

Journal of Materials Chemistry A

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Reaction Mechanism from Quantum Molecular Dynamics for the Initial Thermal Decomposition of 2,4,6-triamino-1,3,5-triazine-1,3,5-trioxide (MTO) and 2,4,6-trinitro-1,3,5-triazine-1,3,5-trioxide (MTO3N), Promising Green Energetic Materials

Cai-Chao Ye,^{†,‡} Qi An,[†] Tao Cheng,[†] Sergey Zybin,[†] Saber Naserifar,[†] Xue-hai Ju[‡] and William A. Goddard III FRSC^{*,†}

[†] Materials and Process Simulation Center, 139-74, California Institute of Technology, Pasadena, California 91125, United States

[‡] Key Laboratory of Soft Chemistry and Functional Materials of MOE, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China

Abstract:

Klapötke and co-workers recently designed two new materials, 2,4,6-triamino-1,3,5-triazine-1,3,5-trioxide (MTO) and 2,4,6-trinitro-1,3,5-triazine-1,3,5-trioxide (MTO3N), envisioned as candidates for green high-energy materials. However, all attempts at synthesis have failed. In order to validate the expected properties for these systems and to determine why these materials are too unstable to synthesize, we used the PBE flavor of Density Functional Theory (DFT) to predict the crystal structures for MTO and MTO3N and then we carried out DFT molecular dynamics simulations (DFT-MD) to determine the initial reaction mechanisms for decomposition. Klapötke estimated that MTO would have a density of $\rho = 1.859$ g/cc with an estimated detonation velocity (D_v) of 8.979 km/s, making it comparable to RDX ($\rho = 1.82$ g/cc, $D_v = 8.75$ km/s) and β -HMX ($\rho = 1.91$ g/cc, $D_v = 9.10$ km/s). His estimated impact sensitivity >30 J, make it much better than HMX (7 J) and RDX (7.5 J). Our predicted crystal structure for MTO (P2(1) space group) leads to $\rho = 1.859$ g/cc, in good agreement with expectations. Our DFT-MD studies find that the first step in the decomposition of MTO is intermolecular hydrogen-transfer reaction (barrier 3.0 kcal/mol) which is followed quickly by H₂O and NO release with reaction barriers of 46.5 and 35.5 kcal/mol. In contrast for MTO3N (P2(1)/c predicted space group), we find that the first steps are a bimolecular decomposition to release NO₂ ($\Delta H = 44.1$ kcal/mol, $\Delta G = 54.7$ kcal/mol) simultaneous with unimolecular NO₂ cleavage ($\Delta H = 59.9$ and $\Delta G = 58.2$ kcal/mol) a unique initial reaction among EMs. These results suggest that MTO3N would be significantly more thermally stable (barrier >6.0 kcal/mol higher) than RDX and HMX, making it an excellent candidate to be insensitive new green energetic materials. However we find that MTO leads to very favorable hydrogen transfer reactions that may complicate synthesis and crystallization, making MTO3N the more promising system.

Keywords: thermal decomposition, Density Functional Theory, green energetic materials, MTO, MTO3N

1. INTRODUCTION

Environmental concerns about current energetic materials (EM) make the development of Green EM a high priority.¹ Moreover developing safe and efficient high-energy content materials is of vital importance to utilization in civil applications as propellants in satellite launch rockets, satellite propulsions system, and naval systems.^{1,2} An ideal green explosive should have higher velocity of detonation, higher detonation pressure, higher density, and lower sensitivity than benchmark explosives, such as RDX and HMX. Simultaneously it is important that the end products from detonation or combustion are environmentally friendly and that the syntheses not yield toxic or non-Green materials that must be disposed. For this reason Klapötke et al designed 2,4,6-triamino-1,3,5-triazine-1,3,5-trioxide (MTO) and 2,4,6-trinitro-1,3,5-triazine-1,3,5-trioxide (MTO3N) as potential new green energetic materials and estimated that velocity of detonation would be 8.979 km/s (compare to 8.855 km/s for RDX and 9.247 km/s for β -HMX) with density is 1.9 g/cc and impact sensitivity >30 J, much better than HMX (7 J) and RDX (7.5 J).³

However, numerous attempts to synthesize MTO and MTO3N have not yet been successful. In order to predict more accurately the properties and to understand the stability, we recently predicted⁴ the crystal packing and cohesive energy of MTO and MTO3N using Monte Carlo simulated annealing methods⁵ with the PBE flavor of Density functional Theory⁶ (DFT) (including the low gradient London dispersion correction⁷ (PBE-ulg) to find that MTO has the P2(1) space group with 2 molecules per cell and a density of 1.859 g/cm³, while MTO3N has the P2(1)/c space group with 4 molecules per cell and a density of 2.016 g/cm³. The two molecular and crystal structures are shown in Figure 1.

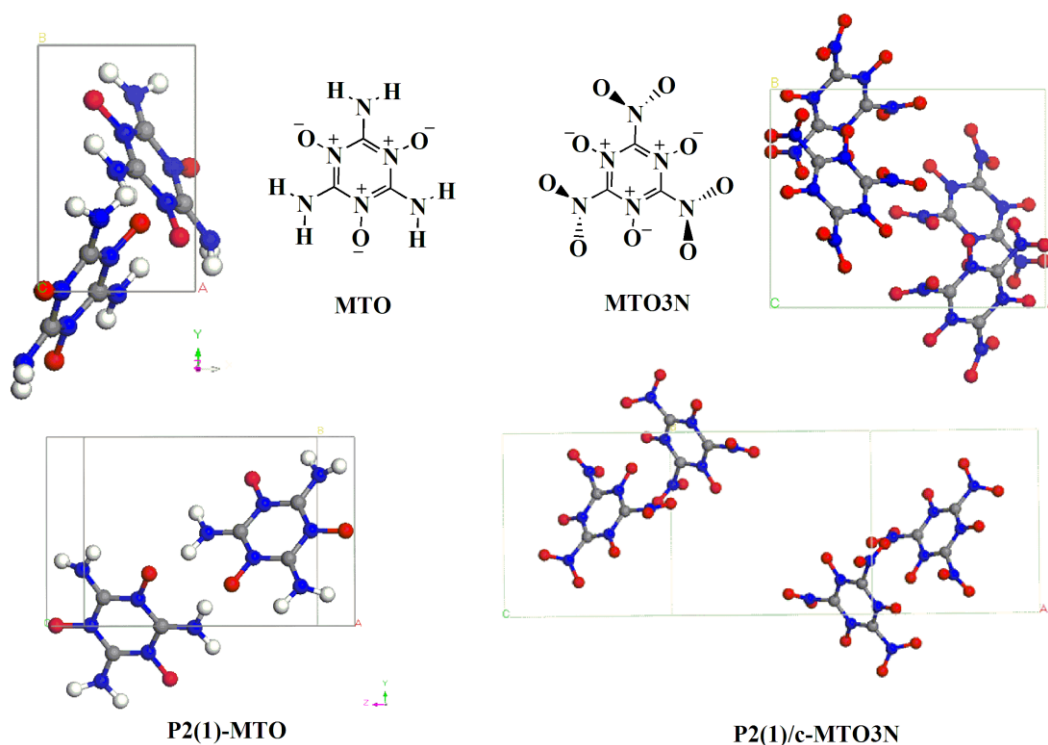


Figure 1. 2,4,6-triamino-1,3,5-triazine-1,3,5-trioxide (MTO) and 2,4,6-trinitro-1,3,5-triazine-1,3,5-trioxide (MTO3N) molecular structures and their most stable crystal structures: P2(1) for MTO and P2(1)/c for MTO3N predicted from previous PBE DFT calculations⁴. The C, O, N, H atoms are represented by grey, red, blue and white balls, respectively.

