MOLECULAR DYNAMICS SIMULATIONS OF HMX CRYSTAL POLYMORPHS USING A FLEXIBLE MOLECULE FORCE FIELD

Dmitry Bedrov[1], Grant D. Smith[1], and Thomas D. Sewell[2]

[1]*Department of Materials Science & Engineering, University of Utah, 122 S. Central Campus Dr., Rm. 304, Salt Lake City, UT 84112*
[2] *Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545*

Abstract. Molecular dynamics simulations using a recently developed quantum chemistry-based atomistic force field [J. Phys. Chem. B **103** (1999) 3570] were performed in order to obtain unit cell parameters, coefficients of thermal expansion, and heats of sublimation for the three pure crystal polymorphs of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). The predictions for β-, α-, and δ-HMX showed good agreement with the available experimental data.

INTRODUCTION

Plastic-bonded explosives (PBXs) are composites of high-explosive crystallites held together by a polymeric binder. Mesomechanical simulation methods, in which the individual explosive grains are resolved within a continuum hydrodynamic framework, are being used to understand ignition and assess the sensitivity of PBXs to various stimuli.[1] Though there are data on bulk properties, simulations on the grain scale require thermophysical and mechanical properties of a single crystal of explosive. Many of these properties are difficult to measure due to the extremely rapid decomposition that occurs for the pressure and temperature regions of interest. Fortunately, judicious application of molecular simulation tools provides a viable path to determine many of the grain-scale properties needed for mesomechanical models.

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) is the energetic component in several important high-performance PBXs, e.g., PBX-9501.[2] We have previously reported values for temperature-dependent density and equilibrium transport coefficients of liquid HMX at atmospheric pressure in the domain 550 K ≤ T ≤ 800 K.[3,4] The predictions were obtained from multi-nanosecond molecular dynamics (MD) simulations using a recently published, fully flexible, quantum chemistry-based atomistic force field for HMX.[5] In this paper we present results of MD simulations using the same force field for the three pure crystal polymorphs of HMX. The β-, α-, and δ- phases of HMX are monoclinic[6] ($P_{21/n}$ spacegroup, Z=2 molecules per unit cell, symmetry axis = *b*), orthorhombic[7] (F*dd*2, Z=8), and hexagonal[8] (P6$_1$, Z = 6, symmetry axis = *c*), respectively. The primary purposes of this work are (1) to validate the force field against the available experimental data for HMX and (2) compare the importance of intra- and intermolecular interactions in determining enthalpy of sublimation of three crystal phases.

SIMULATION PROTOCOL

The force field has been described previously[5] and was used without modification in the present study with the exception that partial atomic charges were increased by 25% in order to take into account the polarization effects in the condensed phases; these scaled charges were also used in Refs. 3 and 4. In our previous simulations of dimethylnitramine[9]

we found that the increase of partial atomic charges by 25% yielded density and cohesive energy in good agreement with experiment. As in our previous studies,[3,4] the covalent bonds were held fixed to constant values determined from quantum chemistry calculations. Since the bond lengths in the force field are constrained, the small differences in lengths observed for chemically similar bonds in the various polymorphs - as well as within a single molecule in a given polymorph - will not be reproduced in our calculations. However, the effects of this on our results are expected to be minor. Moreover, the measured unit cell volumes are predicted quite accurately by the present force field, as shown below. Isothermal-isobaric (NpT) molecular dynamics simulations[10] were performed at atmospheric pressure for each phase using the Rahman-Parrinello approach,[11] with primary simulation cells corresponding to 24 (4 x 2 x 3), 8 (2 x 1 x 4), and 16 (4 x 4 x 1) unit cells for β-, α- and δ-HMX, respectively. Experimental crystal structures[6,7,8] were used to define initial configurations for the simulations. For each system, an equilibration run of 0.5 ns duration was performed, followed by a 1.0 ns production run; the integration step size and sampling interval were 1 fs and 10 fs, respectively. Nonbonded interactions were truncated at 10.0 Å; the standard Ewald summation[12] was used to handle long-range electrostatics. Intramolecular bond lengths were constrained using the SHAKE algorithm.[13]

RESULTS AND DISCUSSION

Cell parameters.

