

# **LEGIBILITY NOTICE**

A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.

LA-UR -89-2718

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

---

LA-UR--89-2718

DE89 016594

TITLE SHOCK-INDUCED REACTION IN SEVERAL LIQUIDS

AUTHOR(S) Stephen A. Sheffield and Robert R. Alcon

SUBMITTED TO American Physical Society Topical Conference on Shock  
Compression of Condensed Matter, Albuquerque, NM,  
August 14-17, 1989

Referred by OSTI  
SEP 2 1989

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

---

 **Los Alamos** Los Alamos National Laboratory  
Los Alamos, New Mexico 87545

## SHOCK-INDUCED REACTION IN SEVERAL LIQUIDS<sup>1</sup>

Stephen A. SHEFFIELD and Robert R. ALCON

Los Alamos National Laboratory, Group M-9, MS P952, Los Alamos, New Mexico 87545

Single-shock experiments have been completed in several liquids using multiple, embedded, electromagnetic Lagrangian particle velocity and impulse gauges to measure shock waveforms. The liquids include acrylonitrile, bromoform, diiodomethane, phenylacetylene, bromocyclopropane, and carbon disulfide. Some of these are known to exhibit shock-induced reaction and others are considered to be candidates for reaction studies. The "universal" liquid Hugoniot, which depends only on initial condition sound speed, was used to calculate the unreacted Hugoniot. Sound velocities were measured for those liquids with no data available. The effects of shock-induced reaction are clearly identified in the particle velocity waveforms for some materials, but there are remaining questions about whether reactions occur in others. The most impressive results are that the full reactive, two-wave structure was measured in phenylacetylene. On the reacting materials with two-wave structures, the particle velocity waveforms had a decrease behind the top of the first wave. This is thought to be evidence of an early reaction which occurs at the top of the first (non-reactive) wave.

### 1. INTRODUCTION

Although a number of experimental studies have been made on shock-induced reactions in liquid materials, little basic understanding concerning why the materials react and what the reactions are has resulted. Our purpose is to find materials that can be studied spectroscopically to gain understanding of the reaction process. The approach is to identify candidate liquids by making measurements of the shock wave profiles resulting from the reactions. Carbon disulfide ( $CS_2$ ),<sup>1-4</sup> acrylonitrile,<sup>5</sup> toluene,<sup>6</sup> benzene,<sup>6</sup> and other organic liquids<sup>6-7</sup> are known to have reactions which result from shock loading up to particular levels. These reactions have usually been established by noting cusps in a plot of measured Hugoniot data. For  $CS_2$ <sup>1-4,8</sup> and acrylonitrile<sup>5</sup> extensive studies have been made with only limited success in understanding the reactions.

Many other materials probably will react in the shock environment but have not yet been identified. A method has been devised to estimate the liquid Hugoniot and then do a few shock experiments to look for deviations from this Hugoniot to see if there is evidence of a reaction. We report here progress made using this approach.

### 2. EXPERIMENT

There are three aspects to this study. First, an estimate of the shock Hugoniot is obtained using the "universal" liquid Hugoniot.<sup>9</sup> This relation requires knowledge of the initial condition sound speed so a method was developed to measure this property. Finally, an electromagnetic gauging technique unique to Los Alamos was used to measure the shock attributes.

#### 2.1. "Universal" Liquid Hugoniot

A "universal" liquid Hugoniot relation was proposed by Woolfolk, Cowperthwaite, and Shaw at SRI in 1973.<sup>9</sup> This empirical form is,

$$U_s/c_0 = 1.37 - 0.37 \exp(-2u_p/c_0) + 1.62u_p/c_0$$

where  $U_s$  is the shock velocity,  $u_p$  is particle velocity, and  $c_0$  is the initial condition sound speed (the only adjustable parameter). This relation allows the  $U_s - u_p$  Hugoniot to start at the initial condition sound speed and still become linear at high pressures.