In order to determine the energy release, detonation properties, and sensitivity of EMs, it is essential to determine the reaction mechanism for the initial steps leading to thermal decomposition⁸⁻¹⁴. For such nitro-based EMs as TNT, RDX, HMX and CL-20, the initial decomposition at low pressure is unimolecular NO₂ cleavage¹⁵⁻²⁰. However for hydrogen containing highly energetic materials such as RDX and HMX, Chakraborty et al^{8, 14, 21} used DFT to show that intramolecular hydrogen transfer to form HONO provides a competitive first step for decomposition²²⁻²⁷ that dominates under high impact conditions²⁸. Since MTO has no -NO₂ group available to cleave off NO₂, and MTO3N has no hydrogen available to form HONO, their decomposition properties should be dramatically different (maybe better) than normal nitro-based explosives.

In this paper, we report the initial thermal decomposition reaction mechanisms of MTO and MTO3N using molecular dynamics simulations based on the PBE-ulg⁷ flavor of DFT. The PBE-ulg corrects the poor description of van der Waals attraction (London dispersion) in PBE⁷. Here we consider MTO and MTO3N starting with their predicted most stable crystal structures (P2(1) for MTO and P2(1)/c for MTO3N).

2. METHODOLOGY

2.1. Quantum molecular dynamics simulation

In these DFT based molecular dynamics (MD) simulations, the interatomic forces were calculated in the framework of DFT^{29, 30}, where exchange and correlation were treated with the generalized gradient approximation (GGA), using the PBE-ulg functional form⁷.

The periodic DFT calculations were performed using the VASP package³¹⁻³⁴. For structure optimization we found that a kinetic energy cut-off of 500 eV for the plane wave expansions gives excellent convergence of the total energies, energy differences, and structural parameters. The same energy cut-offs were used in the DFT-MD calculations. Reciprocal space was sampled with the Γ -centered Monkhorst–Pack scheme using only the gamma point for the supercell calculations. The convergence criteria were set to a 1×10^{-6} eV energy difference for solving the electronic wave function and a 1×10^{-3} eV/Å force for geometry optimization. They were set to 1×10^{-5} eV energy difference for solving the electronic wave function and a 1×10^{-3} eV/Å force for DFT-MD simulation.

Two crystalline phases (MTO: P2(1) and MTO3N: P2(1)/c) were considered in the DFT-MD simulations. The MD considered 8 molecules per periodic cell, obtained by replicating the unit cell twice along the “a” and “b” directions for MTO and replicating the unit cell twice along the “c” direction for MTO3N. Then the structures for the supercells were optimized individually before molecule dynamics simulations. The two initial structures of MTO-P2(1) and MTO3N-P2(1)/c are shown in Figure S1.

The procedure for the DFT-MD cook-off simulations was as follows: First the systems were heated from 20 K to 300 K over a period of 2 ps and then equilibrated at 300 K for 1 ps using the NVT (constant volume, constant temperature and constant number of atoms) ensemble. Finally, we heated the system from 300 K to 3000 K uniformly over the period of 20 ps, but with the volume fixed. The time constant for the Nose-Hoover thermostat was set to 0.1 ps. We used a time step of 1 fs for integrating the equations of motion. To analyse the fragments during the simulation, we used a bond length cut-off of 1.5 times of the normal bond length, as are shown in the Table S1.

2.2. Finite cluster calculation

To analyse the mechanisms for the reactions discovered during the periodic DFT-MD simulations, we extracted the molecule structures involved (generally bimolecular) in the reaction from the periodic DFT-MD trajectories and then carried out finite molecule calculations to locate the nearby transition state (TS) for gas phase reactions at the level of M06/6-311++G** using the Jaguar program³⁵. The TS's were validated to have only one negative eigenvalue for the Hessian. This was followed by intrinsic reaction coordinate (IRC) scans to connect the TS to nearby reactant and the product structures³⁶. To obtain free energies, we diagonalized the mass reduced Hessian to obtain the vibrational frequencies, with which we evaluated the thermodynamic properties at 298.15 K and 1 atm. All gas phase calculations were carried out using the Jaguar 8.2 package³⁵.

3. RESULTS AND DISCUSSION

These DFT-MD simulations provide a very detailed, molecular-level description of the decomposition and reactions of MTO and MTO3N in the condensed phase. This information allows us to extract valuable information about the complex chemistry involved, including uni- and multi-molecular reactions¹². Our goal is to elucidate the reaction pathway as MTO and MTO3N decomposes and evolves to form intermediates that react with each other and with reactant to form eventually the final products observed theoretically and presumably experimentally. In this work, we focus on thermal decomposition of condensed phase MTO and MTO3N crystals, examining the initial reaction pathways to evaluate the stability of these two promising green energetic materials.

3.1. MTO initial reaction

3.1.1. Quantum molecular dynamics simulation

We first examined the initial decomposition reaction of P2(1)-MTO. The molecular fragments during the cook-off simulation are plotted in Figure 2 as a function of temperature. The starting supercell consists of 8 MTO molecules (144 atoms). We see that

1. No reactions are observed from 0 to 7 ps (up to 1250 K).

2. Simultaneous intermolecular H transfer between two MTO monomers is observed during the period 7 to 11 ps (up to 1700 K) to form the dimer containing adjacent NH and N-OH groups in place of NH₂ and N-O⁻, with a structure similar to TS1 in Figure 3.
3. Then, at 11.5 ps (~ 1800 K) the first reaction occurs, a unimolecular reaction involving the intermediate formed in step 2 in which an NH₂ transfer a hydrogen to the N-OH group to release H₂O, leaving behind **INT2** with an opened ring.
4. Later at 13 ps (~2050 K), the first NO molecule is released from **INT2**.

