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Initial Decomposition of HMX Energetic Material from Quantum Molecular Dynamics and the Molecular Structure Transition of β - to δ -HMX

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ABSTRACT

We demonstrate the use of quantum molecular dynamics to identify the β - to δ - molecular structure transition in bulk phase HMX, which has been considered as the main reason of the increased sensitivity in the thermal decomposition of HMX. Both physical and chemical changes accompany this transition, but no previous study has shown conclusively which specific change, or set of changes, is responsible. We find the initial decomposition mechanism of HMX can explain this issue sensitivity. Our DFT simulations of the periodic system followed by detailed finite cluster calculations of the transition states find two distinct initial unimolecular reaction pathways in β -HMX, that operate simultaneously. (1) For the HONO releasing reaction, β -HMX first transformed to an intermediate in which one parallel N-NO₂ group transitions from chair to boat with a low +1.2 kcal/mol barrier, followed by unimolecular HONO release (+42.8 kcal/mol barrier, RDS). (2) For the NO₂ cleavage reaction, β -HMX first transforms to the δ -HMX structure in two steps, with low barriers of +1.9 and +7.6 kcal/mol for each step, followed by unimolecular NO₂ release (+31.3 kcal/mol barrier). Starting with δ -HMX, we find an initial unimolecular NO₂ cleavage and then an independent HONO releasing reaction, with the barriers of +31.6 (NO₂ cleavage) and +38.9 kcal/mol (HONO releasing). We find the constant proportional simulated initial structure transition temperature is 453 K, which is consistent with the experimental results (466 K).

1. INTRODUCTION

There remain many uncertainties about the dynamic behavior of energetic materials (EMs), such as HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), is complicated by the range of structural phases exhibited by many EMs¹. HMX is one such material used as a crystalline high explosive that shows a variety of behaviors when subjected to various thermal fields. HMX exists four polymorphs, labeled α -, β -, γ -, and δ -, with the crystal structures known for α , β , and δ ^{2, 3}. These different crystal types of HMX exhibit different

physico-chemical and detonation properties, and each crystal type can be recrystallized from the appropriate solution at different cooling rates. The β and δ forms are of particular interest because they are the polymorphs used in typical formulations of composites for various applications. β -HMX is a low temperature form, while δ -HMX is a high temperature form. δ is observed as heating of β -HMX when the temperature between 165-210 °C^{4, 5}. Brill et al. reported kinetic measurements of the β - to δ - transition, showing that it is first order with an activation energy and frequency factor resemble the values attributed to chemical decomposition, supporting previous speculation that the initial decomposition step in β -HMX is coupled to, or preceded by, the formation of δ -HMX^{2, 5}. Many *in situ* measurements of the transformation rate has been reported for HMX ignition experiments. Henson et al. used second harmonic generation (SHG) as a fast *in situ* probe of the β - δ transition in HMX, and first demonstrated the technique by monitoring the transition during slow heating^{1, 6}. Although several thermodynamics and kinetics models of HMX crystal transition have been reported⁶⁻⁹, the kinetics of the β - δ transition have not yet been incorporated into any decomposition mechanisms of HMX, because it is very difficult and hazardous to observe and track the decomposition progress of energetic materials, and because the observed products may be the result of several sequential steps.

Recently, we reported great progress in using quantum mechanics (QM) based reactive dynamics to predict the complicated, detailed reaction barriers and kinetics of bulk phase reaction mechanisms¹⁰, especially for energetic materials¹¹⁻¹⁵, with detailed confirmation from experiment and concomitant interpretation of experiment, making it possible to determine the initial decomposition steps of HMX solid phase reactions.

In this work, we want to elucidate the initial thermal decomposition mechanisms of HMX, we report here DFT based molecular dynamics (MD) simulations, using the forces from the PBE-*ulg*¹⁶ flavor of DFT, to examine the initial decomposition of β - and δ -HMX. These studies on the initial reaction of HMX examine the atomistic details of the β - to δ - molecular structure transition and the decomposition mechanisms, providing an enriched understanding the β - to δ -crystal transformation of HMX.

