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RMD simulations applied to the study of energetic materials like HMX smokeless solid propellant: a case study of HMX molecular vacancies

Edemar Kirchhof[a], Rene F. B. Gonçalves[a]*, Marcela G. Domingues[a], Leopoldo Rocco Jr.[b], Bruno T. Rocco[b] , José A. F. F. Rocco[a]

[a] *Department of Chemistry, Aeronautics Institute of Technology, 50 Praça Marechal Eduardo Gomes, São José dos Campos, São Paulo, Brazil 12228-900*
[b] *Flowtest Engenharia e Pesquisa Ltda., 752 R. Goiânia, Caieiras, São Paulo, Brazil 07727-545*
* Corresponding Author*, renefbg@ita.br*

Abstract

Nitramines, like RDX and HMX, are also alternatives to AP as main components in smokeless propellants. They have high specific impulse but are moderately sensitive and have a slightly negative oxygen balance and are therefore unable to contribute positively to the oxygen balance of the propellant. Crystal defects are a constant in applied energetic materials (EMs) and play a crucial role in thermal degradation, combustion and ignition mechanisms, and subsequent aging. Defect engineering is the process of studying how defects affect an EM's qualities and performances in order to design new EMs that meet the required specifications. An emerging field of study in energetic materials is crystal-defect engineering, which offers previously unheard-of opportunities for regulating physical, chemical, and electrical properties as well as propellants, explosives, and pyrotechnics compositions. There are numerous types of crystal defects, including line defects (dislocation), planar defects (twin, shear band, crack, and surface defect), and volume defects (void). Point defects also include orientational defects and element doping. In this study, ReaxFF molecular dynamics simulations were used to examine the effects of molecule vacancies on the reaction kinetics and thermal decomposition mechanisms of condensed-phase - HMX at different temperatures. The thermal decomposition of HMX is the primary event in the combustion process of solid rocket smokeless propellants, directly affecting the related performance of propellants and even rocket engines. Results showed that three primary initial decomposition mechanisms, namely, NNO2 bond dissociation, HONO elimination, and concerted ring fission, exist at both high and lower temperatures. Molecular vacancies affect how much each of the three pathways contributes to the initial breakdown of HMX, and these effects change with temperature. Molecular vacancies significantly enhance N-N bond cleavage and coordinated ring breaking at high temperatures (3200 K), while impeding the production of HONO bonds. The two main competing reaction pathways are N-N bond dissociation and HONO elimination, with the former being more prevalent during the first breakdown. Additionally, we calculated the first decomposition's reaction rate constant and activation barriers for various vacancy concentrations. This RMD study showed that molecular vacancies accelerate the decomposition of condensed-phase HMX by increasing the reaction rate constant and reducing activation barriers.

Keywords: cyclotetramethylene-tetranitramine (HMX), reactive molecular dynamics, vacancies

1. Introduction

Reactive Molecular Dynamics (RMD) simulations have emerged as a powerful and indispensable tool for exploring the complex behaviors of energetic materials at the atomic and molecular scales [1;2]. By accurately modelling chemical reactions and structural transformations under various conditions, RMD provides deep insights into the fundamental processes that govern the stability, sensitivity, and performance of these high-energy systems. This computational approach complements experimental techniques by enabling the investigation of extreme environments and transient phenomena that are often challenging or hazardous to reproduce in laboratory settings, thereby advancing our understanding and facilitating the development of safer and more efficient energetic materials [3].

Among the diverse range of energetic compounds studied using RMD simulations, cyclotetramethylene-tetranitramine (HMX) holds a prominent position due to its exceptional explosive power and widespread applications. HMX is extensively utilized in military ordinances, such as warheads and propellants, as well as in industrial applications that demand high detonation velocities and pressures [4]. Its superior performance characteristics are attributed to its dense crystalline structure and high nitrogen content, which collectively contribute to its substantial energy release upon

decomposition. However, these same properties also render HMX sensitive to external stimuli such as heat, shock, and mechanical stress, necessitating a thorough understanding of the factors influencing its stability and reactivity to ensure safe handling and effective utilization [5;6].