Thus, we find that the unimolecular H₂O release subsequent to H transfers between two monomers is the initial decomposition reaction for P2(1)-MTO. We will discuss these reaction mechanisms in more detail using finite clusters. As the temperature continues to increase, we observe the release of increased numbers of H₂O products.

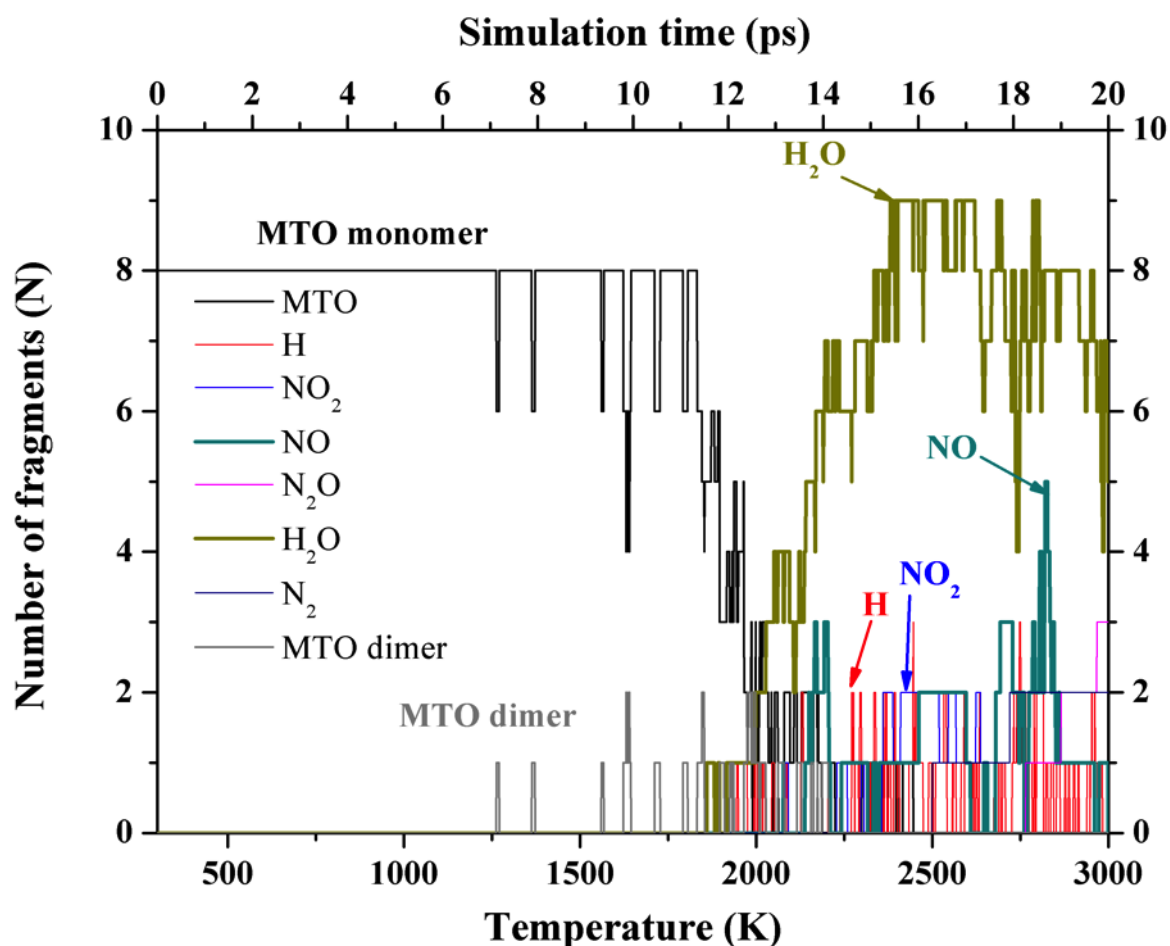


Figure 2. Species analysis for the decomposition of P2(1)-MTO heated from 300 to 3000 K over 20 ps. During 7 to 11 ps, H transfer occurs and at ~11.5 ps ($T = 1800$ K), the first H₂O released. Starting at 13 ps (~2050 K), one NO molecule is released. The main product of MTO decomposition is H₂O.

3.1.2. Finite cluster calculations

To understand the nature of the initial decomposition reactions of P2(1)-MTO, we extracted the activated intermediates from the condensed phase simulation and analyzed the reaction mechanism as a gas phase reaction.

