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Shock Compression of Formic Acid

Author(s):

Virginia W. Manner
Stephen A. Sheffield
Dana M. Dattelbaum
David B. Stahl

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SHOCK COMPRESSION OF FORMIC ACID

V. W. Manner,[1] S. A. Sheffield,[2] D. M. Dattelbaum,[2] and D. B. Stahl[2]

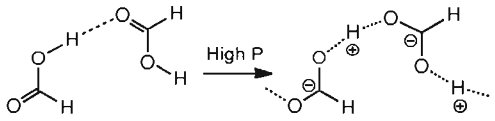
[1] *WX-6, MS-C920, Los Alamos National Laboratory, Los Alamos, NM 87545*
[2] *WX-9, MS-P952, Los Alamos National Laboratory, Los Alamos, NM 87545*

Abstract. Simple molecules such as formic acid, HCOOH, have been suggested to play important roles in the origin of life due to their high pressure and temperature chemistry. The hydrogen bonding characteristics and polymerization of HCOOH under static high pressure have been recently investigated using both molecular dynamics calculations and experimental work. These works suggest that symmetric hydrogen bonding of HCOOH (forming a linear chain polymer where all C-O bonds are equivalent) occurs at 16 – 21 GPa at room temperature. In order to examine the shock compression behavior of this simple carboxylic acid, we present a series of gas gun-driven plate impact experiments on formic acid with shock inputs in the range of 5.5 – 23.0 GPa. Using in-situ electromagnetic gauges, shock wave profiles (particle velocities) were measured at multiple positions as a function of shock input pressure, providing valuable information about its unreacted equation of state. No easily recognizable shock-induced reactions were observed in any of the four experiments, and the four points lie close to a universal liquid Hugoniot based only on the sound speed of formic acid.

Keywords: Shock compression, Hugoniot, formic acid, HCOOH, equation of state, chemical reaction.
PACS: 47.40.Nm, 62.50.Ef, 82.40.Fp

INTRODUCTION

The shock compression of formic acid (HCOOH) has been an area of interest because its polymerization under high pressures suggests it may play a role in the origin of life, where simple molecules combine to form more complex structures. Trunin *et al.* and Voskoboinikov have reported that under the high temperatures and pressures of shock compression, a deviation in the formic acid Hugoniot is seen at ~15 GPa [1,2]. These data indicate that a change in the density of the liquid occurs under shock, supporting reaction (possible polymerization). Additionally, more recent molecular dynamics calculations and low temperature, static high-pressure diamond-anvil cell experiments indicate reaction may occur at roughly 16 – 21 GPa at room temperature, as proposed in Eqn 1 [3,4,5]. In order to investigate the shock wave response of this simple organic carboxylic acid under shock conditions, we have examined its behavior with embedded magnetic-gauge gas gun-driven plate impact experiments at 5.5 – 23.0 GPa.



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EXPERIMENTAL SETUP

Formic acid was either purchased and used as received from Fluka (Lot # BCBB9543), or purified by selective crystallization at ~5 °C from BASF Group Chemical Company. NMR spectroscopy confirmed that the only significant (>0.5%) impurity was water. Density measurements indicated >98% purity (with ~2% water impurity) for the Fluka samples, and >99% purity for the BASF samples. Refractive index measurements were identical for the two samples (1.37120 at 20 °C).

For the gas gun experiments, a fully assembled liquid cell (Fig 1) was filled with formic acid. A 60 µm gauge membrane – a sandwich of two pieces of 25 µm FEP Teflon containing 5 µm thick Al etched in a gauge pattern – was glued at a 30° angle between two pieces of Lexan [6]. A single element gauge (stirrup gauge) was glued to the Kel-F 81 top, and the top was then glued and screwed to the cell using Teflon screws [7].

Of the glues tested with formic acid, only High-Temp Red Silicone Gasket glue (Permatex) was compatible (verified by NMR spectroscopy of a solution of formic acid in contact with the glue for 4h). Therefore all parts of the gauge and cell in contact with the solution were connected using this glue. The outer parts of the cell were glued with 20-minute epoxy to provide additional strength to the glue bonds. Lexan and Teflon were also shown to be compatible with formic acid (although PMMA and most plastics and glues were not).

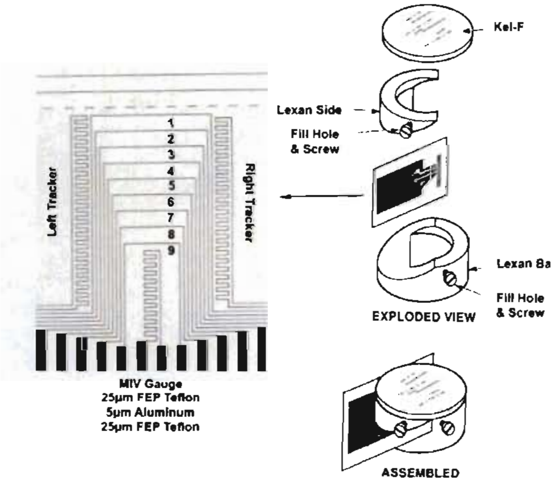

Figure 1. Liquid cell used to contain the formic acid – both an exploded view and the assembled unit, and a picture of the gauge membrane.

