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**FORMIC ACID INVESTIGATION FOR THE PREDICTION OF HIGH EXPLOSIVE
DETONATION PROPERTIES AND PERFORMANCE**

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14. ABSTRACT
The JAGUAR EXP-6 parameters of formic acid were originally optimized by minimizing the difference of experimental detonation velocities to predicted Chapman-Jouguet (C-J) detonation velocities for pentaerythrite tetranitrate (PETN), and were later modified to reproduce experimental overdriven detonation pressures. The resulting parameters are employed in the JAGUAR computer program, which uses direct minimization of free energy to calculate chemical equilibrium for dissociated detonation product species of explosives. JAGUAR was subsequently demonstrated to provide accurate detonation properties for wide ranges of conditions including the C-J state, overdriven detonation, and at seven volume expansions for nearly ideal H-C-N-O based explosives. This work focuses on predicting formic acid thermodynamic properties, including the Hugoniot behavior using experimental data and molecular dynamics modeling. Both the molecular dynamics calculations and experimental data were used to parameterize new sets of EXP-6 potential parameters for use with the extended JCZ3 JAGUAR equation of state. This provides a means for comparison of predicted detonation properties using either the empirically-derived or theoretically-based formic acid potential parameters.

15. SUBJECT TERMS
JAGUAR, EXP-6, C-J, Detonation velocities, Predicting formic acid thermodynamic properties, Predicted detonation properties

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INTRODUCTION

Thermodynamic equations of state for explosives products that are accurate for a wide ranges of specific volumes, including overdriven and expansion regions, are required for the accurate continuum modeling of high explosive systems. Traditionally, thermochemical equations of state, such as the BKW and JCZ3 relationships, do not result in sufficiently accurate detonation properties for the required volume range. In order to improve the accuracy of calculated detonation properties of explosives and of the resulting thermodynamic equations of state, research studies were previously conducted. Variable metric optimization routines were used for the optimization of the JCZ3 EXP-6 potential parameters for H-C-N-O explosive product species.

The JAGUAR thermochemical equilibrium procedure (ref. 1) enables the accurate calculation of the detonation properties of explosives, including Chapman-Jouguet (C-J) points, expansion energies along the principal isentrope, and Hugoniot values. The JAGUAR procedures include the ability to determine constants of the Jones-Wilkins-Lee (JWL) and Jones-Wilkins-Lee-Baker (JWLB) thermodynamic equations of state for hydrocode calculations by the use of variable metric optimization procedures (ref. 2). The thermodynamic equations of state enable the accurate calculation of cylinder velocities, Gurney constants, and other variables with an analytic cylinder model (ref. 3).

JAGUAR uses the JCZ3 equation of state (ref. 4) for fluid mixtures at extreme pressures and temperatures, which requires molecular parameters r^* , ε/k , and l of the EXP-6 intermolecular potential function for each product component. The basic JCZ3 relationships were supplemented with an advanced mixing rule for the effective exponent l of the reaction system, which enable the use of variable values of l for each species.

The JCZ3 equation of state is of the form

$$P = P_0(V, n_1 \dots n_p) + G(V, T, n_1 \dots n_p) \frac{nRT}{V} \quad (1)$$

where $P_0(V, n_i)$ denotes the limiting lattice pressure, and $G(V, T, n_i)$ accounts for the thermal contribution of the intermolecular forces. Expressions for the calculation of P_0 and G are as follows:

$$P_0 = - \left(\frac{\partial E_0}{\partial V} \right) \quad (2)$$

$$G = 1 - V \left(\frac{\partial l}{\partial V} \right) \quad (3)$$

The variables E_0 and l depend on the parameters ε/k , r^* , and l of the Exp-6 potential function. In JAGUAR, the parameters of the mixture are calculated from the combining rules:

$$(r^*)^3 = \sum_i \sum_j x_i x_j \varepsilon_{ij} \quad (4)$$

$$(r^*)^3 = \sum_i \sum_j x_i x_j (r_{ij}^*)^3 \quad (5)$$

$$l = \sum_i \sum_j x_i x_j l_{ij} \quad (6)$$

where

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (7)$$

$$r_{ij}^* = \frac{r_i^* + r_j^*}{2} \quad (8)$$

$$l_{ij} \sqrt{l_i l_j} \quad (9)$$

The compressibility factor, Φ , the residual chemical potential, Γ_i , and the residual energy, e , are calculated from the JCZ3 equation of state by these procedures.

