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Influence of Al and Al₂O₃ Nanoparticles on the Thermal Decay of 1,3,5-Trinitro-1,3,5-triazinane (RDX): Reactive Molecular Dynamics Simulations

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Abstract: Metallic additives, Al nanoparticles in particular, have extensively been used in energetic materials (EMs), of which thermal decomposition is one of the most basic properties. Nevertheless, the underlying mechanism for the highly active Al nanoparticles and their oxidized counterparts, the Al₂O₃ nanoparticles, influencing the thermal decay of aluminized EMs has not fully been understood. Herein, we explore the influence of Al and Al₂O₃ nanoparticles on the thermal decomposition of 1,3,5-trinitro-1,3,5-triazinane (RDX), one of the most common EMs, based on large-scale reactive force field molecular dynamics simulations within three heating schemes (constant-temperature, programmed and adiabatic heating). The presence of Al nanoparticles significantly reduces the induction time and energy required to activate the RDX decay, and greatly increases energy release. The fundamental reason for these results is that Al changes the primary decay pathway from the unimolecular N-NO₂ scission of RDX to bimolecular barrier-free or low-barrier Al-involved reactions, and possesses a strong O-extraction capability and a moderate one to react with C/H/N. It is also responsible for the growth of the Al-contained clusters. And Al₂O₃ nanoparticles can also demonstrate such catalysis capability but contribute less to the enhancement of energy release. Moreover, the detailed evolutions of key thermodynamic properties, intermediate and final gaseous products, and Al-contained products are also presented. Besides, under the programmed heating and adiabatic heating conditions the catalysis of the Al and Al₂O₃ nanoparticles becomes more distinct. Thereby, many properties of aluminized EMs are expected to well be understood by our simulation results.

1. INTRODUCTION

Energetic materials (EMs), including propellants, explosives and pyrotechnics, are a class of important substances applied for military and civilian purposes. In general, the applications of EMs are originated from their energy release after decomposition, on the level of 1~3 kJ/g for common CHON contained EMs. Nevertheless, such energy level cannot meet the increasing requirement of high energy density. Adding metallic fuels particles like Al, Mg, B and Zr to common EMs is feasible to meet the requirement. These metallic fuels usually possess much higher volumetric and gravimetric enthalpies of combustion than those of common CHON contained EMs. Thus, they have widely been utilized as additives in composite EMs to improve detonation and combustion performances. Among them, Al is the most favorable and extensively used because of its high abundance, high reactivity, high enthalpy of combustion, and low cost.¹

Al exhibits several advantages in EMs. For instance, Al particles can improve the specific impulse and burning rate of solid propellants by increasing combustion temperature and thermal conductivity, reducing the molecular weight of gaseous products and increasing energy density.¹⁻² In explosive formulations, Al powders have been added to increase their detonation heat, reaction temperature and combustion time.³⁻⁵ Moreover, Al serves as an essential ingredient of thermobaric and enhanced blast explosives.⁶ As a matter of fact, Al can play different roles in EMs, depending on its content, i.e., a small content of Al will participate in the detonation process and contribute to the enhancement of detonation heat; while, a large one will react with the detonation products and air over a timescale much longer than that of detonation itself, thus demonstrating a striking afterburning effect and contributing significantly to the explosion work.⁶⁻⁷ Besides, the combustion product of Al powders, Al-oxide, is a combustion stabilizer that can enhance the combustion stability of the double-base propellant and reduce the pressure exponent.⁸⁻⁹

The efficiency of Al in EMs seriously depends on its particle size. For example, the coarse or micro-sized metallic Al particles are disadvantaged, due to their low combustion efficiency, low energy release rate, high ignition temperature, and easy agglomeration¹⁰; while, the nano ones can significantly improve the mass and heat transfer rates of solid propellants due to their high specific surfaces and excellent dispersity.¹¹ A small amount of nano-Al particles can effectively increase the combustion efficiency, heat of combustion and decrease the ignition delay of solid propellants.¹²⁻¹³

An Al contained EM is usually called an aluminized EM. Aluminized 1,3,5-trinitro-1,3,5-triazinane (RDX) is currently one of the most extensively applied aluminized explosives. Because thermal decay is a primary and initial process of the combustion and/or detonation of EMs, it is requisite for evaluating any EM to guarantee safety. For the Al-RDX systems, there is a large body of work dedicated to the RDX decomposition catalyzed by Al.¹⁴⁻²² For example, Hou et al.²³ studied the influence of nano-Al on the thermal decomposition of RDX and showed that Al nanoparticles decrease the peak decomposition temperature, the activation energy and the critical explosive temperature of RDX. Zhu et al.¹⁴ interpreted from different perspectives on how nano-Al as a catalyst affects the thermal decomposition of RDX. They found that adding micro-Al does not affect the initial thermal decomposition pathway of RDX, while nano-Al can strongly promote the possibility of C-N bond cleavage of RDX.

It remains challenging to experimentally reveal the thermal decay mechanism of EMs, in particular, on the molecular/atomic level. While, molecular simulation can just remedy the deficiency. A large number of molecular simulations have focused on the initial thermal decomposition mechanism of RDX or Al-RDX mixtures. Schweigert et al.²⁴ investigated the bimolecular thermal decomposition pathways and the gaseous decomposition products of RDX using ab initio molecular dynamics (MD) simulations. Irikura et al.¹⁵ found that RDX decomposition undergoes a bimolecular

