Shock-induced chemistry of phenylacetylene

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Abstract. Gas gun-driven shock compression experiments of phenylacetylene using embedded electromagnetic gauging were used to obtain in situ particle velocity wave profiles at multiple Lagrangian positions at several shock input conditions. At shock conditions above 6 GPa, the input shock wave evolved over time and distance into a complex multiple wave structure due to shock-driven chemical reactions. The 3-wave structure was marked by a fast risetime 2nd wave, slower risetime 3rd wave, and unusual wave dynamics in the 1st wave. From the measured shock and particle velocities, the 1st wave, and intermediate and final product states associated with the chemical reactions were determined. A thermodynamically complete unreacted equation of state was calibrated to estimate the temperature rise along the shock locus. Use of this EOS with the measured 2nd and 3rd wave risetimes yielded highly state-sensitive global reaction rates as a function of the shock locus.

1. Introduction

The study of shock-driven chemical reactions is important for understanding chemical reaction thresholds, their mechanisms and rates, and associated state sensitivities under the extreme conditions generated by shock compression. Phenylacetylene (C₈H₈, ethynyl benzene, PA figure 1) is a compelling “simple” molecular structure for investigation of shock-driven reactions, as it is comprised of covalently-bonded aromatic benzene ring and acetylene moieties, forming a π-electron rich structure. Phenylacetylene has been previously shown by this group to undergo shock-driven reaction(s), as indicated by the formation of multiple shock wave structures, at relatively low shock input conditions [1,2]. In this work, we describe the details of shock-driven reactivity in phenylacetylene obtained by in situ measurements of shock and reactive waves, and their associated dynamics as a function of the shock input condition. Shock wave compression of PA above 6 GPa results in the formation of a multiple (three) wave structure indicative of at least two densification reactions behind the shock front. An inert equation of state for PA was developed using measured thermodynamic properties and the experimental shock states, in order to estimate the temperature rise on the shock adiabat and interpret reaction rates and state sensitivities behind the front.
2. Experimental

Phenylacetylene (99+%) was purchased from Sigma Aldrich and was used without further purification. The ambient pressure bulk sound velocity was measured using a pulse-echo method, driven by a Panametrics HV pulser/receiver model #5058PR acoustic transducer. Selected properties of PA, including those used in developing an inert equation of state (EOS) [3,4], are reported in table 1.

2.1. Plate impact experiments

Gas gun-driven plate impact experiments were performed using a two-stage, 50 mm bore (launch tube) light gas gun at Los Alamos National Laboratory described previously [5]. Kel-F 81 (polychlorotrifluoroethylene) impactors were contained in Lexan projectiles and launched at velocities ranging from 1.59 to 2.79 km/s into instrumented targets containing liquid-phase PA at room temperature. In a single experiment, 1s-786, a z-cut sapphire impactor was used, housed in a projectile launched by a 72 mm diameter launch tube single-stage light-gas gun [6]. Embedded electromagnetic gauges were used as the principal diagnostic for measuring shock and reactive wave profiles in PA [7]. The electromagnetic gauges are thin (5 µm) Al foil elements sandwiched between two FEP-Teflon membranes, forming a gauge package approximately ~60 µm thick, figure 2. The gauge package is inserted on a 30° angle in a LANL-designed liquid cell consisting of a PMMA body, and Kel-F 81 front, positioning the gauges from ~1 to 7 mm into the liquid sample, as shown in figure 2A.

![Figure 1. Chemical structure of phenylacetylene.](image)

**Figure 2.** A) Exploded and assembled views of the liquid target cell used at LANL with embedded electromagnetic gauge membrane inserted on a 30° angle. The cell body is PMMA and the cell front (impact face) is Kel-F 81, producing a symmetric impact condition in the experiments. B) Optical micrograph of the embedded gauge package showing the particle velocity and shock tracker gauges. C) A single gauge element, or “stirrup” gauge is affixed to the rear surface of the Kel-F cell front in contact with the liquid, and is used to obtain the input condition.
A single ~0.94 cm gauge element, called a “stirrup” gauge” (figure 2C) was affixed to the front of the liquid cell in contact with the PA, and was used to obtain the shock input condition. The gauges operate on the principle of Faraday’s law with the measured voltage proportional to the gauge length, electromagnetic field (1.2 kG), and particle (mass) velocity in the material as described previously [6]. Using this technique, particle velocity shock wave profiles are measured at up to 10 Lagrangian positions in material.