JAGUAR FORMIC ACID PARAMETERS

NLQPEB variable metric optimization routines (ref. 3) were used for the optimization of the JCZ3 EXP-6 potential parameters for H-C-N-O explosive product species with available Hugoniot pressure-density data. Close agreement with the Hugoniot data resulted for most of the species considered. For the parameterization of detonation products which dissociate at elevated temperatures and pressures, the U.S. Army Armament Research, Development and Engineering Center (ARDEC), Picatinny Arsenal, New Jersey variable metric optimization routines were applied to determine the equilibrium composition of the reacting system at each Hugoniot condition.

Previous studies have used experimental information for explosives to establish EXP-6 parameter for formic acid, due to a lack of data. The potential parameters initially used in the JAGUAR library for formic acid ($r^* = 4.125$, $\varepsilon/k = 462.5$, $l = 13.5$), were determined to produce agreement with the experimental detonation velocities of PETN for initial densities in the range 1.26 to 1.77 g/cm³ (ref. 5). The JAGUAR procedures with these parameters were found to enable the highly accurate calculation of the detonation properties of near ideal explosives for a wide range of volumes, covering the dilute expansion region, C-J state, and overdriven conditions to about 0.5 Mbar. In order to obtain improved agreement for highly overdriven conditions to 1 Mbar, the EXP-6 parameters of formic acid were subsequently revised (ref. 6) using the experimental Hugoniot data of Fritz et al. (ref. 7) for PBX-9501 (initial density 1.836 g/cm³) for pressures in the range 0.3 to 0.7 Mbar. The parameters were selected to provide minimum error in the following objective function by the NLQPEB procedures:

$$Z = \frac{\sum_i (P_{exp_i} - P_{calc_i})^2}{N} \quad (10)$$

where N is the number of experimental points, P_{exp} is the experimental Hugoniot pressure, and P_{calc} is the pressure calculated with the JAGUAR procedures using the optimized library parameters for the other explosive products. With the optimized parameters $r^* = 4.265$, $\varepsilon/k = 538.85$, and $I = 11.30$, the objective function was substantially lower than for the original formic acid parameters. The optimized parameters of formic acid also resulted in substantially improved agreement with the experimental speed of sound values of Fritz et al. (1996). The optimized formic acid parameters were also found to result in good agreement between JAGUAR values and experimental overdriven Hugoniot data for other explosives, including PETN, TNT, COMP-B, and PBX-9404.

Values of C-J velocities calculated with the JAGUAR Exp-6 libraries were also compared for 47 C-H-N-O explosives (ref. 6). With the original formic acid parameters, the overall error was 1.63%, while the optimized parameters from overdriven Hugoniot data resulted in an overall average error of 1.68%. For both parameter sets, cylinder energies at 6.5 volume expansions calculated with JAGUAR agreed within 2% from the corresponding values obtained from empirical JWL relationships for a number of explosives. Similarly, calculated cylinder velocities at 7 area expansions were within 1% of experimental values by both procedures.

HUGONIOT VALUES FOR FORMIC ACID

As part of the new joint Army Research Laboratory (ARL)/ARDEC Software Application Institute for Multi-Scale Reactive Modeling (MSRM) work, the behavior and effect of formic acid is being investigated. In this study, the EXP-6 parameters for formic acid were re-evaluated by the use of experimental and theoretical information for the individual molecule.

Hugoniot pressure-volume (P-V) values for formic acid calculated with JAGUAR were compared with the experimental data of Trunin et al. (ref. 8) for pressures to 50 GPa. As shown in figure 1, the calculated Hugoniot pressures with the JAGUAR EXP-6 parameters $r^* = 4.265$, $\varepsilon/k = 538.85$, and $I = 11.30$ agree with the experimental values for pressures to about 25 GPa, while the calculated pressures are lower than the data at higher pressures. With these parameters, previously established to obtain optimum agreement with experimental C-J velocities and overdriven pressures, JAGUAR indicates that formic acid is almost completely dissociated into products, including water, carbon dioxide, and carbon at low pressures, while un-dissociated formic acid is the major product for pressures above 30 GPa. Similar Hugoniot values and decomposition resulted with the original JAGUAR parameters determined from C-J data for PETN.