self-catalyzed acceleration chemical reaction process. Kuklja and coworkers²⁵ performed a quantum chemistry study on the initial decomposition path on the bulk RDX and showed that the energy barrier for the scission of N-NO₂ is lower than that for any other pathway. By first-principles MD simulations, Umezawa et al.²⁶ investigated the adsorption and decomposition reaction of RDX molecules on the Al(111) surface, and showed that the initial reaction path is comprised of the rupture of N-O and N-N bonds, and the subsequent redox reactions of O and NO with Al. It showed that the reaction between Al and RDX is a barrier-free process, and many fragments produced from the RDX decay can be adsorbed on the Al surface. Balbuena et al.²⁷⁻²⁸ investigated the infrared and vibration spectra of the RDX molecule on an Al surface (Al₁₆ cluster) using the MD and density functional theory (DFT) combined calculations. They found that the adsorption of the RDX molecules on Al surface leads to a configurational transformation from “AAE” to “AAA”, and the obtained Al-RDX infrared and vibration spectra are in good agreement with experimental observations. Ju et al.²⁹⁻³¹ conducted a series of DFT calculations on the adsorption, decomposition and reaction of common EMs on Al(111) surface, and obtained the related adsorption energy and activation energy. Zhou et al.³² investigated the adsorption and initial decomposition path of a TNT molecule on the Al(111) surface, and obtained the adsorption energy as well as the maximum charge transfer between nano-fragments and Al. Employing MD simulations, Losada et al.¹⁶ explored the reaction mechanism of the shocked aluminized RDX explosive, and traced the gaseous products in the reaction zone. Recently, Ju and coworkers performed reactive force field (ReaxFF) MD simulations of the effect of passivated Al nanoparticle on the thermal decomposition of four EMs, and found that the heat release of the aluminized explosives has been dramatically increased.³³

In spite of progress, a clear understanding on how nano-Al particle and its oxidized counterpart affect the thermal decomposition of RDX at the molecular/atomic level remains still lacking. Herein,

large scale ReaxFF-MD simulations are used to explore the microscopic mechanism of the effect of Al and its oxide on the thermal decomposition of RDX, and reveal their interaction mechanism within the timescale accessible to ReaxFF-MD simulations. By constructing four comparative models and setting different thermal loading conditions, the evolutions of reactants, intermediates and final products, potential energy, pressure, and temperature are analyzed, and the corresponding reaction pathways and activation energies are obtained. We show that, in comparison with pure RDX, the heat of reaction for the Al-RDX system is significantly increased, the activation energy is lowered and the decomposition rate is accelerated due to the catalytic decomposition of RDX and intermediates on the surfaces of nano Al and its oxides. The evolution of Al contained clusters during the decomposition is also recorded. By means of this insight, more perspectives of the thermal decay of Al-RDX systems and the influence of nano Al and its oxides on the decay are presented.

2. METHODOLOGIES

The present simulations were performed using the LAMMPS package³⁴ with the potential functions of the ReaxFF force field.³⁵⁻³⁶ The principle of ReaxFF is based on a combination of bond-order formalism and polarizable charge equilibration scheme to depict both reactive and non-reactive events. The main energy terms contributing to its potential function include ones involving covalent, electrostatic and van der Waals interactions. The power of the ReaxFF force field lies in its capability to simulate the full dynamic evolution of a large-scale system involving chemically reactive events over a longer time scale with a reasonable accuracy comparable to those of quantum chemistry calculations, and its excellent transferability. Hence, in the past less than two decades, the ReaxFF force field has enjoyed tremendous success in many fields of materials.³⁶

The ReaxFF force field parameter set of C/H/O/N/Al used in the present work was optimized by Wang and coworkers.³⁷ Specifically, the separate RDX (C/H/O/N) and Al parameters were cited from

previous literatures.³⁸⁻³⁹ Within the General Multiobjective Force Field Optimization Framework,⁴⁰ Wang et al.^{37,41} added the interaction parameters between Al and C/H/O/N based on extensive first-principles DFT calculations for both nonperiodic molecular clusters and condensed systems. The training set for the molecular clusters includes Al-O-H, AlH₃, Al(CH₃)₃ and Al(NH₂)₃, while that for the condensed systems consists of equation of state for pure Al, α -Al₂O₃, AlH₃, AlN and Al₄C₃. This new ReaxFF force field reasonably well reproduces most properties from first-principles calculations and experiments, as it was recently employed to investigate the interfacial reactions between RDX and Al under shock and thermal stimuli.^{37,41} The reaction pathways, kinetic parameters, and the evolution of the reaction products were thus obtained. Besides, the fragment identification code developed by Goddard's group from CalTech and based on the analysis of the bond connectivity information, was used to trace the evolution of chemical species. And the reaction identification code written by our group was employed to obtain the net reactions and their frequencies. Visualization of the reaction dynamics was primarily performed with the OVITO package.⁴²

Figure 1. Original models of (a) RDX, (b) Void -RDX, (c) Al-RDX, and (d) Al₂O₃-RDX each shown by a slice across the middle of cell and parallel to the AOB face. The C, H, N, O, and Al atoms are represented in gray, white, blue, red, and pink, respectively. Similar representations are considered in the following figures.

Table 1. Parameters and Contents of the Simulation Cells.

Model	RDX	Void-RDX	Al-RDX	Al ₂ O ₃ -RDX
Cell size (Å ³)	57×50×46			
Number of total atoms	10752	8749	9083	9404
Number of RDX molecules	512	411	411	411
Mass percentage of Al and Al ₂ O ₃			9.0%	12.6%

Firstly, a 4×4×4 supercell of α-RDX determined experimentally with a orthogonal crystal system and 512 molecules was constructed (Figure 1a). Thereby, a Void-RDX model with 411 RDX molecules was built by carving a spherical void with a radius of 1.4 nm at the center of the pure RDX model (Figure 1b). Based on the Void-RDX model, an Al-RDX model and an Al₂O₃-RDX model were established by inserting a nano spherical fcc Al cluster and a α-Al₂O₃ cluster both with a radius of 1.1 nm into the void, respectively (Figures 1c and 1d). Key parameters and contents of the four initial models are presented in Table 1. For simplification, these four models or systems are denoted by pure RDX, Void-RDX, Al-RDX and Al₂O₃-RDX, respectively. Thereafter, a classical force field of COMPASS was used to minimize the energy of the four initial models to justify the inappropriate interatomic locations. Subsequently, an isothermal-isobaric (NPT) ensemble equilibration simulation lasting for 10 ps with the ReaxFF force field at 5 K for each model was performed to eliminate the residual stress. The low temperature of 5 K was employed to ensure that RDX molecules do not undergo significant decomposition during equilibration. Based on the equilibrated models, three different simulation schemes were adopted for heating. Firstly, isothermal-isochoric (NVT) simulations at five different temperatures (1500, 2000, 2500, 3000, and 3500 K) were conducted. Considering that the higher temperature leads to the higher decomposition, the simulation time for 1500, 2000, 2500, 3000, and 3500 K was set to be 200, 150, 80, 80, and 40 ps, respectively. Secondly, the programmed heating from 300 to 3500 K at a rate of 16 K/ps for 200 ps was conducted for each model. Finally, it involves a preheating at 1500 K for 2 ps within the NVT ensemble followed by a microcanonical NVE simulation for 100 ps for each system to simulate an adiabatic situation. In all

simulations, the timestep was set to 0.1 fs.