2.2. Inert EOS
An inert equation of state (EOS) for PA was calibrated to ambient state property values and shock data taken along its unreacted (inert) Hugoniot. The EOS was based on the Sesame model [8], wherein pressure and specific internal energy are expressed as a three-part decomposition:

\[
X(\rho, T) = \phi(\rho) + X_{\text{nuc}}(\rho, T) + X_{\text{elec}}(\rho, T)
\]

for \( X = \{ P, E \} \). These terms represent elastic response along the 0K isotherm or “cold curve”, \( \phi(\rho) \), thermal ionic \( (X_{\text{nuc}}(\rho, T)) \), and thermal electronic contributions \( (X_{\text{elec}}(\rho, T)) \), respectively; coupling between the latter two is neglected but expected to be small across the domain of interest. A Debye model was used for \( E_{\text{nuc}} \), from which \( P_{\text{nuc}} \) follows as

\[
P = \rho \Gamma E
\]

in the Mie-Grüneisen (quasiharmonic) approximation [9]. Cold curve properties such as the isothermal bulk modulus were constrained by a quadratic fit to shock data, and the Debye temperature was adjusted to 1400 K in order to recover the ambient specific heat [10]. The Grüneisen parameter, \( \Gamma_0 \), was uniquely determined by thermodynamic consistency by

\[
\Gamma = \frac{\alpha B_0}{\rho C_p},
\]

where all quantities on the right-hand side are taken from experiment. Measured properties of phenylacetylene are compared with those predicted by the EOS in table 1; errors are <4% in every case. Calculated shock loci (figure 4) are also in excellent agreement with data reported below. Given the high level of correspondence between theory and experiment, we used the Sesame EOS to estimate temperature rise on the Hugoniot as a function of shock input condition.

### Table 1. Measured properties of phenylacetylene [3,4,11] compared with those predicted by the inert EOS. The reference state is T = 298 K, P = 1 atm. At this condition, phenylacetylene is a liquid.

| Property                              | Measured | Predicted |
|---------------------------------------|----------|-----------|
| Initial density (g/cm³)               | 0.928    | 0.926     |
| Bulk sound speed (km/s) at 298K\(^a\) | 1.390    | 1.40      |
| Coefficient of thermal expansion (/K)\(^b\) | 8.972 \times 10^4 | 8.667 \times 10^4 |
| \( C_p \) (J/molK)[11]                | 180.1    | 173.2     |
| Isothermal bulk modulus, \( K_f \) (GPa) | -        | 1.45      |
| Grüneisen parameter, \( \Gamma_0 \)  | 0.983    | 0.984     |
| Melting point/boiling point (K)       | 228/416  | -         |
| \( \Delta H_f^{\rho} \) (kJ/mol)[11]  | 284.3 ± 4| -         |
| Molecular weight (g/mol)              | 102.133  | -         |

\(^a\) measured at 298 K. \(^b\) from a linear fit to expansion data near 298 K (reference 4).
3. Results and discussion
Phenylacetylene has been shown to react under static high pressure conditions from a crystalline solid phase at 8.4 GPa to form a colored, polyphenylacetylene polymer arising from polymerization at the acetylene groups [12]. It is notable that acetylene (-C≡C-) is more reactive than the benzene ring, both in PA and as individual molecules, under static compression [13,14]. PA is metastable at ambient conditions, $\Delta G^0 = 86.46$ kcal/mol [11], suggesting a propensity for shock-driven reactivity [11].

A series of gas gun-driven plate impact experiments were performed, imparting several microsecond-duration supported shocks into PA with shock input stresses ranging from 3.3-7.9 GPa. The initial shock states (with subscript $i$) in PA are summarized in table 2. The first wave conditions (subscript 1) for experiments in which reaction was observed were determined using the first wave Rayleigh line, and inert EOS. At shock input conditions above 6 GPa, a multiple shock wave structure was observed to form in PA. The evolution of the initial shock wave into a three-wave structure occurs due to densification reactions in PA, similar to first-order solid-solid phase transitions as described by Dremin and others [15,16].

Table 2. Summary of initial (ini) and first (subscript 1) wave states obtained in phenylacetylene under shock compression. Errors in shock and particle velocities are estimated to be 1-2%. The initial density of phenylacetylene is $\rho_0 = 0.928$ g/cm$^3$.

| Shot No. | $V_{proj}$ km/s | $u_{p,ini}$ mm/µs | $U_x,ini$ mm/µs | $P_{ini}$ GPa | $\rho_{ini}$ g/cm$^3$ | $U_x,1$ mm/µs | $P_1$ GPa | $\rho_1$ g/cm$^3$ | $T$ K |
|--------|----------------|-----------------|----------------|-------------|-----------------|---------------|-------------|---------------|------|
| 1s-786 | 1.423          | 1.546           | 4.35           | 6.24        | 1.440           | 1.42          | 4.24        | 5.59          | 1.395 | 733 |
| 2s-294 | 2.623          | 1.690           | 4.60           | 7.22        | 1.467           | 1.45          | 4.17        | 5.77          | 1.423 | 800 |
| 2s-591 | 2.779          | 1.790           | 4.76           | 7.91        | 1.487           | 1.48          | 4.24        | 5.9           | 1.425 | 846 |
| 2s-662 | 2.712          | 1.710           | 4.69           | 7.55        | 1.461           | 1.46          | 4.20        | 5.7           | 1.409 | 824 |
| 2s-706 | 2.013          | 1.300           | 3.93           | 4.74        | 1.386           | N/A           | N/A         | N/A           | N/A   | 630 |
| 2s-707 | 1.590          | 1.022           | 3.53           | 3.34        | 1.307           | N/A           | N/A         | N/A           | N/A   | 535 |