The formic acid Hugoniot data reported by Trunin et al (ref. 8) were used to determine optimum formic acid EXP-6 parameters for the JCZ3 equation of state by the NLQPEB nonlinear optimization procedures. The objective function minimized is equation 10, the sum of the squares of the differences between calculated and experimental pressures at each volume. The optimum parameters obtained in this manner are $\varepsilon/k = 547.65$, $r^* = 4.115$, $I = 13.85$. In figure 1, these formic acid parameters are seen to result in closer agreement with the experimental Hugoniot pressures than for the previous JAGUAR parameters. With the new parameters, JAGUAR still predicts the formation of substantial amounts of formic acid in the equilibrium products at elevated pressures.

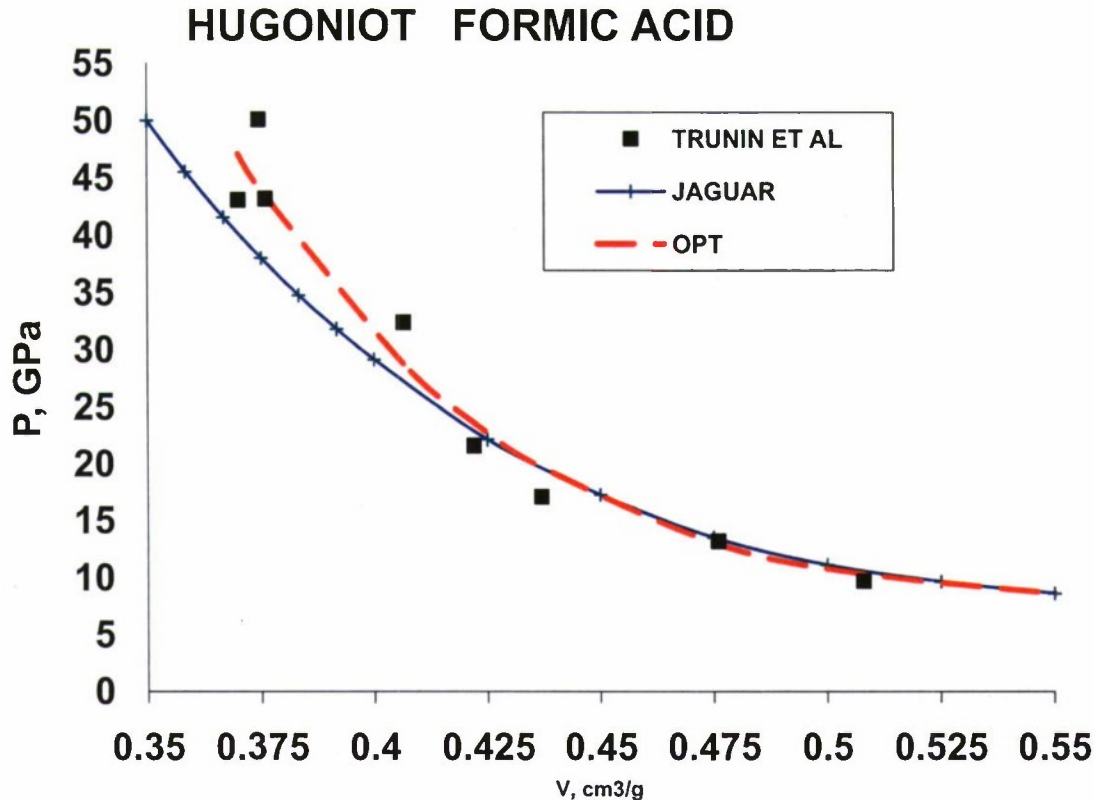


Figure 1
Comparison of formic acid Hugoniot from the original JAGUAR model, the newly optimized JAGUAR output (OPT), and experimental data

MOLECULAR DYNAMICS CALCULATIONS

Hugoniot values were also predicted using isothermal isochoric molecular dynamics simulations for un-dissociated formic acid for a complete range of pressures. The potential parameters used were established by Roszak et al. (ref. 9) for formic acid solid using the Lennard-Jones 9-6 potential function. The resulting calculated Hugoniot curve is shown in figure 2.

The optimization routines for EXP-6 parameters with JAGUAR were revised to enable determination of parameters for un-reacted formic acid consistent with the molecular dynamics calculated formic acid Hugoniot curve. The optimum parameters for formic acid obtained in this manner are $r^* = 3.901$, $\epsilon/k = 1118.96$, $l = 13.251$. The resulting Hugoniot values are in close agreement with the theoretical calculations shown in figure 2.