It should be noted that natural Al nanoparticles are each passivated by an oxide shell of 2-4 nm in thickness.⁴³ The contents of active Al nanoparticles vary depending on their sizes and processing methods. The Al-RDX and Al₂O₃-RDX models adopted here are two extremes of an Al₂O₃-Al-RDX system. The content of active Al in Al-RDX is high up to 100 %, while that in Al₂O₃-RDX is very low. As we will show later, there is a small amount of active Al in the Al₂O₃ nanoparticle. When heated, the oxide shell will be spalled and the small liquid Al clusters are dispersed into the surroundings at a high rate.⁴⁴⁻⁴⁵ Therefore, the aforementioned Al-RDX model can directly describe this kind of scenario. Certainly, the Al₂O₃-RDX model is much closer to practice. The Al oxide always exists in the system, as an oxide shell is naturally present on the Al particles, or the Al nanoclusters burst across the oxide shell will quickly be oxidized. Nevertheless, it remains unclear how these oxide shells and oxide clusters influence the RDX decomposition, on which we focus in the present work. After relaxation, both Al and Al₂O₃ nanoclusters are in an amorphous liquid-like state. By the way, the building of the Void-RDX model is due to its inevitable presence in the RDX-Al or RDX-Al₂O₃ systems. For example, there are moderate gaps in the interface of RDX-Al or RDX-Al₂O₃, shown in Figures 1c and 1d. Thus, it is necessary to build the Void-RDX model to distinguish the effects of the gap and Al or Al₂O₃. Meanwhile, a pure RDX model is established for a comparison purpose.

As aforementioned, the thickness of the Al and Al₂O₃ nanoparticles applied in our simulation is ~1 nm. Even though it is much less than a common one (>50 nm) in experiments, it is enough to efficiently distinguish the effects of Al and Al₂O₃ on the thermal decay of RDX and reveal the underlying microscopic mechanism. Also, these limited sizes of the Al and Al₂O₃ nanoparticles are attributed to the limited simulation capability. Meanwhile, due to the limitation of timescale, the temperatures adopted for the decomposition simulations are systematically higher than those used in

the experiments. However, this setup that is very common among ReaxFF-MD simulations has been confirmed to be feasible to reflect reaction mechanism.⁴⁶⁻⁴⁹ Besides, for convenience, we define R as the ratio of the number of a chemical species to that of RDX to analyze reaction mechanism.

3. RESULTS AND DISCUSSION

3.1. Kinetics of the RDX Decomposition.

Figure 2. Evolution of R of RDX molecules at (a) 1500, (b) 2500, and (c) 3500 K.

Figure 2 shows the number variation of RDX molecules with time at three temperatures. At 1500 K, the decomposition of Al-RDX is the fastest, followed by Al₂O₃-RDX, Void-RDX and pure RDX. Notably, 1500 K is the closest to the temperature adopted in the experiment, below 1000 K.^{14,17,23,50} Therefore, the present result agrees with that the high activity of nano Al has frequently been shown to catalyze the thermal decomposition of RDX.^{14,23} For Al₂O₃, a surprising catalyzing effect is also shown. Generally, Al-oxide is considered to be inert and the presence of oxide shells on Al nanoparticles will decrease the reactivity of Al nanoparticles. However, our result demonstrates that, though Al₂O₃ is not as active as Al, it facilitates the early decay of RDX. It is consistent with an earlier experimental work, in which Zhang et al.⁵¹ demonstrated that α -Al₂O₃ nanoparticles enhanced the thermal sensitivity of HMX. For Void-RDX, the enhanced decomposition should be attributed to a larger specific surface relative to pure RDX.^{25,52-53}

While, comparing the decomposition rates of the four models at different temperatures, we find that the decomposition rate of pure RDX increases much faster with increasing temperature than that of Al-RDX, Al₂O₃-RDX or Void-RDX. As shown in Figure 2b, at 2500 K, after the initial 1 ps, the decomposition rate of RDX exceeds that of Al-RDX. Interestingly, more RDX molecules are decayed in Al₂O₃-RDX and Void-RDX than those in Al-RDX at the final stage. At a high temperature of 3500 K, the pure RDX exhibits first a lower decomposition rate than that of Al-RDX, Al₂O₃-RDX or Void-RDX, and subsequently a fastest decay. Moreover, the decomposition rate of Al₂O₃-RDX also exceeds that of Al-RDX finally, with the longest time required for Al-RDX to fully decompose. This condition under a higher temperature of 3500 K is close to the status of a wave front. Interestingly, our simulated result agrees with a fact that the Al particles (containing an oxide shell and an active Al core) act as inert materials at detonation conditions.⁵⁴⁻⁵⁵ The specific moments at which the RDX molecules undergo 50 % and full decomposition are listed in Table S1 of Supporting Information (SI). This temperature-induced reversal in catalysis effect will be explained in the next section.

Kinetically, the thermal decomposition of EMs is widely assumed to abide by the first order^{47,56-58} as follows

$$-\frac{dc}{dt} = kc \quad (1)$$

$$c(t) = c_0(1 - \exp(-kt)) \quad (2)$$

Herein, t , k , c_0 , and $c(t)$ represent time, the rate constant, the initial and remaining numbers of RDX molecules at moment t , respectively. Equation 2 can be transformed into Eq. 3:

$$k = \frac{1}{t} \ln \frac{c_0}{c_0 - c(t)} \quad (3)$$

The activation energy (E_a) can readily be obtained from the Arrhenius equation:

$$\ln k = \ln A - \left[\frac{E_a}{R} \right] \frac{1}{T} \quad (4)$$

in which A , R and T represent the prefactor, gas constant and temperature, respectively.