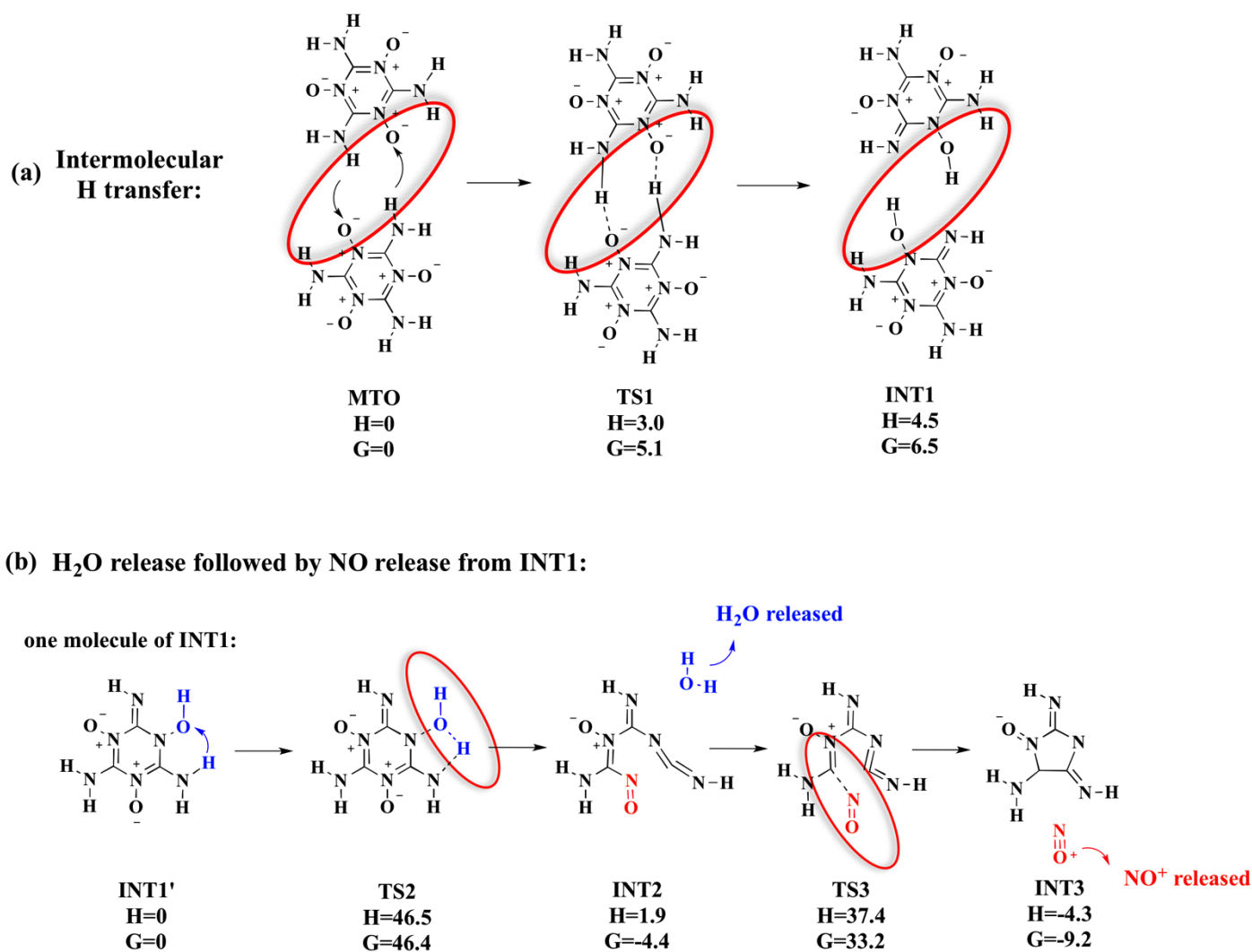


Figure 3. The mechanism of the (a) intermolecular hydrogen-transfer, and (b) H₂O and NO releasing reactions for MTO. First a bimolecular intermolecular hydrogen-transfer take place to form **INT1**, then one H₂O is released to form **INT2**, which is followed quickly by NO release to form **INT3**. Configurations **TS1**, **INT1**, **TS2**, **INT2** and **INT3** were extracted from the DFT-MD trajectory and then optimized as a gas phase reaction. We carried out IRC calculations to show that these steps are connected (that is there is no additional TS between **MTO**, **INT1**, **INT2**, and **INT3**). We calculate that the QM energy of the **INT1** is 7.0 kcal/mol lower than the **TS1** of 7.8 kcal/mol at 0 K, the **INT1** has a higher enthalpy and free energy at 298.15 K than the **TS1**. Whereas including the hydrogen bonding between the two **INT1'** molecules in **INT1**, the QM energy of the **INT1'** is 4.0 kcal/mol above the **INT1**. Here energies are in kcal/mol. The ΔH and ΔG is evaluated at 298.15 K

3.1.2a Intermolecular H transfer to form INT1 (MTO–TS1–INT1) We find that the first reaction is intermolecular hydrogen-transfer in which two MTO molecules each exchange one H atom with the other to form the intermediate **INT1** (Figure 3) via **TS1**. This leads to a very low barrier of only $\Delta H = 3.0$ kcal/mol

($\Delta G = 5.1$ kcal/mol), which is very fast in the QM-MD above 1250 K. Based on this barrier and we estimate that this should take place in a nanosecond in at room temperature, suggesting that the crystallization must be done at low temperature (below 50 K). Although **INT1** has an internal energy of 7.0 kcal/mol, which is lower than the **TS1** of 7.8 kcal/mol at zero temperature, we find that at room temperature **INT1** has a higher enthalpy and free energy than the **TS1**.

3.1.2b Decomposition of INT1' to release H₂O (INT1'–TS2–Int2+H₂O). After formation of the **INT1'** (**INT1** monomer) via the bimolecular H transfer from **MTO**, we find that one H atom of –NH₂ transfers from the N atom to the nearby OH group via **TS2** to release one H₂O molecule and **INT2**, with a barrier of $\Delta H = 46.5$ kcal/mol ($\Delta G = 46.4$ kcal/mol), making it the rate-determining step (RDS) for decomposition. Indeed this is the first decomposition process we see in the DFT-MD on the periodic system (at ~ 11.5 ps)

3.1.2c Decomposition of INT2 to release NO (Int2–TS3–Int3+NO⁺). Starting with **INT2**, the lowest energy pathway to eliminate the NO⁺ molecule is to break the C-N bond via **TS3** to form an intermediate **INT3** (shown in Figure 3), which we find to have a barrier of 35.5 kcal/mol above **INT2**. Indeed we see this process in the DFT-MD on the periodic system at 13 ps.