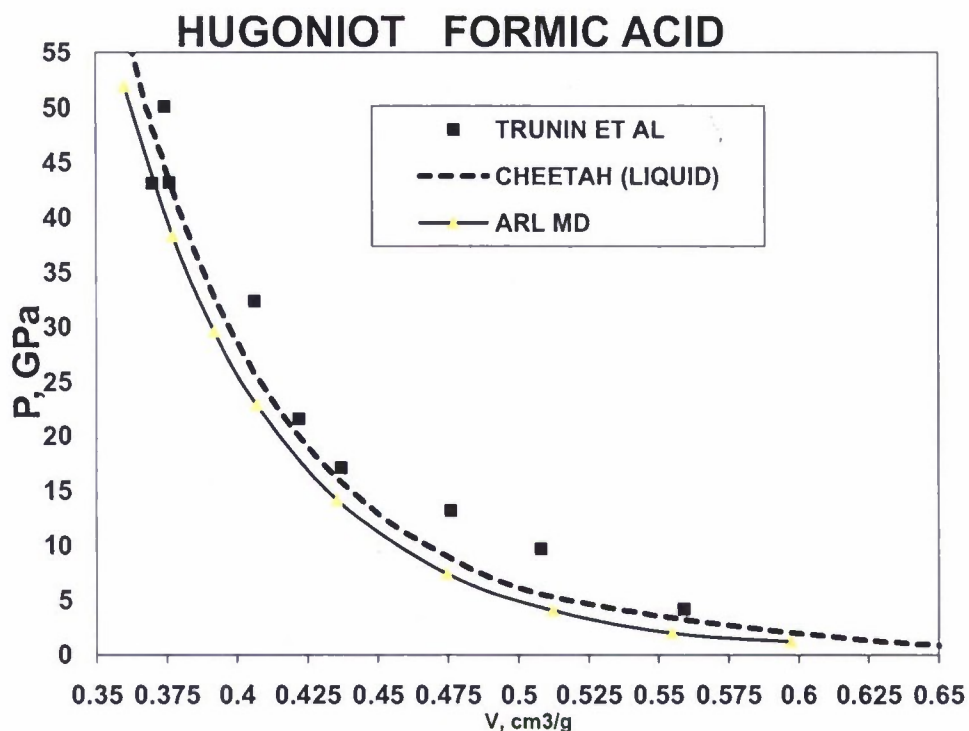


Figure 2
Comparison of formic acid Hugoniot from Cheetah, molecular dynamics calculations (ARL MD), and experimental data

CALCULATIONS FOR LIQUID FORMIC ACID

The calculations performed with JAGUAR with an EXP-6 based equation of state assume that formic acid is gaseous at elevated pressures and temperatures and dissociates to reaction products. Montgomery et al. (ref. 10) used speed of sound data and other experimental information including the Hugoniot data of Trunin et al. (ref. 8), to establish constants of the temperature independent Murnaghan relationship for formic acid:

$$V = V_0(n\kappa P + 1)^{-1/n} \tag{11}$$

with $V_0 = 1.22 \text{ cm}^3/\text{g}$, $n = 6.65$, and $\kappa = 0.613 \text{ (GPa)}^{-1}$. Equation 11 was used in this study to calculate Hugoniot values for un-dissociated liquid formic acid. For the molar heat capacity of the liquid, a linear relationship in temperature was also used. As shown in figure 2, the P-V variation of Hugoniot values with these temperature independent Murnaghan parameters is quite consistent with the experimental Hugoniot data and is similar to those calculated by the molecular dynamic procedure.

The corresponding Hugoniot temperatures for formic acid liquid are shown in figure 3. It can be seen that for a Hugoniot pressure of about 0.6 GPa, the calculated temperature is above the critical temperature of formic acid (580 K). At 10 GPa, the calculated temperature assuming a liquid phase is above 4000 K. Therefore, these results strongly indicate that at elevated pressures on the Hugoniot curve formic acid is gaseous, and its behavior should be represented by an equation of state with possible dissociation to reaction products. The study of Montgomery et al. (ref. 10) indicates that formic acid can also dissociate in the liquid phase at elevated pressures.