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Figure 3. $\ln k$ - $1000/T$ dependences of the thermal decay of RDX in the four models.

The kinetic parameters of the RDX decomposition can be achieved by analyzing the evolution of the number of RDX molecules at various temperatures. The thermal decomposition rate at each temperature can be obtained by fitting the variation of the unreacted RDX molecules with time to Eq. 2. Following the Arrhenius equation (Eq. 4), we plot a $\ln k$ - T correlation as shown in Figure 3. Consistent with the evolution of unreacted RDX molecules shown in Figure 2, we demonstrate in Figure 3 that the RDX decomposition rates of Al-RDX and Al₂O₃-RDX are higher than those of Void-RDX and pure RDX at lower temperatures, while a reversal is exhibited at higher temperatures. The transition temperature is ~ 2000 K.

Table 2. Comparison in E_a of the RDX Thermal Decomposition from Present Work and Existing Results.

Contributors	Model	E_a (kJ/mol)	Average Size
Present work	Al-RDX	48.7	Al particle (1.1 nm), RDX bulk
	Al ₂ O ₃ -RDX	61.7	Al ₂ O ₃ particle (1.1 nm), RDX bulk

	Void-RDX	84.9	Void (1.4 nm), RDX bulk
	RDX	93.5	RDX bulk
Wang et al. ³⁷	Al-RDX	87.7	Al film with oxide shell (10 nm), RDX film (12 nm)
	Al ₂ O ₃ -RDX	154.4	Al ₂ O ₃ film (10 nm), RDX film (12 nm)
	RDX	130.0	RDX bulk
Xiao et al. ¹⁸	Al-RDX	70.8	RDX particle (1 μ m), Al particle (15 μ m)
	RDX	119.6	RDX particle (1 μ m)
Huang et al. ⁵⁹	Al-RDX	98.0	Al particle (40 nm), RDX particle (80 μ m)
	Al-RDX	129.0	Al particle (2.6 μ m), RDX particle (80 μ m)
	Al-RDX	157.0	Al particle (10.7 μ m), RDX particle (80 μ m)
	RDX	135.0	RDX particle (80 μ m)
Miao et al. ⁶⁶	Al-RDX	115.9	Al particle (140 nm), RDX particle (23 μ m)
Zhu et al. ¹⁴	Al-RDX	94.2	Al particle (40 nm), RDX particle (70 μ m)
	Al-RDX	126.8	Al particle (2.6 μ m), RDX particle (70 μ m)
	Al-RDX	156.0	Al particle (10.7 μ m), RDX particle (70 μ m)
	RDX	130.4	RDX particle (70 μ m)
Hou et al. ²³	Al-RDX	164.1	Al particle (60 nm)
	RDX	175.4	RDX particle

The derived E_a from the present work and existing ones are listed in Table 2. The experimentally reported E_a for RDX decomposition and that for aluminized RDX are in the range of 103-272 and 71-349 kJ/mol (the values in Table 2 are not complete), respectively. It shows that the present work underestimates the E_a of Al-RDX and pure RDX in comparison to those from experiments and that from Wang et al.'s simulation with the same ReaxFF force field³⁶. This discrepancy can come from several aspects: (1) The different calculation methods may be the main cause for the E_a discrepancy in. All the studies calculated the kinetics of RDX thermal decomposition using the nonisothermal method, i.e., heating at different rates. Here, we employed the isothermal method, i.e., simulating at different temperatures. (2) the complex experimental conditions which consist of many factors such as particle size, morphology, density, purity, heating rate and stimulus type; (3) the fact that we adopted high temperatures and small nanoparticles to save computational cost; and (4) the assumption that the decomposition kinetics follows a first-order rate equation. Yet, in terms of relative values, we show that nano-Al₂O₃ and nano-Al particles decrease E_a by 31.8 and 44.8 kJ/mol, respectively, which are in good agreement with several existing studies^{14,18,37,59}.

3.2. Initial Decomposition Reactions of RDX.

Table 3. Numbers of Total RDX Decomposition Reactions (Tot), Al-involved RDX Decomposition Reactions (Alu), Unimolecular RDX Decomposition Reactions (Uni), the Four Highest Frequent RDX Decomposition Reactions (Top4), and its Frequencies (Fre) at 1500 and 3500 K for the Four Systems.