2. METHODS

2.1. Simulation method

In this work, we perform the DFT based MD simulations. The interatomic forces were calculated in the framework of DFT¹⁷⁻¹⁸, where exchange and correlation were processed with the generalized gradient approximation (GGA), and we used the PBE functional form plus the *ulg* corrections for London dispersion¹⁶.

We used the VASP package¹⁹⁻²² to perform the periodic DFT calculations. For the crystalline structures optimization, we use a kinetic energy cut-off of 500 eV, and it gives excellent convergence in total energies, energy differences, and lattice parameters. For the DFT-MD calculations, we also use 500 eV energy cut-offs

and only the gamma point for the supercell calculations. For geometry optimization, we set a 1×10^{-6} eV energy difference and a 1×10^{-3} eV/Å force as convergence criteria for solving the electronic wave function. For DFT-MD simulation, we set a 1×10^{-5} eV energy difference and a 1×10^{-3} eV/Å force as convergence criteria for solving the electronic wave function.

Figure 1 Molecular structures of β -HMX and δ -HMX.

Two HMX crystalline phases (β -HMX and δ -HMX) were used in the DFT-MD simulations. We get the initial unit cell from CCSD database, and the β -HMX unit cell structure and δ -HMX unit cell structure can be found in the Supporting Information. For β -HMX, the MD uses a periodic cell which has 8 molecules (224 atoms per cell), obtained by replicating the unit cell twice along the “*a*” and “*b*” directions; For δ -HMX, the MD considered 6 molecules per unit cell. Then before doing the molecule dynamics simulations, we optimized the two structures individually. The two optimized initial structures of β -HMX and δ -HMX for MD simulations are shown in Figure S1.

Then we performed the DFT-MD cook-off simulations: First we heated the optimized initial systems 20 K to 300 K in 2 ps. Then the system was equilibrated at 300 K for 1 ps using the NVT (constant volume, constant temperature and constant number of atoms) ensemble, with the Nose-Hoover thermostat and time constant set to 0.1 ps. Finally, the system was heated from 300 K to 3000 K in 20 ps (heating rate ~ 135 K/ps), and the volume was fixed. A time step of 1 fs was used to integrate the equations of motion. To analyse the fragments in the DFT-MD simulation, a bond length cut-off of 1.5 times of the normal ones were used (see Table S1).

2.2. Reaction mechanism by finite cluster calculation

To examine the detail reaction mechanisms which discovered during the periodic DFT-MD simulations, we extracted the reaction involved molecule structures from the MD trajectories, and using the Jaguar program²³ performed the gas phase reactions locate the nearby transition state (TS), at the level of 6-311++G**. We validated the TSs by only have one negative eigenvalue for the Hessian. And then we do the intrinsic reaction coordinate (IRC) scans, to connect the TS to nearby reactant and the product structures²⁴. In order to get the free energies, we obtained the vibrational frequencies by diagonalized the mass reduced Hessian. And the thermodynamic properties were evaluated at 298.15 K and 1 atm.

3. RESULTS & DISCUSSION

From our DFT-MD simulations, we obtained a detailed, molecular-level reaction pathway of the thermal decomposition in condensed phase β - and δ - HMX. We can extract valuable information about complicated chemical progress involved²⁵. In this work, we studied thermal decomposition of condensed phase β - and δ - HMX crystals, and focus on examining the initial reaction pathways to investigate the β - to δ - molecular structure transition before the initial reaction occurs. As phase transition requires the cell change in the simulation, we didn't study in this work.

3.1. Reaction mechanisms from DFT-MD

Figure 2 (a) Species analysis for β -HMX cookoff DFT-MD simulation (heating from 300 to 3000 K in 20 ps). β -HMX first decomposed at 2200~2250 K (~14 ps), first HONO and NO_2 molecules releasing almost at the same time. (b) Species analysis for δ -HMX cookoff DFT-MD simulation (heating from 300 to 3000 K in 20 ps). δ -HMX first decomposed at ~2010 K (12.6 ps), one NO_2 molecule released and followed by one HONO released.