A critical aspect affecting the behavior of HMX is the presence of molecular vacancies and other crystallographic defects within its lattice structure. These imperfections can arise during the synthesis, processing, or aging of the material and have been shown to profoundly influence its physical and chemical properties. Molecular vacancies [7] can act as initiation sites for decomposition reactions, altering the thermal stability and increasing the sensitivity of HMX to external perturbations [8]. They can also affect mechanical properties, such as hardness and elasticity, which are crucial for the material's performance under operational conditions. Understanding the nature, distribution, and effects of these defects is therefore essential for predicting the behavior of HMX and mitigating potential hazards associated with its use.

RMD simulations offer a robust framework for investigating the impact of molecular vacancies on the properties of HMX at a fundamental level. By simulating the dynamic evolution of the crystal lattice under various conditions, researchers can elucidate the mechanisms by which vacancies influence initiation pathways, energy release rates, and decomposition products. These simulations enable the exploration of different defect configurations and concentrations, providing comprehensive insights into their effects on the material's response to thermal and mechanical stimuli. Furthermore, RMD studies can aid in identifying strategies for defect mitigation through controlled processing techniques or the design of novel HMX-based formulations with enhanced stability and reduced sensitivity.

In summary, the application of Reactive Molecular Dynamics simulations to the study of molecular vacancies in HMX represents a significant advancement in the field of energetic materials research. This approach not only deepens our fundamental understanding of the interplay between structural defects and material behavior but also contributes to the optimization of explosive performance and safety. The insights gained from such studies have far-reaching implications, guiding the development of next-generation energetic materials with tailored properties for a wide range of military and industrial applications.

2. Methodology

The reactive molecular dynamics (RMD) simulations were performed using the software LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [9] and the ReaxFF force field [10] for hydrocarbons. The simulation began with the generation of a crystalline HMX structure, followed by the deliberate introduction of molecular vacancies to simulate defects that might occur during material processing, aging, or under stress conditions [11].

The reactive molecular dynamics simulations enable the calculation of kinetic parameters, with proved accuracy. In this case, three different temperatures (static) were applied to the system, varying from 2100 to 2500 K. The temperature in the canonic ensemble was controlled using a Berendsen thermostat. NVT was used for the determination of parameters as the results were smoother than with NVE. Temperature and energy fluctuations were smaller, and the correlation coefficient was higher. For the species analysis, a cutoff distance of 2.2 Å was considered.

3. Results and Discussion

Figs. 1 and 2 below present the energy variation of the systems in different temperatures, with and without the vacancies.

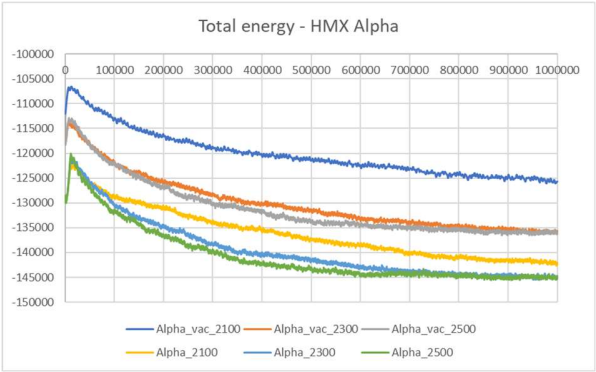

Figure 1. Energy variation for HMX alpha

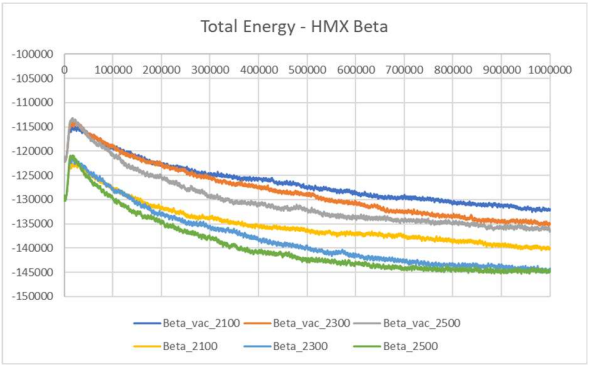

Figure 2. Energy variation for HMX beta

The two graphs illustrate the total energy of HMX in its alpha and beta polymorphs over time, as a function of simulation steps. Each graph compares the energy profiles for both pristine (no vacancies) and defected

(with vacancies) crystal structures at three different temperatures: 2100 K, 2300 K, and 2500 K. The legend labels correspond to these different conditions [LAMMPS].