T (K)	Model	Tot	Alu	Uni	Top4	
					Fre	Primary Reactions
1500	Al-RDX	428	149	11	20	$C_3H_6O_6N_6 + CH_2O \rightarrow C_4H_8O_7N_6$
					13	$C_3H_6O_6N_6 + CH_2O \rightarrow C_3H_6O_5N_6 + CH_2O_2$
					10	$C_3H_6O_6N_6 + H \rightarrow C_3H_7O_6N_6$
					7	$C_3H_6O_6N_6 + CHN \rightarrow C_4H_7O_6N_7$
	Al ₂ O ₃ -RDX	518	73	42	34	$C_3H_6O_6N_6 + CH_2O \rightarrow C_4H_8O_7N_6$
					15	$C_3H_6O_6N_6 + CH_2O \rightarrow C_3H_6O_5N_6 + CH_2O_2$
					13	$C_3H_6O_6N_6 \rightarrow C_3H_6O_4N_5 + NO_2$
					13	$C_3H_6O_6N_6 + CH_2ON_2 \rightarrow C_4H_8O_7N_8$
	Void-RDX	472	-	87	67	$C_3H_6O_6N_6 \rightarrow C_3H_6O_4N_5 + NO_2$
					41	$C_3H_6O_6N_6 + NO_2 \rightarrow C_3H_6O_8N_7$
					23	$C_3H_6O_6N_6 + CH_2O \rightarrow C_4H_8O_7N_6$
					15	$C_3H_6O_6N_6 + CH_2O \rightarrow C_3H_6O_5N_6 + CH_2O_2$
	RDX	705	-	107	70	$C_3H_6O_6N_6 \rightarrow C_3H_6O_4N_5 + NO_2$
					61	$C_3H_6O_6N_6 + NO_2 \rightarrow C_3H_6O_8N_7$
					23	$C_3H_6O_6N_6 + CH_2O \rightarrow C_4H_8O_7N_6$
					19	$C_3H_6O_6N_6 + O_2N \rightarrow C_3H_6O_5N_6 + NO_3$
3500	Al-RDX	340	111	46	14	$C_3H_6O_6N_6 \rightarrow C_3H_6O_5N_6 + O$
					12	$C_3H_6O_6N_6 \rightarrow C_3H_6O_4N_5 + NO_2$
					12	$C_3H_6O_6N_6 + H \rightarrow C_3H_7O_6N_6$
					5	$C_3H_6O_6N_6 + O \rightarrow C_3H_6O_7N_6$
	Al ₂ O ₃ -RDX	389	37	61	22	$C_3H_6O_6N_6 \rightarrow C_3H_6O_4N_5 + NO_2$
					16	$C_3H_6O_6N_6 \rightarrow C_3H_6O_5N_6 + O$
					8	$C_3H_6O_6N_6 + H \rightarrow C_3H_7O_6N_6$
					7	$C_3H_6O_6N_6 + O \rightarrow C_3H_6O_5N_6 + O_2$
	Void-RDX	380	-	163	90	$C_3H_6O_6N_6 \rightarrow C_3H_6O_4N_5 + NO_2$
					32	$C_3H_6O_6N_6 \rightarrow C_3H_6O_5N_6 + O$
					11	$C_3H_6O_6N_6 + C_3H_6O_6N_6 \rightarrow C_3H_6O_5N_6 + C_3H_6O_7N_6$
					11	$C_3H_6O_6N_6 + C_3H_6O_6N_6 \rightarrow C_6H_{12}O_{12}N_{12}$
	RDX	368	-	154	87	$C_3H_6O_6N_6 \rightarrow C_3H_6O_4N_5 + NO_2$
					31	$C_3H_6O_6N_6 \rightarrow C_3H_6O_5N_6 + O$
					18	$C_3H_6O_6N_6 + C_3H_6O_6N_6 \rightarrow C_6H_{12}O_{12}N_{12}$
					14	$C_3H_6O_6N_6 + C_3H_6O_6N_6 \rightarrow C_3H_6O_5N_6 + C_3H_6O_5N_6 + O_2$

To interpret the aforementioned temperature-induced reversal in catalysis effect and reveal the initial decomposition pathways of RDX, we present in Table 3 the numbers of total RDX decomposition reactions, Al-involved RDX decomposition reactions, unimolecular RDX

decomposition reactions, the four highest frequent RDX decomposition reactions, and its frequencies at the lowest temperature of 1500 K and the highest temperature of 3500 K for the four models. It shows that in the temperature range of 1500-3500 K, the self-catalyzed bimolecular reaction is always the dominant mechanism for RDX decomposition in terms of the total number of reaction events, verifying an existing result¹⁵ that the intermediate radicals can react with RDX molecules, thus accelerating the decomposition. While, the present work and previous quantum chemistry calculations⁶⁰ both show that the unimolecular break is the primary pathway for RDX decomposition at early stages for RDX.

It is known that the interaction between Al and RDX is a barrier-free process.³¹ To clearly show how Al and Al₂O₃ nanoparticles activate the thermal decomposition of RDX, we carried out ReaxFF-MD simulations of single RDX molecule adsorbing on Al and Al₂O₃ surfaces, and single RDX molecule in the vacuum (see Videos 1-5 in SI). As can be seen from Video 1 that the RDX molecule is quickly adsorbed onto the Al surface, forming a N-O-Al linkage. Then, the N-O bonds are quickly broken, with Al-O bonds formed. This process is completed within the initial several picoseconds at a temperature as low as 1 K, indicating a strong reactivity between RDX and Al. We also performed another simulation at 5 K, with Video 2 showing that all O atoms in the RDX molecule are extracted by the Al surface within 3 ps. For the Al₂O₃ surface, we first performed a programmed heating from 1 K to 1000 K (Video 3). We also observed the formation of N-O-Al bond relationship and the scission of N-O bonds. However, only one N-O bond dissociates and it occurs at ~300 K. We performed another constant temperature simulation at 300 K for the Al₂O₃ surface, further confirming the result (Video 4). This suggests that the Al₂O₃ surface does possess a moderate reactivity, weaker than that of Al. In contrast, for a single RDX molecule in vacuum, we observed the scission of -NO₂ from the RDX molecule at 2000 K after ~10 ps (Video 5).

As we have demonstrated, the Al-involved barrier free or low-barrier reactions are much faster than the energetically favorable early unimolecular decomposition of the N-NO₂ cleavage of the pure RDX, which has an energy barrier of 34.2-42.4 kcal/mol.^{15,25,61-62} As can be seen in Table 3, Al-RDX undertakes a total of 149 of Al-involved barrier-free or low-barrier RDX decomposition events with only 11 relatively high-barrier unimolecular reactions; while the pure RDX has to undergo 107 unimolecular reactions. Al₂O₃-RDX also undergoes 73 of Al-involved RDX decomposition reactions, thus accelerating its thermal decomposition. Void-RDX also exhibits a significant number (87 in total) of unimolecular reactions. But considering that the energy barrier for N-NO₂ bond rupture can be lowered by 8-15 kcal/mol²⁵ for the RDX molecules placed near the surface, it is expected that the presence of void surface in Void-RDX will accelerate the thermal decomposition at the early stage. Nonetheless, at later stage, when bimolecular reactions become dominant, the high probability of the intermolecular collision in the pure RDX model will become increasingly important. Thus, we observe that the RDX decomposition in the pure RDX finally surpasses that of Void-RDX at 1500 K (Figure 2a). With temperature increasing, the initial unimolecular reactions are also increasingly activated, and the advantage of barrier-free or low-barrier Al-involved reactions becomes decreasingly significant. At 2500 K (Figure 2b), Al-RDX only shows a slight advantage in the first 1 ps over the pure RDX; whereas even this initial advantage is almost completely lost due to a high unimolecular reaction rate at the high temperature of 3500 K (Figure 2c).