First, we examined the initial decomposition of β -HMX. Figure 2(a) shows a function of temperature of molecular fragments during the cook-off simulation. The system consists of 8 β -HMX molecules (224 atoms). When the temperature increases to ~2200 K and instantaneous pressure increased to ~1.0 GPa, the first reaction occurs, and two β -HMX molecules decomposed one by one almost at the same time, but leading to two distinct types of unimolecular decompositions, one releasing HONO and the other releasing NO_2 molecule almost at the same time (NO_2 cleavage later than HONO release from another β -HMX molecule). Later after 2250 K, there are more NO_2 molecules released, see Figure 2(a). Thus, we consider that, for β -HMX, both unimolecular HONO releasing and NO_2 cleavage reaction are the initial reactions. We will discuss the reaction

mechanisms detailly below in the “Reaction mechanism from finite cluster calculations” section.

For the initial chemical reactions of δ -HMX, the DFT-MD results is shown in Figure 2(b). Here δ -HMX molecules start to react at ~ 2010 K, involving both NO_2 cleavage and HONO releasing mechanisms. Different from the initial reactions of β -HMX, the NO_2 molecule and the HONO molecule are released from the *same* HMX molecule. Thus, the initial reaction in δ -HMX is different than for β -HMX case. Then ~ 1 ps later, at ~ 2200 K, HMX molecules decrease one by one, and more NO_2 and HONO molecules releasing. This is similar to the RDX's initial reaction mechanism which the hydrogen-transition to form HONO occurs at the beginning

3.2. Reaction mechanism from finite cluster calculations

To identify the initial thermal decomposition mechanism of β - and δ -HMX detailly, we first extracted the activated intermediates, which involved in the first reactions, from the condensed phase DFT-MD simulation. Then we addressed the reaction mechanism as a gas phase reaction from finite cluster calculations as below.

3.2.1. β -HMX structure transitions before initial decomposition.

Figure 3. Mechanism of β -HMX structure transitions prior to initial decomposition. The gas phase calculations are performed here and start from the activated intermediates which extracted from the condensed phase DFT-MD trajectory (Configurations TS1 and TS3 were obtained at ~ 1800 - 1900 K, and configurations INT2 and INT4 were obtained at $\sim$

2200 K. Configurations **INT1**, **TS2**, **INT3** and **TS4** are obtained from finite cluster DFT calculations.). This leads to release of one NO₂ molecule and one HONO molecule. Unit is in kcal/mol.

First, we consider the β -HMX periodic system. As can be seen from Figure 2(a), at about 2200 K, the two β -HMX molecules started to decompose simultaneously. We analyzed the DFT-MD trajectory to find that the first HONO releasing event and the NO₂ cleavage event show two quite distinct kinds unimolecular decompositions ($\sim 1/2$ β -HMX molecules transfer to **INT1** when the temperature increases to 1800 K before decomposition at ~ 2200 K in DFT-MD simulation, see Figure S2). Here the simulated initial structure transition temperature is 1800 K as the decomposition temperature is 2200 K for β -HMX (554 K in experiment), so the constant proportional transitions temperature is ~ 453 K, which is similar to the experimental results (~ 466 K)²⁹. Then we separately optimized both two kinds of unimolecular decompositions as gas phase reactions. As described below for both cases, the nearby transition state (TS) were found with a single saddle point, and then we minimize them to find the nearby stable reactant and product species. In Figure 3, we addressed the observed reaction pathways and the free energy of each species and discussed below in detail.