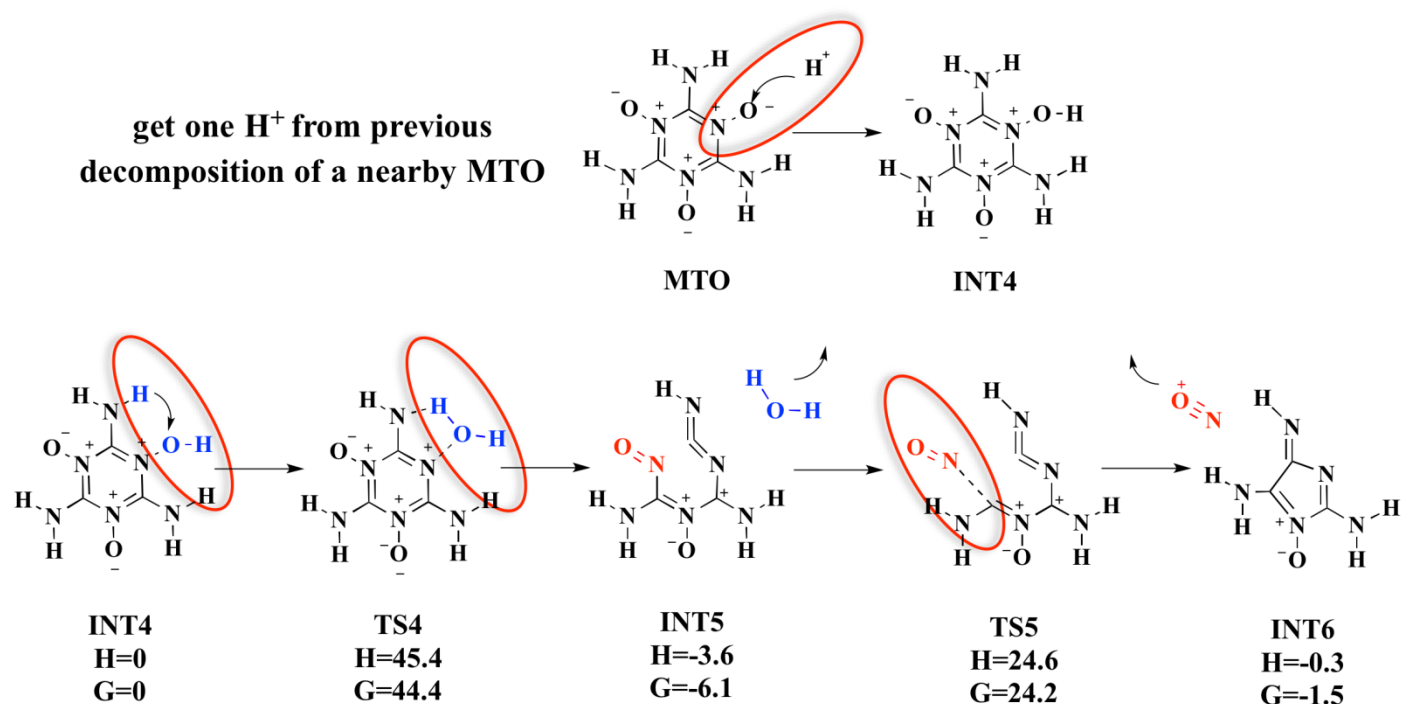


Figure 4. The mechanism of our proposed pathway for the reactions releasing H₂O and NO⁺ from MTO, which starts with an H⁺ transfer from a previously decomposed MTO molecule to an oxygen atom (see the red lines in Figure 2, which indicate dissociated H atoms) of an unreacted MTO to form **INT4**. Then **INT4** releases one H₂O to form **INT5**, which is followed quickly by NO⁺ release to form **INT6**. Units are in kcal/mol.

3.1.2d MTO get one H⁺ from previous decomposed nearby fragments. Between 12.5 and 15.0 ps (2000 K and 2300 K) in the DFT-MD simulations on MTO crystal, we found intermediates **INT4**, **INT5** and **INT6** after the first H₂O and NO releasing reaction, (shown in Figure 4). The mechanism for forming these species

is as follows. First, the MTO molecule adds a dissociated H^+ from some previous decomposition to the O atom to form the intermediate **INT4**. Then starting from **INT4**, one H atom of $-\text{NH}_2$ transfers via **TS4** to the nearby OH group to release one H_2O molecule, forming **INT5**. This has a barrier of $\Delta\text{H} = 45.4$ kcal/mol ($\Delta\text{G} = 44.4$ kcal/mol), making it the rate-determining step (RDS) for this decomposition pathway. Then from **INT5** the easiest decomposition pathway is to eliminate the NO^+ molecule by breaking the C–N bond via **TS5** to form intermediate **INT6** (shown in Figure 4), This has a barrier of $\Delta\text{H} = 28.2$ kcal/mol ($\Delta\text{G} = 30.3$ kcal/mol) above **INT5**.

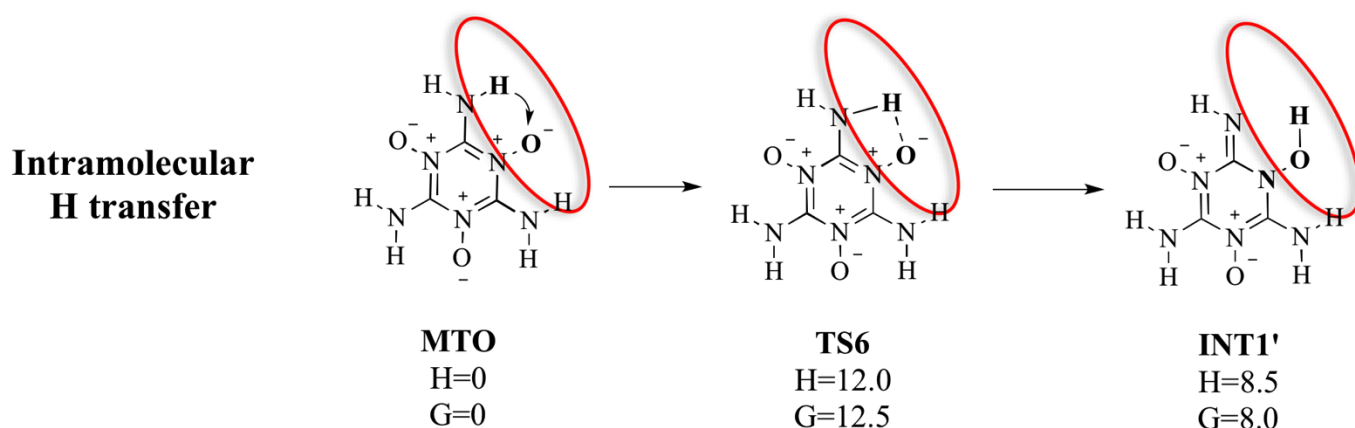


Figure 5 The reaction mechanism for the intramolecular H transfer path **MTO–TS6–INT1'** that forms one molecule of **INT1**, this path was observed in gas phase but was not observed in the DFT-MD simulations. Here energies are in kcal/mol.

3.1.2e Intramolecular H transfer (MTO-TS6-INT1'). Although our DFT-MD studies of MTO did not find an intramolecular hydrogen-transfer, we carried out QM calculations to examine the barrier for this intramolecular hydrogen-transfer pathway (**MTO-TS6-INT1'**), as shown in Figure 5. Here one H atom of the $-\text{NH}_2$ group transfers to the adjacent O atom to form the **INT1** via **TS6**. This leads to a barrier of $\Delta\text{H} = 12.0$ kcal/mol ($\Delta\text{G} = 12.5$ kcal/mol), which is 9.0 kcal/mol higher than the simultaneous intermolecular hydrogen-transfer reaction. This explains why we did not observe intramolecular hydrogen-transfer events in the DFT-MD for periodic MTO. This pathway would form the same **INT1'** intermediate (one molecule in **INT1**) in the gas phase as shown in Figure 5. As described above we also found a nearby transition state (**TS6**) with one saddle point and then the nearby stable reactant (**MTO**) and product (**INT1'**) species. Compared with the intermolecular H transfer (discussed above in Figure 3), The first **INT1** in Figure 3 has lower energy than **INT1'** in Figure 5 because of the hydrogen bonding between the two **INT1'** molecules in **INT1** (the hydrogen bond distance is 1.560 Å).