After the early Al-involved reactions and the unimolecular reactions, bimolecular reactions between light gaseous species take place. It was demonstrated that high pressure facilitates bimolecular reactions.⁶⁰ Figure 4 presents the evolution of pressure at 1500, 2500, and 3500 K for the interested systems. It shows that the pure RDX exhibits distinctly a higher pressure increase rate firstly and a higher pressure later than the other three models. A higher pressure implies a higher

number density of gaseous species and a higher collision rates between RDX molecules with these species. As for Al-RDX and Al₂O₃-RDX, after the early reactions, the Al and Al₂O₃ particles are transformed into Al contained clusters in the condensed phase, which contribute little to the later bimolecular reactions. Apart from that, the light gaseous species can be physically or chemically adsorbed onto these clusters, further reducing the self-catalyzed bimolecular decomposition reactions. It is thus unsurprising that the pure RDX is the first to fully decompose for temperatures above 2000 K. It is interesting to note that the lower increase rates of pressure and pressure in Al-RDX and Al₂O₃-RDX are in excellent agreement with the experimental results that Al particles with natural oxide shell decrease the detonation pressure of aluminized explosives⁵ and the pressure exponent of aluminized propellants.^{8,9} The detailed Al-contained cluster evolution will be discussed in the next section. In terms of the specific initial RDX decomposition pathways, we show in Table 3 that the most frequent reactions in the pure RDX and Void-RDX are the most energetically favorable N-NO₂ dissociation both at low and high temperatures, consistent with numerous prior studies.^{15,24-25,61-62} However, the pathways also exhibit a temperature dependence. At a low temperature of 1500 K, the N-NO₂ dissociation in the pure RDX and Void-RDX is complemented by the bimolecular interactions between RDX and NO₂ or CH₂O radicals. Previous quantum chemistry calculations⁶⁰ of shock wave induced decomposition of RDX also showed that radicals like NO₂ play an important role in facilitating the decay of RDX. When the temperature increases to 3500 K, the N-O bond rupture and bimolecular reactions between RDX molecules become important. As for Al-RDX and Al₂O₃-RDX, besides the primary Al-involved barrier-free or low-barrier reaction events, RDX molecules prefer to decompose through the bimolecular pathways such as the interaction between RDX and CH₂O or H radicals at a low temperature of 1500 K; while the unimolecular N-NO₂ and N-O scission, and bimolecular reactions between RDX and H or O radicals are both very frequent. Interestingly, we also

observe numerous NO_3 radicals due to the oxidation of NO_2 by RDX in the pure RDX at 1500 K, verifying its existence.⁶³

Figure 4. Evolution of pressure with time at (a) 1500, (b) 2500, and (c) 3500 K.

3.3. Evolution of Al-contained clusters.

The number of gaseous products and condensed detonation or combustion products are both of great significance in that they affect the detonation properties of aluminized explosives, the specific impulse of propellants, and the stability of rocket motors. Besides, we can know from Figure 4 that the pressures of Al_2O_3 -RDX and Al-RDX are lower than that of the pure RDX, due to the fewer light gaseous products. Also, it is strongly related with the big molecular cluster formation. Moreover, it should be pointed out that the clusters with the maximum molecular weight (MW) in the pure RDX and Void-RDX are orders of magnitude smaller than the largest Al contained clusters, and are thus not shown.

Figure 5. Evolution of the molecular weight (MW) of the largest molecular cluster at different temperatures for (a) Al-RDX, and (b) Al₂O₃-RDX. The largest cluster always contains Al.

Thus, much attention is paid to the systems of Al₂O₃-RDX and Al-RDX. After a careful checking, we find that each largest molecular cluster contains Al during the thermal decay of these two systems. Figure 5a demonstrates that, for both Al₂O₃-RDX and Al-RDX, the MW of the largest cluster tends to be steady, and decreases with temperature increasing. It suggests that a high temperature does not favor an Al-contained molecule cluster formation with a larger MW. Comparing Figures 5a with 5b, we find that MW of the largest molecular of Al-RDX first increases steeply and then tends to be steady; while that of Al₂O₃-RDX increases slowly. It should be reasonable. For Al-RDX, the initial largest cluster is in fact an Al nanoparticle; it becomes larger and larger after reactions proceed with more and more other atoms combined with Al; when the oxidation of Al is saturated, the cluster size keeps steady. As to Al₂O₃-RDX, because the oxidation of Al has been saturated already, the cluster size increases slowly, due to some adsorption of reaction intermediates and products, with a limited amount. It also suggests that Al₂O₃ is still stable till 3500 K.

Figure 6. Evolution of the numbers of the Al-contained molecular clusters at different temperatures for (a) Al-RDX, and (b) Al_2O_3 -RDX. The simulation time is shown in logarithm.

Figure 6a shows a first increase and a subsequent decrease of the total number of Al-contained clusters during the simulation time for Al-RDX. Combined with the MW evolution shown in Figure 5a, we can deduce that the MW increase results from the combination of small clusters to big ones. For example, at 3000 K, the MW of the largest molecular cluster increases steeply, due to the fusion of two and several clusters (Figure 5a). This can also be verified by two close key moment of the steep increase of MW and the maximal amount of the clusters: around 10 ps. In addition, since the condensed detonation or combustion products in the aluminized EMs are composed of the Al-contained clusters, the trends of the plot suggest that the temperature increasing can reduce the cluster size or increase the number of the residual products. As to Al_2O_3 -RDX, Figure 6b exhibits also a first increase and a subsequent decrease of the total number of Al-contained clusters; besides, it demonstrates a smaller amount of clusters and a fewer change of the numbers. The number of the Al-contained clusters in Al-RDX is one order of magnitude higher than that of Al_2O_3 -RDX. This agrees

with the fewer changes of the MW of the largest cluster shown in Figure 5b.

Figure 7. Configurations of Al particles with RDX molecules in the initial period when heated at 3500 K.