All experiments were conducted on a gas-driven two-stage gun with a launch tube bore with 50 mm diameter and a maximum projectile velocity capability of ~3.5 km s^{-1}. A small TV camera was mounted to the back of the cell so we could observe that no leaking or reaction occurred after it was filled with the formic acid and placed under vacuum in the target chamber for 2 – 3h. The air temperature was 21 ± 3 °C during the loading and firing of each shot.

The gun had an electromagnet mounted in the target chamber that produced a uniform 1200 gauss field in the gauge region. The Lexan gun projectiles had Kel-F 81 or polycrystalline Sapphire (Vistal) impactors on the front, and the projectile velocity was measured to an accuracy of ~0.1%. The gauge membrane had 9 particle velocity and three "shock tracker" gauges (Fig 1) [6]. The stirrup gauge, glued to the Kel-F 81 top and in contact with the liquid, provided a measurement of the particle velocity at the liquid input interface.

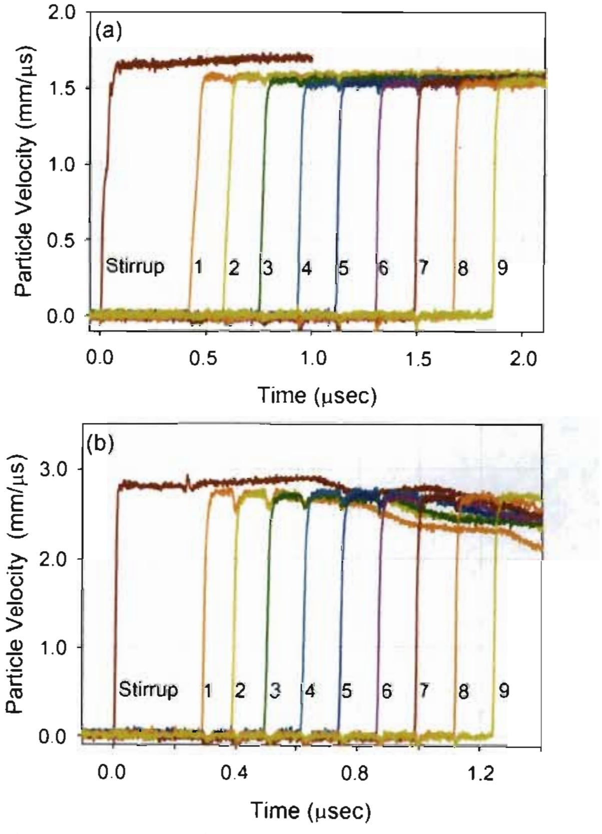

Figure 2. (a) Particle velocity (mm/µs) *vs* time for formic acid shot at 9.24 GPa (Kel-F impactor) and (b) 23.0 GPa (Vistal impactor), showing the stirrup gauge and gauges 1 – 9. The labels on Gauges 1 – 9 correspond to the labels in Fig 1.

RESULTS AND DISCUSSION

Four gas gun experiments were performed in this study. Fig 2 shows plots of particle velocity *vs* time for each gauge at shock inputs of 9.24 and 23.0 GPa. The input particle velocity (u_P) profile was taken from the voltage trace of the stirrup gauge, which is proportional to the gauge length, magnetic field, and u_P as a function of time [6]. At both input pressures, a flat profile is observed (Fig 2), indicating that no changes in density occur after the shock wave passes into the formic acid. At 23.0 GPa (Fig 2b), the decrease in particle velocity at longer times is due to release waves generated from the Vistal/Lexan surface of the projectile. The shock velocity (U_S) was calculated from a distance-time plot obtained from the position and time-of-arrival of the left and right trackers and the gauges (Fig 1) [6]. These data are summarized in Table 1 for all four experiments, where the relative volume change of the solution $\Delta V/V_0 = (V_0-V_1)/V_0 = u_P/U_S$, and the pressure $P = \rho_0 U_S u_P$, are taken from the jump conditions.

In shock wave experiments, Hugoniot curves are used to evaluate the material's equation of state (EOS). Equation 2 shows the empirically derived Universal Liquid Hugoniot [8],

$$U_S = 1.37C_0 - 0.37C_0\exp\left(\frac{-2u_P}{C_0}\right) + 1.62u_P \qquad (2)$$

where $C_0 = 1.28$ km s^{-1} for formic acid [9], plotted with the current data as well as previous published work [1]. All of the measured data in the present work falls on the line of the unreacted Hugoniot in the U_S–u_P plot (Fig 3).