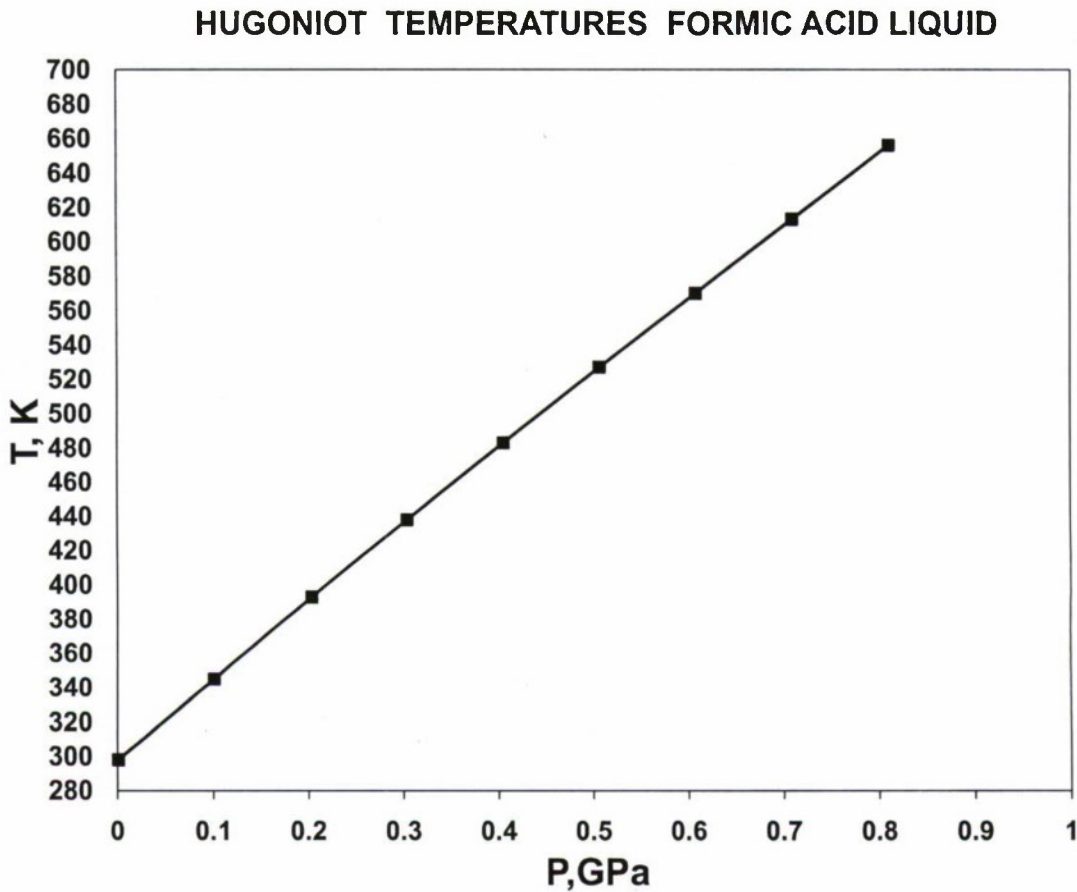


Figure 3
Predicted Hugoniot temperature as a function of pressure for formic acid

COMPARISONS WITH C-J DATA FOR EXPLOSIVES

Experimental C-J values for PETN for initial densities 1.263 to 1.77 g/cm³ were compared with calculated values from JAGUAR with varying Exp-6 parameters for formic acid. The results are summarized in table 1. The current JAGUAR formic acid parameters result in an average absolute deviation of 1.16%. These parameters were determined previously by optimization of overdriven Hugoniot pressures and C-J values for several explosives. With the set determined by directly optimizing experimental C-J values, the average deviation is 0.69%. Parameters determined recently by optimizing agreement with formic acid experimental Hugoniot data result in higher deviations for the C-J values (2.21%). The errors are also large for C-J velocities calculated with parameters optimized for agreement with the molecular dynamics calculated Hugoniot values for un-dissociated formic acid. The various parameter sets are included in table 1. In addition, for 47 C-H-N-O explosives considered previously (ref. 6), the average absolute error in C-J velocities from table 2 is 1.66% for the current JAGUAR parameters, 1.87% with the parameters resulting from experimental Hugoniot data, and 3.33% for the parameters for un-dissociated formic acid.