Besides, the melting, dispersion and agglomeration of Al atoms are found when heating Al-RDX, as illustrated in Figure 7. These heated and dispersed small Al particles with a large specific surface area undergo fast barrier-free reactions or low-barrier ones with RDX molecules, contributing to the decomposition of RDX at the early stage. With regard to Al_2O_3 -RDX, because of its high melting point, Al_2O_3 could more effectively keep its structural integrity, and only a few small clusters are spalled. Subsequently, the highly dispersed Al-contained clusters will continue adsorbing intermediates, leading to the cluster growth and the slowing down of the subsequent RDX decomposition. In contrast to the highly dispersed Al-contained clusters in Al-RDX, the number of Al-contained clusters and the corresponding specific surfaces in Al_2O_3 -RDX are much smaller, with less adsorption of the intermediates and a slower cluster growth. Hence, the higher bimolecular

reaction rate in Al_2O_3 -RDX is responsible for its higher RDX decomposition rate than that of Al-RDX at the later stage.

Figure 8. Evolution of the elemental composition of the largest Al contained clusters at different temperatures. (a) Al-RDX at 1500 K, (b) Al-RDX at 3500 K, (c) Al_2O_3 -RDX at 1500 K, and (d) Al_2O_3 -RDX at 3500 K.

Table 4. Ratios of the Elemental Composition of the Largest Al contained Molecular Clusters at Different Temperatures in the Final Steady State.

T (K)	Model	Composition	Al:C	Al:H	Al:O	Al:N
1500	Al-RDX	$\text{C}_{145}\text{H}_{261}\text{O}_{848}\text{N}_{123}\text{Al}_{306}$	2.11	1.17	0.36	2.49
	Al_2O_3 -RDX	$\text{C}_{57}\text{H}_{108}\text{O}_{695}\text{N}_{58}\text{Al}_{259}$	4.54	2.4	0.37	4.47
3500	Al-RDX	$\text{C}_{23}\text{H}_{42}\text{O}_{331}\text{N}_{18}\text{Al}_{169}$	7.35	4.02	0.51	9.39
	Al_2O_3 -RDX	$\text{C}_{18}\text{H}_{17}\text{O}_{509}\text{N}_{13}\text{Al}_{251}$	13.94	14.76	0.49	19.31

We further present in Figure 8 the evolution of the elemental composition of the largest Al contained clusters at different temperatures. Regarding Al-RDX (Figures 8a and 8c), an initial violent Al dispersion can be reflected by a sharp fluctuation of the numbers of Al atoms. The most prominent feature is that a large number of O atoms are extracted by Al from RDX and the intermediates. Apart from O atoms, a number of C/H/N atoms are adsorbed by the Al contained clusters too. Al_2O_3 -RDX (Figures 8b and 8d) only exhibits a slight fluctuation in the Al numbers initially, suggesting its much

higher cohesive energy in keeping structural integrity. Al_2O_3 -RDX nevertheless displays a weaker O-extraction and adsorption capability due to the initial saturated Al-O coordination of Al_2O_3 . The specific elemental compositions of the final clusters are listed in Table 4. It shows two similar final Al:O ratios at a given temperature for both systems. The capability of Al nanoparticles to adsorb C/H/N approximately doubles that of the Al_2O_3 ones. Notably, increasing temperature significantly weakens the capability of Al and Al_2O_3 nanoparticles to adsorb and interact with the other chemical species, which also contributes to the smaller size of the Al contained at higher temperatures.

3.4. Evolution of Potential Energy (PE).

Figure 9. Evolution of potential energy per RDX molecule at (a) 1500 K, (b) 2500 K, and (c) 3500 K.

The primary contribution to the heat of detonation or combustion is the enthalpy change from the initial metastable state to the final stable state. Within the NVT ensemble, the enthalpy change is equivalent to the change of PE. We thus present in Figure 9 the PE evolution. It can be seen that the PE of the four systems each first increases, and then undertakes an exothermic thermal decomposition with a significant PE decrease. This endothermic stage is analogous to the experimentally termed “ignition delay”, and is commonly called “induction time”.^{46,64} Whereas the amount of energy absorption required to “ignite” is usually an indicator for ignition temperature. Based on the PE

profile, it is found that the enthalpy change between the initial and final states for Al-RDX is about one magnitude higher than those of the other three systems. This result is in excellent agreement with the experimental conclusion that the addition of nano-Al dramatically increases the heat of detonation or combustion of the composite EMs.¹⁻⁵

Table 5. Energy Variation during the Decomposition.

<i>T</i> (K)	Model	<i>t_i</i> (ps)	<i>E_B</i> (kcal/mol)	ΔU (kcal/mol)
1500	Al-RDX	0.4	53.0	-326.1
	Al ₂ O ₃ -RDX	2.0	87.3	-83.0
	Void-RDX	4.1	100.4	-27.5
	RDX	6.6	103.2	-42.6
2000	Al-RDX	0.4	77.3	-416.2
	Al ₂ O ₃ -RDX	1.9	124.5	-244.3
	Void-RDX	2.6	128.0	-223.6
	RDX	2.8	137.7	-249.8
2500	Al-RDX	0.5	70.5	-405.0
	Al ₂ O ₃ -RDX	1.5	154.8	-249.3
	Void-RDX	2.2	152.6	-238.6
	RDX	1.7	166.5	-250.4
3000	Al-RDX	0.5	82.6	-399.4
	Al ₂ O ₃ -RDX	1.6	180.7	-252.8
	Void-RDX	1.4	170.7	-255.1
	RDX	1.3	194.2	-245.4
3500	Al-RDX	0.5	98.0	-336.9
	Al ₂ O ₃ -RDX	1.3	204.6	-179.1
	Void-RDX	1.2	191.0	-194.6
	RDX	0.8	211.9	-196.3

Note: *T* is the temperature, *t_i* is the equilibration-induction time, and *E_B* is the PE increase per RDX Molecule during the induction period. ΔU denotes the PE decrease during the entire simulations. We should note that the models at 1500 K is still far from the final equilibrium state due to slow reaction rate at the low simulation temperature.