3.2. MTO3N initial reaction

3.2.1. Quantum molecular dynamics simulation

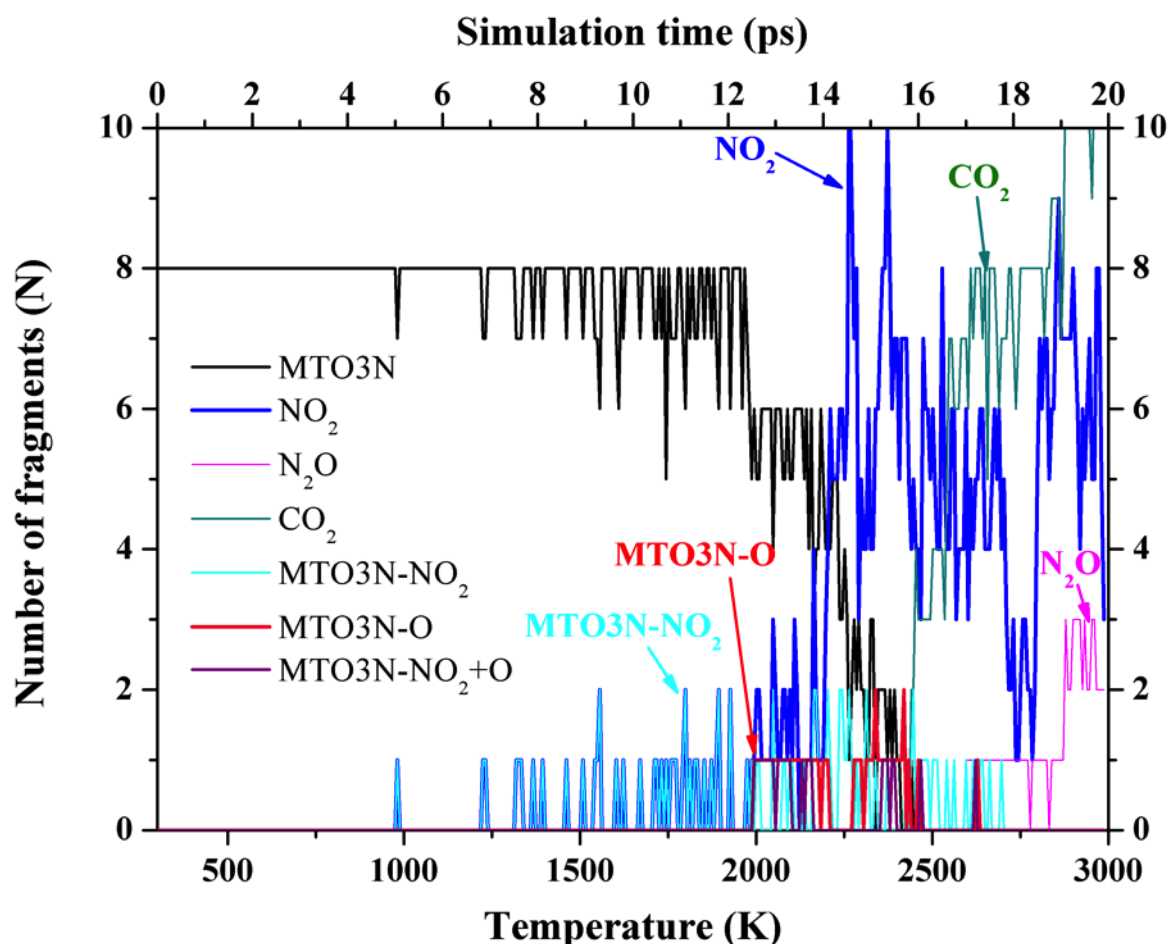


Figure 6. Species analysis for the decomposition of P2(1)/c-MTO3N heated from 300 to 3000 K over 20 ps. From 5 to 12.5 ps, we observe only N–N bond stretching vibration (no reactions), and then at 12.5 ps (~2000 K), we observe release of two NO_2 molecules. At the same time, we observe three new fragments (MTO3N-NO_2 , MTO3N-O , and $\text{MTO3N-NO}_2+\text{O}$), which indicate that the two NO_2 molecules come both from a bimolecular NO_2 releasing reaction and a unimolecular NO_2 cleavage reaction. This event is illustrated in Figure 7.

For P2(1)/c-MTO3N the initial decomposition fragments during the cook-off simulation are plotted in Figure 6 as a function of time (temperature). The starting supercell consists of 8 MTO3N molecules (144 atoms).

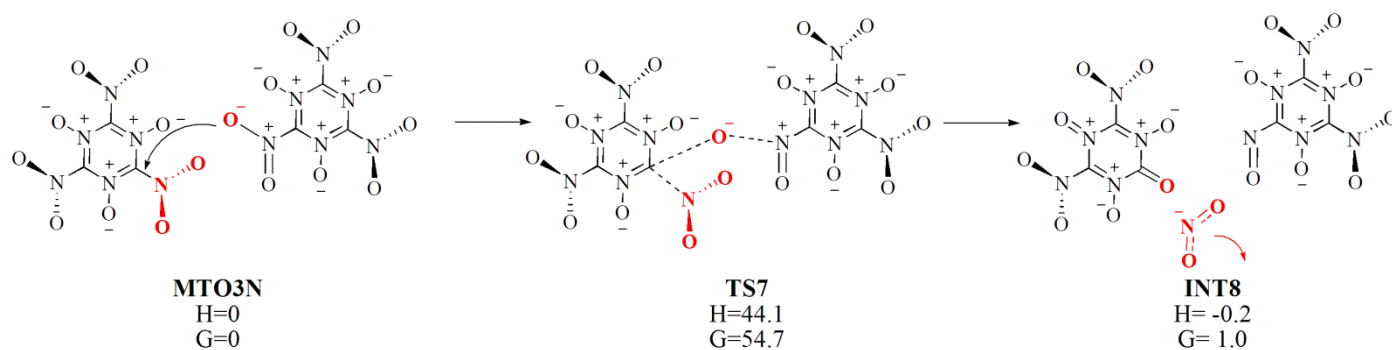
- From 5 to 12.5 ps, the amplitude of the N–N bond stretching vibration leads to fluctuations beyond our NN cut-off, but no real reactions
- Then at 12.5 ps (~2000 K), we observe release of two NO_2 molecules simultaneously with three new fragments: MTO3N-NO_2 , MTO3N-O , and $\text{MTO3N-NO}_2+\text{O}$ as shown in Figure 6. Here one NO_2 molecule comes from a bimolecular NO_2 releasing reaction while the other is from a unimolecular NO_2 cleavage reaction.

We will discuss the reaction mechanisms in more detail in the next section using finite cluster calculations. As the temperature continues increasing, we observe release of additional NO_2 products.

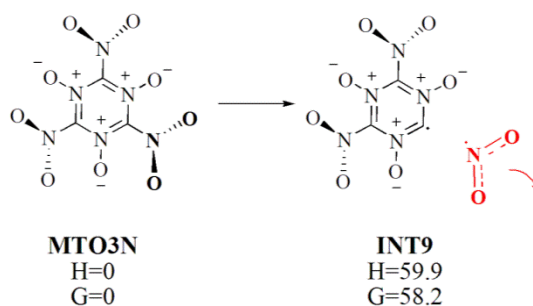
3.2.2. Finite cluster calculation

In order to understand the nature of the initial decomposition reactions of P2(1)/c-MTO3N, we extracted the activated intermediates from the condensed phase simulation and analyzed the reaction mechanism as a gas phase reaction, just as for P2(1)-MTO. We find that both an initial bimolecular NO_2 releasing reaction and a unimolecular NO_2 cleavage reaction takes place simultaneously.