Table 1
PETN C-J comparisons

| rho | exptl | C-J VALUE | | | | Md Opt |
|-------|--------------|------------------|----------------------|--------------|--------------|--------|
| | | JAGUAR | Opt Hug | Opt C-J | | |
| 1.77 | 8.3 | 8.371 | 8.555 | 8.337 | 8.776 | |
| 1.7 | 8.08 | 8.12 | 8.268 | 8.066 | 8.466 | |
| 1.6 | 7.75 | 7.791 | 7.887 | 7.714 | 8.056 | |
| 1.507 | 7.47 | 7.504 | 7.557 | 7.415 | 7.698 | |
| 1.45 | 7.18 | 7.337 | 7.363 | 7.24 | 7.485 | |
| 1.263 | 6.59 | 6.755 | 6.748 | 6.686 | 6.81 | |
| | | | ABSOLUTE % DEVIATION | | | |
| | | 0.855 | 3.072 | 0.446 | 5.735 | |
| | | 0.495 | 2.327 | 0.173 | 4.777 | |
| | | 0.529 | 1.768 | 0.465 | 3.948 | |
| | | 0.455 | 1.165 | 0.736 | 3.052 | |
| | | 2.103 | 2.549 | 0.836 | 4.248 | |
| | | 2.504 | 2.398 | 1.457 | 3.338 | |
| | | 1.157 | 2.213 | 0.685 | 4.183 | |
| | | EXP-6 PARAMETERS | | | | |
| | r^* | 4.256 | 4.115 | 4,125 | 3.901 | |
| | ϵ/k | 538.85 | 547.65 | 462 | 1119 | |
| | l | 11.3 | 13.85 | 13.5 | 13.251 | |

Both the current JAGUAR parameters and those optimized with C-J data (table 2) result in agreement with Hugoniot data at moderate pressures, but produce larger deviations at high pressures. The experimental Hugoniot data shows considerable scatter. In particular, this provides considerable uncertainty at high pressures. Additionally, the JAGUAR calculations indicate disassociation for pure formic acid in the high pressure region, which introduces more uncertainty.