We have used this empirical relation to estimate the Hugoniot for over 40 liquids (with available Hugoniot data), including liquid argon, mercury, benzene,  $CS_2$ , and water. The calculated Hugoniot fits

<sup>1</sup>Work performed under the auspices of the U.S. Department of Energy

TABLE I  
SOUND SPEED DATA FOR LIQUIDS

Chemical Name and Formula	Density $\text{g/cm}^3$	Measured Sound Speed $\text{mm}/\mu\text{s}$
Acrylonitrile $\text{H}_2\text{C}=\text{CHCN}$	$0.806^{20^\circ\text{C}}$	$1.19^{26^\circ\text{C}}$
Benzonitrile $\text{C}_6\text{H}_5\text{CN}$	$1.102^{15^\circ\text{C}}$	$1.43^{27^\circ\text{C}}$
Diiodomethane $\text{CH}_2\text{I}_2$	$3.325^{20^\circ\text{C}}$	$0.966^{27^\circ\text{C}}$
Phenylacetylene $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$	$0.928^{20^\circ\text{C}}$	$1.39^{24^\circ\text{C}}$
Bromocyclopropane $\text{C}_3\text{H}_5\text{Br}$	$\approx 1.51$	$1.01^{24.5^\circ\text{C}}$
2-Bromopropene $\text{CH}_3\text{CBr}=\text{CH}_2$	$1.362^{20^\circ\text{C}}$	$0.907^{25^\circ\text{C}}$
2-Butyne $\text{CH}_3\text{C}\equiv\text{CCH}_3$	$0.691^{20^\circ\text{C}}$	$1.27^{18^\circ\text{C}}$

the experimental data well for this diverse set of liquids; this is fairly strong evidence that it provides a good unreacted Hugoniot estimate for liquids for which no experimental data exists. Deviation of data from this curve is assumed to result from some type of reaction.

### 2.2. Sound Speed Measurements

We put together a setup and measured liquid sound speeds for the liquids where this property had not been previously reported. This equipment consisted of a Mitutoyo digital height gauge, together with a Panametrics transducer/receiver system. Measurements made with this system are considered to be accurate to about 1%. Table I contains data for some of the liquids measured to date.

### 2.3. Shock Experimental Setup

All the experiments were done using an 8-m-long, 72-mm-diameter bore, single-stage gas gun capable of projectile velocities to  $1.43 \text{ mm}/\mu\text{s}$  in magnetic gauging experiments. An electromagnet was installed in the target chamber to provide the magnetic field (up to 825 gauss).

Electromagnetic gauging in shock experiments was first reported by Zaitsev, et al. in the Soviet Union in 1960.<sup>10</sup> We are using a system developed by Vorthman and Wackerle in the early 1980's.<sup>11</sup> The gauge package includes, in addition to particle velocity gauges, impulse gauges which were first reported

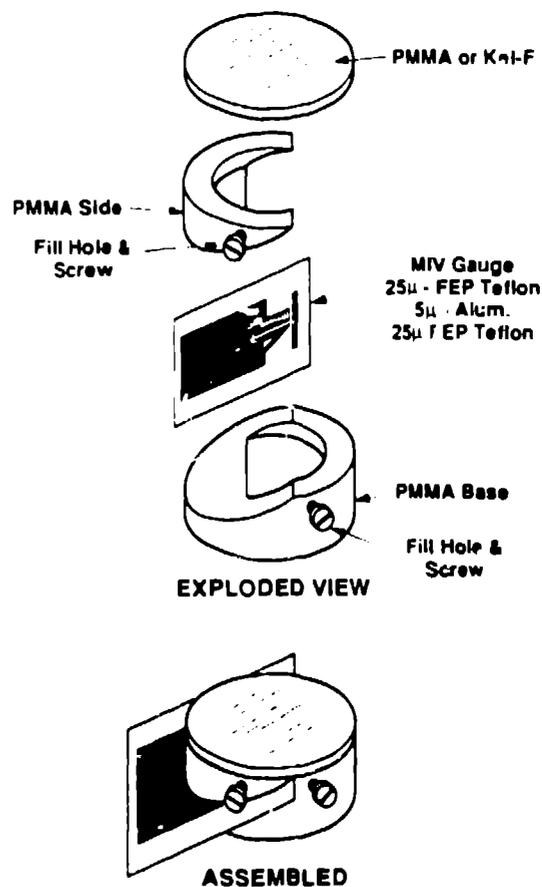


Figure 1.  
Plexiglas (PMMA)/Kel-F liquid cell and MIV gauge construction details.

by Young, et al.<sup>12</sup> We call our gauge package an MIV (Magnetic Impulse and Velocity) gauge. The gauge membrane was suspended at a  $30^\circ$  angle (with the shock plane) providing particle velocity and impulse measurements at each of five Lagrangian positions,  $\approx 1 \text{ mm}$  apart. Details of the gauge and cell are shown in Figure 1. The inside of the cell (40.6-mm dia. by 9-mm thick) was lined with Teflon film to prevent chemical attack on the Plexiglas. Before the unlined Kel-F cell front was attached, the gauge positions were measured with a depth microscope.