In the first graph, which depicts the total energy of the HMX alpha polymorph, the pristine structures show a clear trend where the total energy decreases as the simulation progresses, eventually reaching a more stable state. At higher temperatures, specifically 2500 K, the total energy begins at a more negative value compared to lower temperatures, such as 2100 K, indicating that the system starts with higher internal energy, which subsequently decreases as the system stabilizes.

The defected HMX alpha structures, on the other hand, display higher total energy across all temperatures compared to their pristine counterparts, reflecting the destabilizing effect of molecular vacancies. While the trend in energy stabilization is similar to that of the pristine structures, the defected systems maintain a generally higher energy level, suggesting that vacancies lead to a less stable crystal structure. Additionally, the difference in energy between defected and pristine structures appears more pronounced at higher temperatures, which suggests that vacancies may exacerbate thermal instability in the HMX alpha polymorph.

In the second graph, which illustrates the total energy of the HMX beta polymorph, a similar energy reduction trend over time is observed. The pristine HMX beta structures also show a starting point with more negative total energy at higher temperatures, with a gradual decrease as the system approaches a stable state. Notably, the energy drop at higher temperatures, like 2300 K and 2500 K, is more significant, indicating increased thermal energy dissipation as the system stabilizes.

For the defected HMX beta structures, the starting total energy is again higher compared to the pristine beta structures across all temperatures, indicating the destabilizing influence of molecular vacancies. The stabilization process in these defected structures shows that even at higher temperatures, they eventually reach a stable energy state, though at higher overall energy levels than the pristine structures.

Comparatively, the energy behavior across the alpha and beta polymorphs shows that both exhibit a general trend of decreasing total energy over time, indicating a movement toward a stable state. The beta polymorphs, both pristine and defected, appear to stabilize at slightly lower energy levels compared to their alpha counterparts, suggesting a marginally higher inherent stability for the beta form under the same conditions.

Temperature has a noticeable impact, with increased temperatures, such as 2500 K, corresponding to higher initial total energy. This effect is more pronounced in defected structures, indicating that molecular vacancies could lead to increased thermal sensitivity. The presence of molecular vacancies results in consistently higher total energy across both polymorphs, underscoring the destabilizing effect of these defects. This effect becomes more pronounced at higher temperatures, which suggests that vacancies may significantly impact the thermal stability of HMX, making it more sensitive to external conditions.

The data suggest that while both polymorphs exhibit similar trends in energy reduction over time, the beta form may be slightly more stable. Furthermore, molecular vacancies significantly increase the total energy, especially at higher temperatures, indicating a potential increase in sensitivity and reduced stability for defected structures.

Figure 3 below shows the kinetic treatment for the different systems.

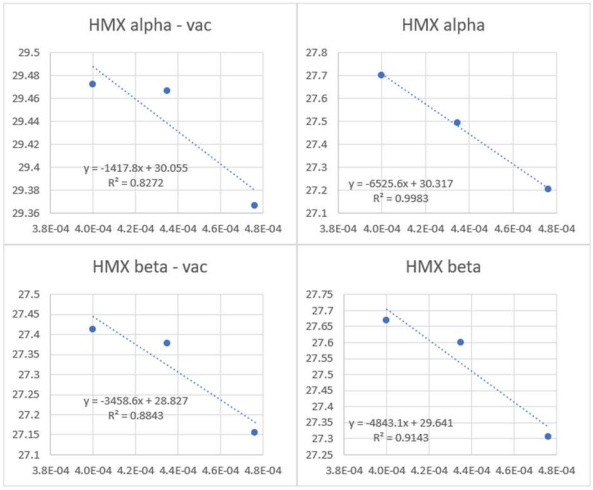

Figure 3. Arrhenius plots for the different systems

The figure presents four Arrhenius plots, which are used to analyse the temperature dependence of reaction rates in the different HMX systems: HMX alpha with vacancies, pristine HMX alpha, HMX beta with vacancies, and pristine HMX beta. The Arrhenius equation is linearized to the form $\ln(k) = -Ea/R(1/T) + \ln(A)$, where k is the reaction rate, Ea is the activation energy, R is the gas constant, and T is the temperature. The slope of the line in these plots gives the activation energy divided by the gas constant, while the intercept provides information about the pre-exponential factor A.