We find (see Figure 3) the first HONO releasing unimolecular reaction pathway is β -HMX – **TS1** – **INT1** – **TS2** – **INT2** + **HONO**, which involves two steps. Starting with β -HMX, the one of the parallel N-NO₂ groups (left and right N-NO₂ group in β -HMX) changes over time from a chair conformation to a boat conformation via **TS1** (at +1.2 kcal/mol) to form **INT1** (+0.6 kcal/mol above β -HMX). Then after formation of **INT1** via the **TS1** from β -HMX, we find that one H atom near the parallel NO₂ group move from C atom to the parallel NO₂ group via **TS2**, then forms **INT2** and release one **HONO** molecule. The barrier is $\Delta G = +42.8$ kcal/mol, and this step is the rate-determining step (RDS). This is the first decomposition pathway we observed in the DFT-MD cookoff simulation (at ~ 14 ps), Then 0.2 ps later, we find the first NO₂ cleavage unimolecular decomposition process in the DFT-MD periodic system.

For the first NO₂ cleavage unimolecular reaction, the pathway is β -HMX – **TS3** – **INT3** – **TS4** – δ -HMX – **INT4** + **NO₂**, which involves three steps, with β -HMX transforming to δ -HMX before NO₂ cleavage. Starting with β -HMX, the first step involves one of the vertical N-NO₂ groups (up and down N-NO₂ group in β -HMX) changing over time from chair conformation to boat conformation via **TS3** (at +1.9 kcal/mol) to form **INT3** (0.2 kcal/mol above β -HMX). The second step starts with the new formed vertical N-NO₂ group (right parallel N-NO₂ group in β -HMX) over time from a vertical position to a parallel position to form a boat conformation via **TS4** to form the intermediate, which is δ -HMX. This reaction has a +7.6 kcal/mol barrier. The third step to eliminate the NO₂ molecule observed in the MD simulation involves breaking one parallel N-N bond of δ -HMX to form **INT4**, which have a reaction energy of 31.3 kcal/mol above δ -HMX. The barrier of **INT1** – **TS2** – **INT2** + **HONO** is 9.7 kcal/mol higher than the δ -HMX-**INT4** reaction, but in the DFT-MD simulation HONO releasing and NO₂ cleavage reaction are almost at the same time because in our cookoff simulations,

we found that four molecules transform to **INT1** molecular structure ($\sim 1800\text{K}$) and while only one molecule transforms to full δ -HMX ($\sim 2100\text{K}$). and the HONO was observed from INT1 while the NO_2 dissociation from δ - phase. This increase the probability of HONO releasing even the reaction barrier of HONO reaction is higher than NO_2 dissociation. In addition, the fast quenching rate and small simulation cell also may accelerate the HONO reaction.

Figure 4. The mechanism of the proposed reaction pathway of HONO releasing and NO_2 cleavage in β -HMX. The HONO releasing reaction has a barrier (**TS5**) of 43.6 kcal/mol, and the NO_2 cleavage reaction energy (barrier) is 33.2 kcal/mol above β -HMX. Units are in kcal/mol.

Although in the β -HMX periodic system, DFT-MD did not find a direct HONO or NO_2 releasing reaction for at the first step, we also performed the adiabatic QM calculations and proposed one direct HONO releasing and one direct NO_2 cleavage reaction (shown in Figure 4). For the HONO releasing reaction, the β -HMX molecule stretches the N-N bond via **TS5** (at +43.6 kcal/mol) to release a HONO molecule, leading to a barrier of 43.0 kcal/mol above **INT1** (at +0.6 kcal/mol). For the NO_2 releasing reaction, the β -HMX stretches the N-N bond directly to **INT6** which have a reaction energy of 33.2 kcal/mol above β -HMX. As the barrier of β -HMX – **TS5** – **INT5** is 0.2 kcal/mol higher than the **INT1** – **TS2** – **INT2** reaction, and β -HMX – **INT6** is 1.9 kcal/mol higher than the δ -HMX – **INT4** reaction, this explains why we did not find this direct NO_2 releasing reaction at the beginning decomposition.