The bimolecular NO_2 releasing reaction **MTO3N-TS7-INT8** shown in Figure 7(a) takes place between two MTO3N molecules at about 12.5 ps (~ 2000 K). In this reaction one oxygen atom of an $-\text{NO}_2$ group in MTO3N reacts with the carbon atom of the nearby MTO3N to make a new $\text{C}=\text{O}$ double bond via **TS7**, accompanied by breaking of the $\text{C}-\text{N}$ bond, to release one NO_2 . This bimolecular NO_2 releasing reaction (**MTO3N-TS7-INT8**) is the rate-determining step (RDS) with a barrier of $\Delta H = 44.1$ kcal/mol ($\Delta G = 54.7$ kcal/mol), which is similar to the barrier of H_2O releasing reaction (**INT1'-TS2-INT2**) in MTO initial reactions.



(a) The mechanism of the bimolecular NO_2 releasing reaction in MTO3N



(b) The mechanism of unimolecular NO_2 cleavage reaction in MTO3N

Figure 7 (a) The mechanism of the bimolecular NO_2 releasing reaction **MTO3N-TS7-INT8**, which takes place between two MTO3N molecules at 12.5 ps (~ 2000 K). In this reaction one oxygen atom of the $-\text{NO}_2$ group in MTO3N reacts with the carbon atom of a nearby MTO3N to make a new $\text{C}=\text{O}$ double bond via **TS7** while displacing the NO_2 from this C atom. (b) The unimolecular NO_2 cleavage reaction for MTO3N. **MTO3N-INT9** also takes place at 12.5 ps (~ 2000 K) Energies in kcal/mol. This reactions have very different ΔH with (a) much more favorable, but the ΔG at 298.15 K is similar.

Figure 7(b) shows, the energetics for the unimolecular NO_2 cleavage reaction pathway (**MTO3N-INT9**) found in the fragment analysis of Figure 6 at 12.5 ps (~ 2000 K). The reaction barrier (and endothermicity) is

calculated to be $\Delta H = 59.9$ kcal/mol (see Figure 7(b)), which is 15.8 kcal/mol higher than the bimolecular NO_2 releasing reaction barrier. However the transition state free energy $\Delta G = 58.2$ at 298.15 K is similar to the $\Delta G = 54.7$ for the bimolecular reaction, explaining why the DFT-MD simulation observes both at the same time at 12.5ps (~ 2000 K).

To understand why the reaction energy (barrier) for the unimolecular NO_2 cleavage reaction in MTO3N is much higher than the barrier of the bimolecular NO_2 releasing reaction, we examined the molecular structure of MTO3N in both the gas phase and crystal. We found that optimizing the MTO3N molecular structure in the gas phase leads to a structure in which, the planes of the three $-\text{NO}_2$ group are all perpendicular to the plane of 6-member ring. However, in the optimized MTO3N crystal, the angles between the planes of the $-\text{NO}_2$ groups on one MTO3N molecule and the plane of 6-member ring are 30° , 60° , and 90° , respectively. Moreover in the MTO3N crystal the shortest distance between the oxygen atom of $-\text{NO}_2$ and the oxygen atom of nearby $\text{C}=\text{O}$ group is 2.655 Å, much shorter than in gas phase MTO3N (3.274 Å). We conclude that the strong intermolecular repulsive force between $-\text{NO}_2$ group and the nearby $\text{C}=\text{O}$ group makes the bimolecular release of the $-\text{NO}_2$ group more favorable in the crystal. In contrast for unimolecular NO_2 cleavage unimolecular NO_2 cleavage in MTO3N requires a very long atom transfer process, giving it a very high reaction energy (barrier), but this is favored at high temperature because of the increased entropy from the bond breaking process.

4. SUMMARY AND CONCLUSIONS

The condensed phase DFT-MD temperature programmed simulations uncover competing unimolecular and bimolecular reactions for the initial thermal decomposition reactions of the MTO and MTO3N energetic materials. We find that these MD results can be explained in terms reaction pathways on just the one or two molecules involved. Key points of our simulations are:

1) For P2(1)-MTO, the initial reaction is a bimolecular hydrogen-transfer reaction, followed first by H_2O release with ring opening and then by NO release. This intermolecular hydrogen-transfer reaction has a very low barrier of $\Delta H = 3.0$ and $\Delta G = 5.1$ kcal/mol, suggesting that that this reaction may proceed in less than an hour even at 100 K. This could be tested by examining the IR and Raman of the crystalline form to find evidence of both OH and $\text{C}=\text{N}$ bonds. For the **INT1** species formed after the intermolecular hydrogen transfer reactions, it is now most favorable for intramolecular release of H_2O ($\Delta H = 46.5$ and $\Delta G = 46.4$ kcal/mol) to form **INT2**. From this **INT2** intermediate, it is favourable ($\Delta H = 35.5$ and $\Delta G = 37.6$ kcal/mol) to break the $\text{C}-\text{N}$ bond, to release NO while forming an imidazole ring.

2) For P2(1)/c-MTO3N, the bimolecular NO_2 releasing reaction and unimolecular NO_2 cleavage reaction take place simultaneously in the DFT-MD. In the bimolecular NO_2 releasing reaction, one oxygen atom of the $-\text{NO}_2$ group in MTO3N reacts with the carbon atom of a nearby MTO3N to form a new $\text{C}=\text{O}$ double bond while releasing the NO_2 from this carbon, with a $\Delta H = 44.1$ and $\Delta G =$

54.7 kcal/mol barrier. The reaction energy (barrier) for the unimolecular NO₂ cleavage is calculated to be $\Delta H = 59.9$ and $\Delta G = 58.2$ kcal/mol. leading to a ΔG just slightly higher than the bimolecular NO₂ releasing reaction.

The predicted initial reaction barriers for MTO ($\Delta H = 46.5$ kcal/mol) and MTO3N ($\Delta H = 44.1$ kcal/mol) are higher than the NO₂ dissociation barrier RDX ($\Delta H = 39.0$ kcal/mol)⁸ and for HMX¹⁴ ($\Delta H = 39.8$ kcal/mol). This suggests that both crystals should be more thermally stable. However the favourable hydrogen transfer processes in MTO may lead to problems with synthesis and crystallization. Thus we recommend MTO3N as the more promising material.

We have used carried out similar DFT-MD simulations to investigate the initial thermal decomposition reaction of TKX-50³⁷ and DTTO³⁸, which also have been suggested to be insensitive energetic materials. There we found the first decomposition barrier of TKX-50 (45.1 kcal/mol) and DTTO (45.9 kcal/mol), which are similar to the value we find for MTO (46.5 kcal/mol) and MTO3N (44.1 kcal/mol). These the high decomposition barriers for MTO and MTO3N suggest that these newly designed green energetic materials: MTO and MTO3N would be thermally insensitive.

