-2). This bromoform is 99+ % pure, the major impurity being a small amount of ethanol stabilizer added by Aldrich.

Projectiles were made of Lexan and faced with impactors of either Vistal (pressed polycrystalline sapphire) or single crystal z-cut sapphire.

TABLE 1. Gas Gun Shot and Unreacted Hugoniot Data for Liquid Bromoform.

Shot No.	Type of Experiment	Impactor Material	Impact Velocity (mm/μs)	Particle Velocity (mm/μs)	Shock Velocity (mm/μs)	Shock Pressure (GPa)	Relative Volume (V/V_0)
741	Stirrup	Vistal	0.603	0.534	2.05	3.17	0.740
742	Stirrup	Vistal	0.798	0.680	2.45†	4.83	0.723
743	Stirrup	Vistal	1.000	0.840	2.58	6.26	0.674
744	Stirrup	Sapphire	(1.25)*	1.07	2.95	9.10	0.638
745	Stirrup	Sapphire	1.410	1.14‡	3.07‡	10.1‡	0.629‡
1033	MMG	Sapphire	0.964	0.83	2.542	6.09	0.674
1034	MMG	Sapphire	1.267	1.06	3.035	9.30	0.651
1035	MMG	Sapphire	1.391	1.16	3.147	10.6	0.631

† Back gauge data not good * Projectile velocity estimated. ‡ Evidence of reaction so data suspect.

RESULTS AND DISCUSSION

With these techniques, it was possible to measure the shock velocity in the bromoform quite accurately. In the stirrup experiments, the cell was rigid and the distance between gauges accurately known. Shock velocity was the distance between gauges divided by the wave transit time. In the MMG experiments, there were several gauges at fixed depths. The slope of a line fitted to the gauge depth vs. the wave arrival time gave a good shock velocity measurement. These quantities were determined for each of the experiments, even those suspected of having reaction, and are presented in Table 1. They are also plotted in Fig. 2 along with the data of Refs. 1 and 2 and the universal liquid Hugoniot for bromoform. With both the shock and particle velocity known, the mechanical state of the bromoform could be completely determined. Relevant quantities are also presented in Table 1.

Figure 2 clearly shows that Ramsay's lower pressure data are different from ours. Since his data were obtained from explosively driven experiments, at relatively low pressures, the inputs may not be accurately known. Our gun data should be more accurate because the pressure input is constant and easily controlled with the projectile velocity. That our data fall on or near the expected liquid Hugoniot is another indication of their accuracy.

Starting at pressures between 10-15 GPa the data of Refs. 1 and 2 lie below the expected liquid bromoform Hugoniot. This is evidence that a reaction is occurring. Since the data are below the line, the products of the reaction are expected to be more dense than the reactants. This is similar to what has been observed in carbon disulfide (CS_2) (6), acrylonitrile (7), and other organic liquids. It is unknown whether or not this reaction causes the shocked bromoform to emit as indicated by McQueen and Isaak (2).

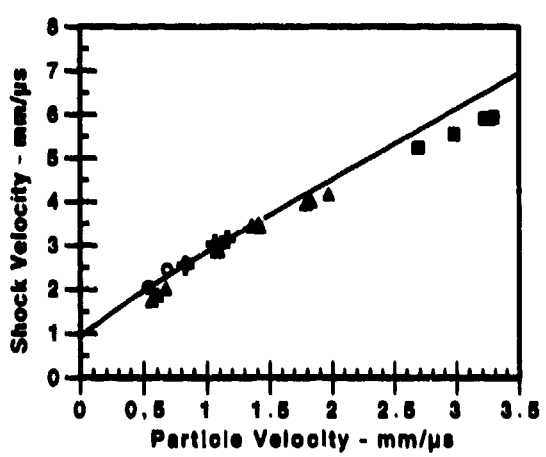

FIGURE 2. Hugoniot data for liquid bromoform. The line is the universal liquid Hugoniot using an initial condition sound speed of 0.931 mm/μs (5) Triangles are data from Ref. 1, and squares are data from Ref. 2. Data from our "stirrup" experiments are shown as circles and "MMG" data are shown as crosses.

Ramsay states that bromoform becomes opaque at pressures above 6 GPa with an induction time of 1 to 2 μs (1). Neither the Hugoniot measurements nor the particle velocity waveforms measured in our study show any mechanical evidence of a reaction in the 6 to 9 GPa range. Particle velocity waveforms from a 9.3 GPa input MMG experiment are shown in Fig. 3a. There is no evidence in the waveforms of a chemical reaction. However, the bromoform has been held at pressure for scarcely one microsecond before the pressure is reduced by a rarefaction from the back of the impactor. It is possible that the reaction is too slow to be seen in this experiment. If a reaction does occur within one microsecond it does not result in a large enough volume change to be measurable with our particle velocity gauges. We do observe subtle waveform differences in this pressure regime but they are so small it would be unwise to interpret them as an indication of a reaction.