For the HMX alpha system with vacancies, the plot shows a linear relationship between ln(k) and (1/T), with a relatively low slope compared to the other systems. The equation of the line is y = -1477.8x + 30.055, and the coefficient of determination R2 = 0.8272. The relatively shallow slope suggests a lower activation energy for the decomposition process in the HMX alpha system when vacancies are present. The R2 value indicates a moderate

fit, suggesting some variability in the data that may not be fully explained by a simple Arrhenius relationship.
The pristine HMX alpha system exhibits a much steeper slope in its Arrhenius plot, with the equation y = -6525.6x + 30.317 and an R2 value of 0.9983, indicating an excellent linear fit. The steep slope suggests a higher activation energy for the pristine HMX alpha system compared to the defected version. This indicates that the pristine structure is more thermally stable, requiring more energy to initiate decomposition.
The HMX beta system with vacancies also shows a linear relationship in the Arrhenius plot, with the equation y = -3458.6x + 28.827 and an R2 value of 0.8843. The slope is steeper than that of the alpha system with vacancies but not as steep as the pristine alpha system. This suggests that the beta polymorph with vacancies has an intermediate activation energy, higher than the alpha with vacancies but lower than the pristine alpha.
For the pristine HMX beta system, the Arrhenius plot shows a slope and intercept of y = -4843.1x + 29.641, with an R2 value of 0.9143. The slope indicates that the activation energy is higher than that of the defected beta system but lower than the pristine alpha system. The good R2 value suggests that the relationship between temperature and reaction rate is well described by the Arrhenius equation.
Overall, the Arrhenius plots reveal that pristine HMX systems (both alpha and beta) have higher activation energies compared to their defected counterparts, indicating greater thermal stability. The presence of vacancies in the crystal structure lowers the activation energy, making the material more susceptible to decomposition at lower temperatures. The pristine HMX alpha polymorph has the highest activation energy, implying it is the most stable of the four systems analyzed. The HMX beta polymorph, whether pristine or with vacancies, shows intermediate activation energies, suggesting a balance between stability and reactivity.

4. Conclusions

The total energy analysis reveals that both alpha and beta polymorphs of HMX exhibit a general trend of decreasing energy over time, indicating stabilization as the simulation progresses. However, the presence of molecular vacancies in both polymorphs consistently leads to higher total energy levels, which suggests that these defects have a destabilizing effect on the crystal structure. This effect is particularly pronounced at higher temperatures, where the difference in energy between defected and pristine structures becomes more significant, indicating increased thermal sensitivity and reduced stability in the presence of vacancies.

The Arrhenius plots further underscore the impact of vacancies on the thermal stability of HMX. Pristine HMX systems, especially the alpha polymorph, exhibit higher activation energies compared to their defected counterparts, indicating greater resistance to thermal decomposition as described by many researchers [12;13;14]. The HMX alpha polymorphin, is shown to be the most stable, with the highest activation energy among the systems studied. Conversely, the introduction of vacancies lowers the activation energy, making the material more prone to decomposition at lower temperatures, which could lead to heightened sensitivity in practical applications.

In conclusion, the findings highlight the critical importance of controlling defects within HMX crystal structures to ensure their thermal stability and safety in energetic material applications. The alpha polymorph, particularly in its pristine form, demonstrates superior stability, making it a preferable choice in scenarios where thermal stability is paramount. However, the presence of vacancies significantly compromises this stability, underlining the need for meticulous material engineering to minimize defects and enhance the performance and safety of HMX-based explosives and propellants.

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