Electronic Supplementary Information (ESI) available: Atomic coordinates of all intermediates and TSs shown in this study, coordinates for structures of P2(1)-MTO and P2(1)/c-MTO3N, and the bond cut-off in the fragment analysis. See DOI: 10.1039/b000000x/

AUTHOR INFORMATION

Corresponding Author:

*Email: wag@wag.caltech.edu

Notes:

The authors declare no competing financial interest.

ACKNOWLEDGEMENT

This research was funded by ONR (N00014-09-1-0634, Cliff Bedford). C.-C. Ye was sponsored by the China Scholarship Council, and thanks the Innovation Project for Postgraduates in Universities of Jiangsu Province (Grant No. CXZZ13_0213).

REFERENCE:

1. M. B. Talawar, R. Sivabalan, T. Mukundan, H. Muthurajan, A. K. Sikder, B. R. Gandhe and A. S.

- Rao, *J Hazard Mater*, 2009, **161**, 589-607.
2. D. M. Badgajar, M. B. Talawar, S. N. Asthana and P. P. Mahulikar, *J Hazard Mater*, 2008, **151**, 289-305.
 3. T. M. Klapötke, personal communication, 2014.
 4. S. Naserifar, S. V. Zybin, C-C, Ye and W. A. Goddard III, 2015, unpublished.
 5. M. Arellano and S. Bond, *Review of Economic Studies*, 1991, **58**, 277-297.
 6. R. G. Parr and R. G. P. W. Yang, *Density-functional theory of atoms and molecules*, Oxford university press, 1989.
 7. H. Kim, J. M. Choi and W. A. Goddard III, *J Phys Chem Lett*, 2012, **3**, 360-363.
 8. D. Chakraborty, R. P. Muller, S. Dasgupta and W. A. Goddard III, *J Phys Chem A*, 2000, **104**, 2261-2272.
 9. N. Umezawa, R. K. Kalia, A. Nakano, P. Vashista and F. Shimojo, *J Chem Phys*, 2007, **126**, 234702.
 10. R. A. Fifer, *Fundamentals of Solid-Propellant Combustion*, AIAA, New York, 1984.
 11. M. R. Manaa, L. E. Fried, C. F. Melius, M. Elstner and T. Frauenheim, *J Phys Chem A*, 2002, **106**, 9024-9029.
 12. S. P. Han, A. C. van Duin, W. A. Goddard III and A. Strachan, *J Phys Chem B*, 2011, **115**, 6534-6540.
 13. A. Strachan, E. M. Kober, A. C. van Duin, J. Oxgaard and W. A. Goddard III, *J Chem Phys*, 2005, **122**, 54502.
 14. D. Chakraborty, R. P. Muller, S. Dasgupta and W. A. Goddard III, *J Phys Chem A*, 2001, **105**, 1302-1314.
 15. S. N. Bulusu, *Chemistry and physics of energetic materials*, Kluwer Academic, Boston Norwell, MA, U.S.A., 1990.
 16. C. J. Wu and L. E. Fried, *J Phys Chem A*, 1997, **101**, 8675-8679.
 17. K. K. Irikura, *J Phys Chem A*, 2013, **117**, 2233-2241.
 18. R. Cohen, Y. Zeiri, E. Wurzburg and R. Kosloff, *J Phys Chem A*, 2007, **111**, 11074-11083.
 19. X. F. Chen, J. F. Liu, Z. H. Meng and K. L. Han, *Theor Chem Acc*, 2010, **127**, 327-344.
 20. S. Okovytyy, Y. Kholod, M. Qasim, H. Fredrickson and J. Leszczynski, *J Phys Chem A*, 2005, **109**, 2964-2970.
 21. D. Chakraborty, R. P. Muller, S. Dasgupta and W. A. Goddard III, *J Comput-Aided Mater*, 2002, **8**, 203-212.
 22. B. Wang, D. Wright, D. Cliffler, R. Haglund and S. T. Pantelides, *J Phys Chem A*, 2011, **115**, 8142-8146.
 23. D. Furman, R. Kosloff, F. Dubnikova, S. V. Zybin, W. A. Goddard III, N. Rom, B. Hirshberg and Y. Zeiri, *J Am Chem Soc*, 2014, **136**, 4192-4200.
 24. C. A. Mayhew, P. Sulzer, F. Petersson, S. Haidacher, A. Jordan, L. Mark, P. Watts and T. D. Mark, *Int J Mass Spectrom*, 2010, **289**, 58-63.
 25. Z. Takats, I. Cotte-Rodriguez, N. Talaty, H. W. Chen and R. G. Cooks, *Chem Commun*, 2005, 1950-1952.
 26. L. M. Minier, K. R. Brower and J. C. Oxley, *J Org Chem*, 1991, **56**, 3306-3314.
 27. L. L. Davis and K. R. Brower, *J Phys Chem*, 1996, **100**, 18775-18783.
 28. A. Strachan, A. C. van Duin, D. Chakraborty, S. Dasgupta and W. A. Goddard III, *Phys Rev Lett*, 2003, **91**, 098301.
 29. W. Kohn and L. J. Sham, *Phys Rev*, 1965, **140**, A1133-A1138.
 30. P. Hohenberg and W. Kohn, *Phys Rev*, 1964, **136**, B864-B871.
 31. G. Kresse, *J Non-Cryst Solids*, 1995, **193**, 222-229.
 32. G. Kresse and J. Furthmuller, *Comp Mater Sci*, 1996, **6**, 15-50.

33. G. Kresse and J. Furthmuller, *Phys Rev B*, 1996, **54**, 11169-11186.
34. G. Kresse and D. Joubert, *Phys Rev B*, 1999, **59**, 1758-1775.
35. A. D. Bochevarov, E. Harder, T. F. Hughes, J. R. Greenwood, D. A. Braden, D. M. Philipp, D. Rinaldo, M. D. Halls, J. Zhang and R. A. Friesner, *Int J Quantum Chem*, 2013, **113**, 2110-2142.
36. K. Fukui, *Accounts Chem Res*, 1981, **14**, 363-368.
37. Q. An, W. Liu, W. A. Goddard III, T. Cheng, S. V. Zybin and H. Xiao, *J Phys Chem C*, 2014, **118**, 27175–27181.
38. C.-C. Ye, Q. An, W. A. Goddard III, T. Cheng, W.-G. Liu, S. V. Zybin and X.-H. Ju, *J Mater Chem A*, 2015, **3**, 1972-1978.

TABLE OF CONTENTS:

A variety of initial decomposition reactions are favorable for MTO and MTO3N, two possible candidates for green high-energy materials.