All chemicals were used as received. Shock-wave input to the cell was by a Lexan projectile faced with a single-crystal (z-oriented) sapphire impactor.

### 3. RESULTS AND DISCUSSION

Although large numbers of experiments have not been completed on each material, a single multiple gauge experiment provides better information than several experiments where only one measurement is made. Since particle velocity, shock velocity, and impulse (pressure) are all measured, the Hugoniot state is overdetermined and an idea of the internal consistency of the various data for each experiment can be obtained. We will provide here only a brief description of the measurements in each material. Several experiments on bromoform and diiodomethane provided no concrete evidence of reaction below pressures of 10 and 11 GPa, respectively, although there were unexplained anomalies in the waveforms.

#### 3.1. Carbon Disulfide

Although several new experiments have been completed on  $\text{CS}_2$ , the conclusions reached in a previous paper<sup>4</sup> remain valid. The cusp in the Hugoniot occurs at  $\approx 5.1$  GPa, the state measured at the top of the first wave in the reactive wave structure. It has not yet been possible to measure the full two-wave structure in this material with our gas gun. An interesting aspect of the latest experiments is that there is a decrease in particle velocity (or "pull back") at the top of the first wave. A re-examination of the two-wave structures produced in earlier double-shock experiments<sup>3</sup> also indicates similar behavior. There is a possibility that this could be the result of an early reaction at the top of the first wave (the condition of incipient reaction) but more work must be done to demonstrate this. The same behavior was noted for acrylonitrile and phenylacetylene below.

#### 3.2. Acrylonitrile

A single MIV gauge experiment was completed on acrylonitrile to see if a two-wave structure could be recorded. Unfortunately, only the first wave could be measured, although there was evidence that a second wave formed but rapidly fell behind the first wave. The sound speed was measured for this material (Table I) and the corresponding calculated Hugoniot agreed well with the data from the Soviet Union;<sup>6</sup> they estimated the Hugoniot cusp at a pressure of

4.3 GPa. From our measurements of particle velocity, shock velocity, and impulse (pressure) we estimate that the Hugoniot cusp occurs at 4.1 GPa. However, our measured Hugoniot state for the first wave does not agree as well as the Soviet data with the calculated Hugoniot so the exact pressure of the cusp is still in question. The waveforms from this experiment showed some particle velocity "pull back", similar to that observed in the  $\text{CS}_2$  experiments.

#### 3.3. Bromocyclopropane

Bromocyclopropane was studied because it has very high ring strain in its three-membered ring. We felt that the rather large ring strain would make it a likely candidate for ring opening in a shock environment, thereby producing bromopropene. The energies and densities of these two materials appear to be such that this reaction should have a "detonation like" behavior. One MIV gauge experiment was recently completed with an input pressure of  $\approx 7.5$  GPa. We did not observe a two-wave structure or a detonation like waveform. However, there appeared to be some slight rounding in the later particle velocity waveforms. This may be the result of a considerably overdriven reaction. It will take several experiments at lower pressures to check this out.

#### 3.4. Phenylacetylene

We had a desire to look at a carbon-carbon triple bond liquid and phenylacetylene was chosen because it has a high density and sound speed. It is an acetylene molecule with a benzene ring in place of one of the hydrogens, i.e., the carbon-carbon triple bond is attached to a benzene ring. Benzene has a cusp in the Hugoniot at about 13 GPa<sup>1,6</sup> and it was felt that if the carbon-carbon triple bond was very reactive in a shock environment, it might break considerably below this; perhaps at a condition we could obtain with our gas gun. Recently, an MIV gauge experiment was completed on this material. Beautiful developing two-wave particle velocity profiles were measured; the waveforms are shown in Figure 2. These experimental results were gratifying because this is the first time that the evolution of a full two-wave structure in a reacting liquid has been measured in

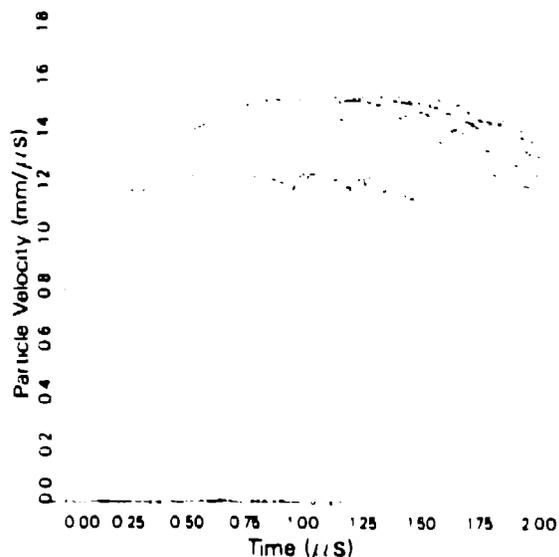


Figure 2.