In Table 1 we report atmospheric pressure lattice parameters and unit cell volumes for β-, α-, and δ-HMX as obtained from MD simulations at 295 K. Also shown for comparison are the experimental data obtained at 295 K. It can be seen that the simulation results are in good agreement with experiment. The largest percent error in unit cell volume, 1.4%, occurs for α-HMX. The lattice angles are essentially exact with the exception of β-HMX, for which the angle β is 3.6% too small. This error is compensated by errors of −4.7% and 3.7% in lattice lengths b and c, respectively, to yield nearly perfect agreement with experiment for the unit cell volume. (The errors in those two lattice parameters are the largest obtained in the present work.) Overall, the current predictions are more accurate than those based on the force field of Dzyabchenko et al.[14] and comparable to those reported by Sorescu et al.[15] More detailed comparisons among the force fields are somewhat problematic, however, since in the former case molecular packing was used while in the latter case the temperatures at which the isothermal-isobaric calculations were performed for α- and δ-HMX did not correspond to those for which experimental structural determinations have been reported (295 K).

Coefficients of Thermal Expansion.

In order to determine the coefficients of thermal expansion (CTEs), simulations for each polymorph were performed at several temperatures in the associated stability domains,[16] as well as at 295 K; we used $250 < T < 350$ K (250, 280, 295, 320, and 350 K) for β-HMX, $295 < T < 450$ K (295, 350, 380, 400, 420, and 450 K) for α-HMX and $295 < T < 520$ K (295, 480, 500, and 520 K) for δ-HMX. The resulting temperature dependencies of the lattice parameters were adequately described by straight lines; thus, the CTE χ_X for a given lattice parameter at 295 K was determined from $\chi_{X,295K} = 1/X_{295K}(\partial X/\partial T)$ where X = a, b, c, and V. The CTEs thus obtained are reported in Table 1 and are in generally good agreement with the experimental data at 295 K,[17,18] which are included for comparison. The largest deviation of the predicted χ_V from experimental data is observed for β-HMX and is 11.4%. The CTEs of the individual cell parameters are in best agreement with experiment for α- and δ-HMX, and somewhat less so for β-HMX.

Enthalpy of Sublimation.

The accuracy with which a force field predicts enthalpies of sublimation is another crucial test of its overall validity. The sublimation enthalpy can be determined as:

$$\Delta H_s = H_{gas} - H_{solid} = RT + \Delta E_{inter} + \Delta E_{intra} \quad (1)$$

where ΔE_{inter} and ΔE_{intra} are the differences in intermolecular and intramolecular potential energies of HMX molecules in the ideal gas and relevant

crystal phases, respectively. We note that for HMX ΔE_{intra} is not negligible: quantum chemistry calculations[5] at the B3LYP/6-311G** level indicate that the energy difference between

based on a combined analysis of experimental data due to others.[21,22] Good agreement between experimental and MD predicted enthalpies is obtained. The predicted ΔH_s for α-HMX lies in

Table 1. Properties of HMX polymorphs from MD simulations[a] and experiments at 295 K.