Using equation 2 and the relations $P = \rho_0 U_S u_P$ and $\Delta V/V_0 = u_P/U_S$, the unreacted Hugoniot can also be plotted in terms of input pressure and relative volume change. Fig 4 shows the same trend as Fig 3, where the data lie on the predicted P–$\Delta V/V_0$ Hugoniot for the unreacted liquid. In summary, at 23.0 GPa under shock conditions (~2000 K and μs timescales), formic acid either does not polymerize or does not undergo any significant volume change. The same trend is observed at pressures of 5.53 – 17.7 GPa, where there is no visible deviation from the unreacted liquid Hugoniot, and no discernable wave structure under shock (as in Figure 2a).

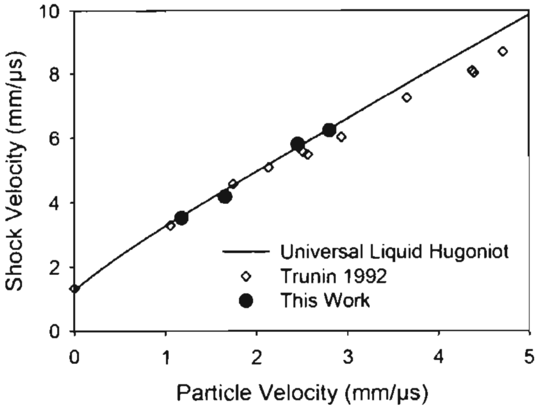

Figure 3. Universal Liquid Hugoniot (solid line) for shock velocity *vs* particle velocity (mm/μs), plotted with the present work and literature data.

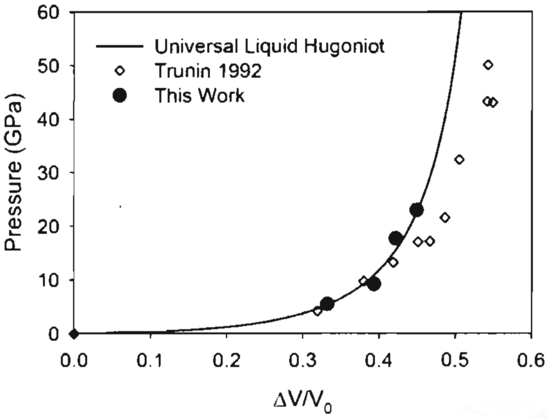

Figure 4. Pressure *vs* relative volume change of formic acid for all data in Figure 3.

Using formic acid thermodynamic parameters, an EOS model developed by Hayes [10] can be constructed based on the Helmholtz free energy.

TABLE 1. Summary of results from plate impact experiments on formic acid.

Projectile Velocity (mm/μs)	Impactor	Pressure (GPa)	u_P (mm/μs)	U_S (mm/μs)	$\Delta V/V_0$ (u_P/U_S)
2.00	Kel-F 81	5.53	1.17	3.53	0.332
2.78	Kel-F 81	9.24	1.65	4.19	0.393
2.75	Vistal	17.7	2.45	5.81	0.422
3.29	Vistal	23.0	2.80	6.24	0.449

Calculations based on this model give a rough estimate of temperature under shock conditions for each input pressure, using the following parameters: C_V = 1.699 J/gK, ρ_0 = 1.214 g/cc, $K_{T,0}$ = 0.025 Mbar, $\alpha = 1.076 \times 10^{-3}$ K^{-1}, $\Gamma = K_{T,0}\alpha/C_V\rho_0$ = 0.846, and N = 6.65. The calculations estimate a shock temperature of ~600 K at 5.53 GPa, and ~2100 K for 23.0 GPa. Even using our calculated temperatures as a minimum value [11], these pressures and temperatures place the shocked formic acid states in the decomposition region of the static P–T phase diagram reported by Montgomery *et al* [5]. However, under our shock conditions, we do not observe any indication of the volume change expected with reaction.

Formic acid has been suggested as a potentially important building block in the origin of life, in part due to its presence in the interstellar medium and comets [12] as well as its similarities with simple amino acids. In simulations of cometary impacts, amino acids and other simple organic compounds have survived shock conditions of over 20 GPa for several μs [13]. We have created similar conditions to these in laboratory experiments.

CONCLUSIONS

We have shocked pure formic acid using a two-stage gas gun, at shock input pressures of 5.5–23.0 GPa. We have experimentally defined the Hugoniot in this region for the first time, and see no evidence of a multi-wave structure or a density/volume change associated with reaction.

Fig 4 shows that Trunin *et al.*'s data deviates from the unreacted Hugoniot at ~15 GPa, suggesting that a volume change associated with polymerization or decomposition of formic acid should occur at ≥15 GPa under shock conditions. In contrast, our data shows no volume change at input pressures of ≤23 GPa.

These findings also disagree with previous static high-pressure studies and molecular dynamics calculations where polymerization occurs at ≤21 GPa. However, static high-pressure experiments are performed over long timescales (hours) where pressure and temperature are adjusted separately. In future work, formic acid will be shocked to higher input pressures, spectroscopic diagnostics will be pursued, and the shock compression of close relatives such as acetic acid will be investigated.

ACKNOWLEDGEMENTS

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