MIV gauge particle velocity waveforms obtained from phenylacetylene experiment with a shock input of 6.8 GPa.

a single-shock input experiment. The input shock to the phenylacetylene was  $\approx 6.8$  GPa. Although careful data analysis is not yet complete, the first wave appears to have a pressure of  $\approx 4.8$  GPa. The second wave has more than one slope, a possible indication of a multistep reaction. There is considerable pull back in the particle velocity waveforms behind the first wave in this material also.

Because phenylacetylene reacted at such a low pressure, it appears that the acetylene part of the molecule (the C $\equiv$ C bond) is much more reactive than the benzene ring (4.8 GPa compared to 13 GPa for benzene). Although this supports some ideas which we and others have had pertaining to the carbon-carbon triple and double bonds being more reactive in a shock than single bonds, much work yet remains before these ideas are well founded.

#### ACKNOWLEDGMENTS

We thank W. J. Spencer and M. Whitehead for their help in obtaining the data. Many valuable discussions on chemistry with Ray Engelke are also appreciated.

#### REFERENCES

1. R. D. Dick, Shock Wave Compression of Benzene, Carbon Disulfide, Carbon Tetrachloride, and Liquid Nitrogen, Los Alamos Scientific Lab. Report LA-3915 (1968).
2. R. D. Dick, Bull. Am. Phys. S. 27(4) (1982) 507.
3. S. A. Sheffield, J. Chem. Phys. 31 (1984) 3048; S. A. Sheffield, Shock-Induced Reaction in Carbon Disulfide, Ph.D. Thesis at Washington State University, Pullman, WA (1978).
4. S. A. Sheffield, Onset of Shock-Induced Reaction in Liquid CS<sub>2</sub>, in: Shock Waves in Condensed Matter-1987, eds. S. C. Schmidt and N. C. Holmes (North-Holland, New York, 1988) pp. 463-466.
5. V. V. Yakushev, S. S. Nabatov, and O. B. Yakusheva, Comb. Expl. and Shock Waves 10(4) (1975) 509.
6. R. D. Dick, J. Chem. Phys. 71 (1979) 3203; R. D. Dick, J. Chem. Phys. 74 (1981) 4053; R. D. Dick, J. Chem. Phys. 52 (1970) 6021.
7. O. B. Yakusheva, V. V. Yakushev, and A. N. Dremin, High Temp.-High Pres. 3 (1971) 261.
8. K. M. Olgilvie and G. E. Duvall, J. Chem. Phys. 78 (1983) 1077; G. E. Duvall, R. H. Grandholm, P. M. Bellamy, and J. E. Hegland, Effects of Temperature on the UV-Visible Spectrum of Dynamically Compressed CS<sub>2</sub>, in: Shock Waves in Condensed Matter-1985, ed. Y. M. Gupta (Plenum Press, New York, 1986) pp. 221-229; C. S. Yoo, G. E. Duvall, J. Furrer, and R. Grandholm, J. Phys. Chem. 93 (1989) 3012.
9. R. W. Woolfolk, M. Cowperthwaite, and R. Shaw, Thermochemica Acta 5 (1973) 409.
10. V. M. Zaitsev, P. F. Pokhil, and K. K. Shvedov, Doklady Akademii Nauk. SSSR 132 (1960) 1339.
11. J. Vorthman and J. Wackerle, Multiple-Wave Effects on Explosives Decomposition Rates, in: Shock Waves in Condensed Matter-1983, eds. J. R. Asay, R. A. Graham, and G. K. Straub (North-Holland, New York, 1984) pp. 613-616.
12. C. Young, R. Fowles, and R. P. Swift, Chapter 9. An Electromagnetic Stress Gauge, in: Waves and the Mechanical Properties of Solids, eds. J. J. Burke and V. Weiss (Syracuse University Press, 1971) pp. 203-223.