Property	β-HMX		α-HMX		δ-HMX	
	MD	expt	MD	expt	MD	expt
a [Å]	6.5306	6.5347[b]	14.9912	15.14[e]	7.6200	7.711[f]
b [Å]	10.5086	11.0296[b]	23.9080	23.89[e]	7.6100	7.711[f]
c [Å]	7.6246	7.3549[b]	6.0531	5.913[e]	33.5340	32.553[f]
α	89.999	90.0[b]	89.990	90.0[e]	89.999	90.0[f]
β	98.946	102.69[b]	90.000	90.0[e]	89.994	90.0[f]
γ	90.000	90.0[b]	89.999	90.0[e]	120.170	120.0[f]
volume [Å³]	516.86	517.16[b]	2168.86	2138.7[e]	1681.85	1676.3[f]
$\chi_a \times 10^5$ [K^{-1}]	2.07	-0.29[c]	3.65	3.65[c]	4.02	4.1[c]
$\chi_b \times 10^5$ [K^{-1}]	7.2	11.6[c]	4.26	4.86[c]	4.19	4.1[c]
$\chi_c \times 10^5$ [K^{-1}]	2.56	2.30[c]	1.44	1.21[c]	3.94	2.6[c]
$\chi_V \times 10^5$ [K^{-1}]	11.60	13.1[c]	9.34	9.6[c]	12.76	13.5[c]
ΔH_s [kcal/mol]	45.5	44.16[d]	44.2	-	41.0	42.04[d]
ΔE_{inter} [kcal/mol]	48.0		53.0		53.0	
ΔE_{intra} [kcal/mol]	-0.8		-7.0		-10.0	

[a] The first uncertain digit is the last one shown, corresponding to the standard deviations of the mean among contiguous 100 ps subaverages along the overall trajectory.
[b] Ref.[6]; [c] Refs.[17,18]; [d] Ref.[20]; [e] Ref.[7]; [f] Ref. [8].

the lowest energy gas-phase geometry and that of an optimized gas-phase molecule in the nominal α-HMX conformation is 3.5 kcal/mol. Also, in the crystal phase, bends and torsions of a particular conformer can be distorted from the optimal values of the corresponding gas-phase conformer due to condensed-phase effects. While the difference in intramolecular energies of gas- and solid-phase molecules can make a significant contribution to ΔH_s, this effect has been ignored in the assessment of other force fields.[14,15] In order to obtain the intramolecular energy difference in the present work, simulations of an HMX ideal gas were performed at 295 K using a stochastic dynamics algorithm described elsewhere.[19] The calculated sublimation energies for each polymorph are provided in Table 1, where they are compared (for β- and δ-HMX) to values derived by Lyman et al.[20]

between the values of β- and δ-HMX, which is consistent with the polymorph stability ranking[16] ($\beta > \alpha > \delta$) at room temperature. The ΔE_{inter} and ΔE_{intra} contributions to ΔH_s obtained from MD simulations are also reported in Table 1. ΔE_{intra} makes an important contribution to the ΔH_s of α- and δ-HMX (7.0 and 10.0 kcal/mol, respectively) and is only about 0.8 kcal/mol for β-HMX. It is worth noting that the polymorph dependence of the intermolecular energy contribution to ΔH_s is opposite to that of ΔH_s itself, i.e., the intermolecular interactions for δ- and α-HMX are more favorable than for β-HMX. However, this relative "stabilization" of δ- and α-HMX due to intermolecular interactions is compensated by the unfavorable intramolecular energy of HMX molecules in these phases, resulting in smaller

enthalpies of sublimation relative to β-HMX.

CONCLUSIONS

We have used a quantum chemistry-based intra- and intermolecular force field to predict the crystal structures, coefficients of thermal expansion, and heats of sublimation of the three pure polymorphs of HMX; and the sound speeds of β-HMX at 295 K; all at atmospheric pressure. The results for the lattice parameters and their temperature dependencies are in good agreement with experiment. The predicted enthalpies of sublimation are consistent with experimental measurements. Detail analysis of contributions to the enthalpy of sublimation (ΔH_S) reveals that the change in intramolecular energy (between ideal gas and crystal polymorph) makes an important contribution to ΔH_S of α- and δ-HMX. We found that the polymorph dependence of the intermolecular energy contribution to ΔH_S is opposite to that of ΔH_S itself ($\beta > \alpha > \delta$), i.e., the intermolecular interactions for δ- and α-HMX are more favorable than for β-HMX. However, this relative "stabilization" of δ- and α- phases due to intermolecular interactions is compensated by the unfavorable intramolecular energy of HMX molecules in these phases, resulting in smaller ΔH_S relative to β-HMX.

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