3.2.2. Unimolecular NO_2 cleavage and HONO releasing reaction in δ -HMX.

Next, we consider the δ -HMX case. Here the first reaction is an N- NO_2 cleavage and HONO releasing reaction in the same δ -HMX molecule, leading to the unimolecular NO_2 releasing and HONO releasing reaction, as shown in Figure 5. These two reactions take place in one δ -HMX molecule in the condensed phase at about 2020 K. At first, starting with δ -HMX, we find that the preferred pathway to release the NO_2 molecule is stretching one vertical N-N bond to form **INT7** (with a reaction energy of 31.6 kcal/mol above δ -HMX). Then from **INT7**, we find that one H atom near the parallel NO_2 group moves from C atom to the nearby

parallel NO₂ group via **TS6**, then **INT8** and one HONO molecule released, with a barrier of $\Delta G = 39.0$ kcal/mol and release -44.3 kcal/mol energy. In the gas phase calculation, we also investigate the other pathway to eliminate the HONO molecule from **INT7** to form **INT10** with +49.0 kcal/mol barrier. This barrier is +10 kcal/mol higher than the barriers of **INT7** – **TS6** – **INT8** pathway, explaining why we do not observe it in the initial decomposition of δ -HMX from DFT-MD simulations.

Figure 5 Mechanism of initial δ -HMX unimolecular decomposition. The gas phase calculations are performed here and start from the activated intermediates which extracted from the condensed phase DFT-MD trajectory (Configurations **INT7** were obtained at ~ 2010 K and configurations **INT8** were obtained at ~ 2050 K. Configurations **TS6** and **TS7** are obtained from finite cluster DFT calculations). This leads to release of one NO₂ molecule and one HONO molecule. Configurations **INT9** is the pathway to eliminate the NO₂ molecule breaking one parallel N-N bond from δ -HMX is not observed in the initial decomposition of δ -HMX from DFT-MD simulations but obtained from finite cluster DFT calculations. Unit is in kcal/mol.

4. CONCLUSION

The goal of this work was to identify the initial reaction mechanism of β - and δ -HMX decomposes to find the events in this well-used EM, as it evolves to different structures transitions before decomposition that followed different reaction pathways to eventually form the different final products observed theoretically and experimentally. Indeed, from our DFT-MD simulations, we obtained a detailed, molecular-level reaction

pathway of the thermal decomposition in condensed phase β - and δ - HMX. This enables information about the complex physics or chemistry involved to be extracted, including structure transition, single versus multiple steps reaction sequences. Key points of our simulations are

- (1) There are two different initial unimolecular reaction pathways in β -HMX, both operating simultaneously. One releases the first HONO while the other releases the first NO_2 molecules.
- (2) For the HONO releasing reaction, β -HMX first transforms the structure to an intermediate in which one of the parallel N- NO_2 groups changes over time from chair to boat conformations, with a low barrier of +1.2 kcal/mol, suggesting that this reaction may proceed very easily before decomposition reaction. This is followed by unimolecular HONO release (42.8 kcal/mol barrier, RDS).
- (3) For the NO_2 cleavage reaction, β -HMX first transforms to the δ -HMX structure via **INT3** in which one of the vertical N- NO_2 groups changes over time from chair to boat conformations in two steps, with low barriers of +1.9 and +7.6 kcal/mol for each step, followed by unimolecular NO_2 release (+31.3 kcal/mol barrier).
- (4) δ -HMX initially performs a both unimolecular NO_2 cleavage and HONO releasing reactions in one δ -HMX molecule, with the barriers of +31.6 (NO_2 cleavage) and +38.9 kcal/mol (HONO releasing) for each step.

These simulations addressed and rationalized the decomposition mechanisms of β -HMX, showing that the formation of δ -HMX occurs first, as experimental studies had previously speculated. We expect these theoretical studies of the initial reaction of β - and δ - HMX might stimulate further experimental mechanisms studies of HMX, particularly the ignition, and characterization.

ASSOCIATED CONTENT

Supporting Information

Unit cell information and initial simulation structures of β -HMX and δ -HMX, the bond type and bond cutoff value which used in the fragment analysis, atomic coordinates of all intermediates and TS shown in this study. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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