In contrast to the 9.3 GPa experiment of Fig. 3a very interesting waveforms were obtained at 10.6 GPa as can be seen in Fig. 3b. The four waveforms obtained from the MMG gauges in Fig. 3b are much like those obtained in homogeneous NM shock initiation experiments (8). In those experiments a reaction starts behind the shock front producing a spread out wave that then begins to move toward the shock front. As the reactive wave moves it steepens into a shock which grows in amplitude and eventually overtakes the initial shock. After overtake it has the character of a detonation wave. Analysis of the four waveforms shown in Fig. 3b indicates that bromoform is initiating in the same manner as the NM. In addition to this experiment, Shot 745 at 10.1 GPa had comparable behavior. Because there were only two gauges, one at the front and the other at the back of the bromoform, we did not understand what the waveforms meant until we saw the records obtained in Shot 1035.

Because bromoform has not been mentioned as an explosive material, these results were quite

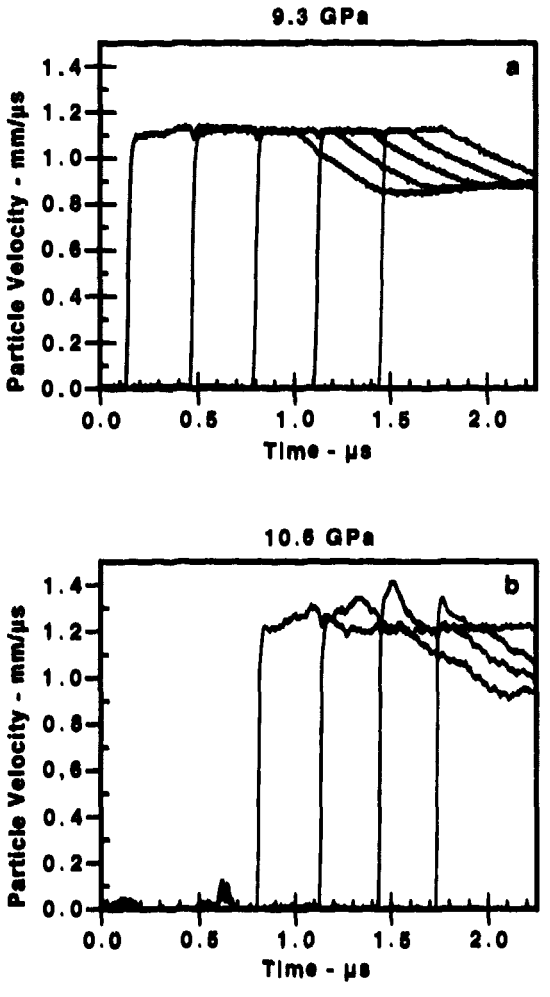

FIGURE 3. Magnetic particle velocity gauge waveforms from MMG experiments 1034 (a) and 1035 (b). Shot 1034 was at 9.3 GPa and showed no unusual behavior. Shot 1035 was at 10.6 GPa and has totally different waveforms. The two sets of waveforms are not time correlated because the gauges were at different depths.

surprising. A further evidence of bromoform's explosive behavior was that the aluminum shroud surrounding the target was expanded and cracked. This shroud protects the gun's target chamber from shrapnel originating from reacting explosive targets. It is never damaged during experiments on inert materials.

After this experiment was completed, we obtained BKW calculations on bromoform (9). These indicate that the expected reaction products are the gases HBr, Br_2, and CBr_4, and carbon as a solid. Further, a detonation could occur with a C-J pressure of 3.2 GPa. This C-J pressure does not agree with our measurements, but it does indicate that a regime in which the products are less dense than the reactants exists and explosive initiation like waveforms are expected. It is unknown at this time whether or not bromoform would detonate in a cylinder of finite diameter. Ours are 1-D measurements and do not really indicate what may happen in 2-D geometry.

Above 15 GPa, the Hugoniot data in Refs. 1 and 2 fall below the expected liquid Hugoniot, indicating the products are more dense than the reactant. Thus, either the reaction mechanism changes at this pressure or else some of the product gases are compressed to the point they become condensed. This remains to be determined, perhaps in MMG experiments at higher pressures on our two-stage gas gun.

In summary, some very interesting reactions occur in shocked bromoform. It apparently becomes opaque beginning at about 6 GPa but either in a slow reaction or with a small volume change. At 10 GPa a detonation like reaction (products less dense than the reactant) is observed. This changes in nature somewhere above an input of 15 GPa to be a reaction in which the products are more dense than the reactants. Clearly, there is room for more research to determine the exact nature of these reactions.

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