Table 2
Comparison of C-J velocities

| | Density (g/cm ³) | EXPTL D (Km/s) | JAGUAR D (Km/s) | OPT Hug D (Km/s) | MD OPT D (Km/s) |
|-----------------|---------------------------------|-------------------|--------------------|---------------------|--------------------|
| CH3NO2 | 1.14 | 6.37 | 6.629 | 6.550 | 6.567 |
| CH3NO3 | 1.21 | 6.75 | 6.774 | 6.733 | 6.828 |
| CH4N4O2 | 1.7 | 8.2 | 8.473 | 8.547 | 8.829 |
| CH4N4O4 | 1.73 | 9.0 | 9.076 | 9.079 | 9.124 |
| CH5N5O2 | 1.65 | 8.6 | 8.651 | 8.724 | 8.955 |
| C2H4N2O6 | 1.48 | 7.3 | 7.458 | 7.452 | 7.496 |
| C2H6N4O4 | 1.66 | 8.24 | 8.182 | 8.233 | 8.417 |
| C2H10N4O6 | 1.6 | 7.67 | 7.829 | 7.784 | 7.904 |
| C3H5N3O9 | 1.6 | 7.74 | 7.735 | 7.732 | 7.751 |
| C3H6N6O3 | 1.57 | 7.8 | 7.892 | 7.921 | 8.096 |
| C3H6N6O6 | 1.8 | 8.8 | 8.691 | 8.859 | 9.212 |
| C3H7NO3 | 1.04 | 5.4 | 5.909 | 5.860 | 5.850 |
| C4H2N8O10 | 2.01 | 9.15 | 9.403 | 9.405 | 9.409 |
| C4H4N8O14 | 1.96 | 8.85 | 8.919 | 8.919 | 8.919 |
| C4H6N4O6 | 1.52 | 7.1 | 7.042 | 7.023 | 7.045 |
| C4H6N4O11 | 1.64 | 8.19 | 8.122 | 8.123 | 8.201 |
| C4H8N2O7 | 1.384 | 6.6 | 6.867 | 6.801 | 6.575 |
| C4H8N4O8 | 1.67 | 8.0 | 7.892 | 7.940 | 7.987 |
| C4H8N8O8 | 1.9 | 9.15 | 9.074 | 9.319 | 9.748 |
| C5H4N6O15 | 1.85 | 8.06 | 8.219 | 8.219 | 8.220 |
| C5H6N8O13 | 1.86 | 9.0 | 9.001 | 9.014 | 9.077 |
| C5H8N4O12 | 1.77 | 8.27 | 8.377 | 8.447 | 8.782 |
| C5H9N3O9 | 1.46 | 7.18 | 7.177 | 7.150 | 7.032 |
| C6H3N3O6 | 1.69 | 7.35 | 7.377 | 7.419 | 7.626 |
| C6H3N3O7 | 1.71 | 7.35 | 7.350 | 7.388 | 7.568 |
| C6H4N2O4 | 1.492 | 6.1 | 6.052 | 6.004 | 5.884 |
| C6H4N4O6 | 1.72 | 7.3 | 7.342 | 7.370 | 7.588 |
| C6H5N5O6 | 1.84 | 7.69 | 7.847 | 7.903 | 8.135 |
| C6H6N4O7 | 1.63 | 7.15 | 6.952 | 6.935 | 6.955 |
| C6H6N6O6 | 1.94 | 8.0 | 8.323 | 8.449 | 8.731 |
| C6H6N6O14 | 1.78 | 8.3 | 8.436 | 8.472 | 8.680 |
| C6H8N6O18 | 1.73 | 8.26 | 8.105 | 8.106 | 8.113 |
| C6H10N6O10 | 1.73 | 8.1 | 8.035 | 8.106 | 8.226 |
| C7H5N3O6 | 1.64 | 6.94 | 6.847 | 6.833 | 6.856 |
| C7H5N3O7 | 1.61 | 6.8 | 6.902 | 6.901 | 7.009 |
| C7H5N5O8 | 1.7 | 7.56 | 7.607 | 7.660 | 7.909 |
| C7H7N9O21 | 1.8 | 8.16 | 8.285 | 8.286 | 8.289 |
| C8H7N3O7 | 1.6 | 6.8 | 6.651 | 6.604 | 6.423 |
| C10H16N6O19 | 1.63 | 7.53 | 7.594 | 7.624 | 7.669 |
| C12H4N6O12 | 1.6 | 7.1 | 7.187 | 7.216 | 7.351 |
| C12H4N8O8 | 1.85 | 7.25 | 7.610 | 7.654 | 7.785 |
| C12H5N7O12 | 1.6 | 7.14 | 7.138 | 7.165 | 7.319 |
| C12H6N8O12 | 1.79 | 7.5 | 7.598 | 7.644 | 7.820 |
| C14H6N6O12 | 1.74 | 7.13 | 7.236 | 7.268 | 7.454 |
| C18H59O18 | 1.78 | 7.56 | 7.651 | 7.692 | 7.795 |
| C18H6N8O16 | 1.8 | 7.33 | 7.474 | 7.514 | 7.645 |
| C24H6N14O24 | 1.78 | 7.6 | 7.781 | 7.823 | 7.915 |
| Avg. Abs. Error | | | 1.664 | 1.87 | 3.327 |

CONCLUSIONS

Optimum formic acid EXP-6 parameters were established to minimize deviations with both experimental formic acid Hugoniot data and predicted Hugoniot values for un-dissociated formic acid from molecular dynamic procedures. However, lower deviations from experimental C-J values for pentaerythrite tetranitrate (PETN) resulted using previous EXP-6 parameters for formic acid that were parameterized using detonation properties, indicating that the Hugoniot data for formic acid may be error at elevated pressures. Calculations for the un-dissociated molecule have determined that formic acid is liquid on the Hugoniot curve to about 0.6 GPa. At higher Hugoniot pressures and temperatures, JAGUAR indicates that formic acid dissociates into C-H-O products. This dissociation and uncertainty of the formic acid data may explain the deviation from experimental Hugoniot data observed by the molecular dynamic calculations in the high pressure region and thus the deviation observed in the predicted PETN detonation properties using either EXP-6 parameters based on the data or the molecular dynamics calculations. Additional theoretical and experimental information for formic acid and other explosive product molecules are required to explain the observed behaviors of formic acid at higher pressures and to provide increased accuracy EXP-6 potential parameters for use in JAGUAR. Further atomistic and molecular dynamics calculations are planned.

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