Figure 3 (left) shows the evolution of particle velocity wave profiles following shock compression of PA to 7.2 GPa, shot 2s-294. The figure has been annotated to illustrate the salient features of the wave dynamics. The initial shock wave compresses PA to a metastable state on the unreacted Hugoniot. Following an induction time ($\tau$), the particle velocity at the input interface, as measured at the stirrup gauge, increases due to completion of the densification reaction(s) at the input interface. A three-wave structure forms over space ($x$) and time ($t$), which is marked by a first wave, a fast risetime second wave (P2), and a slow risetime third wave (P3).

Figure 3. (left) Particle velocity wave profiles for shot 2s-294, in which PA is initially shocked to 7.2 GPa and ~800 K. (right) Selected wave profiles from each of the plate impact experiments, described in table 2, illustrating wave dynamics as a function of input condition. Inert shocks are observed below $P_{ini} = 5$ GPa. A nearly steady multi-wave structure is observed at $P_{ini} = 7.9$ GPa.
The evolution of the initial wave, and risetimes and delays of 2nd and 3rd waves are related to the global reaction rate(s) of shock-driven reactions transforming PA to at least two higher density states (intermediate and final). Varying the shock input condition (in $P,T$) affects the wave dynamics [2], as shown in figure 3 (right). Selected wave profiles approximately 4 mm into the PA sample from each of the experiments are shown. Below 5 GPa, single (non-reactive) waves were observed at each of the Lagrangian gauge positions in material. Above 6 GPa, chemical reaction was observed. Increasing the shock input pressure above the reaction threshold (cusp condition) increases the shock input temperature (table 2), and accelerates the reactions, as evidenced by shortened reactive wave risetimes and delays behind the first wave. PA was also observed to exhibit unusual dynamics on the first wave, with a propagating wave instability forming with increasing $t$ and $x$. Note the variation and decay in the first wave particle velocity in figure 3 (left). It is unclear what the origin of the instability is, but it could be related to competing reaction pathways, or local variations in volume- or temperature-dependent reactions at the first wave condition.

When not overdriven, the first wave state (or shock reaction threshold) for PA is estimated to be $P_1 = 5.6$ GPa and $T_1 \approx 710$ K. By applying conservation of mass [16], analysis of the multiple wave structures in Lagrangian coordinates was performed to estimate the densities and pressures of the intermediate ($\rho_2, P_2$) and final states ($\rho_3, P_3$) [17]. The initial, first, intermediate and final states (for $P_\text{in} > 6$ GPa) are shown in figure 4 in the $U_\rho-U_p$ (left) and $P-U_p$ (right) planes, along with the inert Hugoniot for PA, calculated using the EOS described above. The intermediate and product states in the figures show the marked discontinuities in the principal Hugoniot, giving rise to the complex wave structures observed. From the wave analysis, the first reaction(s) results in a volume collapse of $\approx 10\%$, followed by the second reaction(s) resulting in $\approx 3\%$ further densification. The densification of PA under shock conditions is consistent with polymerization reactions induced by shock compression, as recently indicated by reactive molecular dynamics simulations [17].

![Figure 4. Initial, 1st wave, intermediate and final states reached in PA in the $U_\rho-U_p$ (left) and $P-U_p$ (right) planes. The solid line in both figures is calculated Hugoniot from the inert EOS. Additional lines through the intermediate and final states are drawn to guide the eye.](image)

From the multi-wave dynamics, global reaction rates (estimated as $1/t$, where $t$ is the risetime of 2nd and 3rd waves) were found to be $1.2-2.5 \times 10^7$ s$^{-1}$ for reaction 1, and $2.8-6.6 \times 10^6$ s$^{-1}$ for reaction 2, depending on the input condition. These global rates are similar to those observed in detonating high explosives, and are highly sensitive to initial shock state; the wave dynamics vary substantially with input conditions over $< 2$ GPa and 150 K. An Arrhenius analysis using the global reaction rate constants, $\ln(k)$ (s$^{-1}$), and calculated initial shock temperatures, indicates that the activation energies for shock-driven reactions are $\approx 72$ and 53 kcal/mol, for the 1st and 2nd reaction, respectively.
4. Conclusions
PA has been demonstrated to react at shock input conditions above 6 GPa on its principal Hugoniot to form a three-wave structure indicative of the formation of at least two higher density species. The input shock reaches a metastable state on the unreacted Hugoniot, which evolves over measureable $t$ and $x$ (ns, mm) into a three-wave structure with fast risetime 2nd wave, and slow risetime 3rd wave. The global reaction rates were found to be similar to detonating high explosives; $10^6 - 10^7$ s$^{-1}$ at the initial conditions reached in this study: $P_{ini} = 6-8$ GPa, and $T \approx 700$ to $900$ K.

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