Table 5 lists the relevant parameters to potential energy during the decomposition of RDX. In terms of the induction time and the energy absorption needed to “ignite”, we show that, at a given temperature, the Al-RDX model exhibits a much smaller induction time, and it requires much less energy to activate the exothermic process than other three models. These results strongly indicate that EMs containing Al nanoparticles should have a much shorter ignition delay and a lower ignition

temperature. We also recognize that the presence of Al_2O_3 only makes a small contribution to the energy absorption and release at the low temperature of 1500 K, and this contribution has not been observed at higher temperatures. This result indicates that, despite its moderate capability to adsorb chemical species, the adsorption contributes little to the energy release. It suggests that the adsorption of chemical species on the highly active Al nanoparticles is more chemical, whereas it is more physical on the less active Al_2O_3 particles.

3.5. Evolution of Key Intermediates and Final Products.

We select the evolution of several representative intermediates like CH_2O , CHN , CHON , HO , NO_2 , NO , and NO_3 to analyze the reactions. $\text{C}_3\text{H}_6\text{O}_4\text{N}_5$ and $\text{C}_3\text{H}_6\text{O}_5\text{N}_6$ are mainly formed through the scission of N-NO_2 and N-O bonds. The case of 2500 K is presented in Figure 10. It is found that, at 2500 K, Al-RDX generates distinctly less O contained NO_2 , NO , O_2 , CHON and $\text{C}_3\text{H}_6\text{O}_4\text{N}_5$ than void-RDX and the pure RDX, especially at the early stage; whereas it generates more CHN fragments without O. It further indicates the strong O-extraction capability of the highly active Al nanoparticles. As we have described in Section 3.3, the RDX molecules in Al-RDX undertake completely different decomposition path initially, which starts with the barrier-free or low-barrier reaction between the Al nanoparticle and RDX molecules followed by a series of bimolecular reactions (Table 3). In contrast, because the primary initial decomposition pathways for the pure RDX and Void-RDX are the scission of N-NO_2 and N-O bonds, it is unsurprising to detect the initial increase in population of $\text{C}_3\text{H}_6\text{O}_4\text{N}_5$, $\text{C}_3\text{H}_6\text{O}_5\text{N}_6$, NO_2 , and NO in this case. Most of these species have been detected experimentally.^{14,65}

Figure 10. Evolution of key intermediates for (a) Al-RDX, (b) Al₂O₃-RDX, (c) Void-RDX, and (d) RDX at 2500 K.

Table 6. Numbers of Chemical Reactions Related to RDX, the Key Intermediates, and the Final Products (N₂, H₂O, and CO₂) at 1500 and 3500 K for the Four Systems. “Total” and “Al” Denote the Total Number of Reactions and the Al-involved Reactions, Respectively.

T (K)	1500				3500			
Model	Al-RDX	Al ₂ O ₃ -RDX	Void-RDX	RDX	Al-RDX	Al ₂ O ₃ -RDX	Void-RDX	RDX
Total	19093	19924	14666	29730	19106	21266	17628	25637
Al	8698	3966	-	-	8190	3249	-	-
C ₃ H ₆ O ₆ N ₆	512	635	545	924	353	433	405	499
HO	5338	4472	2361	4548	5125	6453	4913	7135
CH ₂ O	5100	4944	2185	3992	1466	1121	970	1371
NO ₂	2706	4642	3570	7249	986	1347	1538	2034
NO	3246	4401	2260	4558	1970	2497	2376	3157
NO ₃	218	670	1023	2074	60	116	132	222
C ₃ H ₆ O ₅ N ₆	907	1081	871	1449	466	536	455	516
CN	1553	121	28	24	2830	2868	1884	2385

CHN	821	405	211	257	1378	1248	1064	1258
O	522	643	457	570	1396	1522	1533	1686
CHON	508	275	183	187	2132	3333	2182	3691
O ₂	715	747	78	197	1065	1291	814	1214
CHO	559	257	64	184	941	792	665	845
H	269	122	75	46	1636	1340	1074	1143
NH ₂	134	12	42	22	972	1021	845	1254
HONO	522	514	354	535	344	558	634	793
C ₃ H ₆ O ₄ N ₅	128	251	383	652	150	163	269	381
N ₂ O	70	142	101	143	118	238	281	322
H ₂	61	30	21	4	315	235	207	202
CO	36	6	0	0	345	275	191	204
N ₂	1187	532	352	539	3370	2447	1423	2119
H ₂ O	650	609	434	765	3168	4159	3031	4812
CO ₂	98	54	46	77	1305	1514	814	1292

Regarding both population and life time, CH₂O, CHN and CHON are the most important intermediates for all four systems. Table 6 lists the statistics of chemical reactions related to RDX, the key intermediates, and the final products (N₂, H₂O, and CO₂) at 1500 and 3500 K. The total number of reactions and the Al-involved number of reactions have also been listed. It is demonstrated that, the Al-involved reactions of Al-RDX is approaching one half of the total ones. However, as we have noted, this high-involvement of Al contained species actually reduces the subsequent bimolecular reactions. Consistent with the population evolution of these key species, the intermediates account for a majority of the total reactions, which are predominantly bimolecular reactions. Intriguingly, comparing Figure 10 and Table 6, we realize that radicals like HO, H, and O are very active in the bimolecular reactions, they are thus relatively much less than some stable species like CH₂O. This phenomenon suggests that radicals such as HO, H, and O are highly active, yet they have a very short lifetime.

It is worthwhile to note that N₂O is an important intermediate comparable to that of NO₂ during the thermal decomposition of RDX based on experimental observations.¹⁴ While, we do not observe any significant presence of N₂O in any system. This may be resulted from the much higher

temperature of the present simulations than that in experiments. In addition, it can be seen that a moderate amount of NO_3 is detected in Void-RDX and the pure RDX, verifying our analysis in Section 3.2. With regard to the number dependence of the intermediates on the temperature, we find an obvious population increase of CO at higher temperatures.

Figure 11. Evolution of final products (a) N_2 , (b) CO_2 , and (c) H_2O at 3000 K.

Apart from the Al contained clusters as condensed final product, N_2 , H_2O , and CO_2 are the most important final products. These stable gaseous products play an important role in augmenting the performance of CHNO EMs. Comparatively, N_2 , H_2O , and CO_2 can be quickly generated in Al-RDX at low temperatures, while their generation is apparently delayed in the pure RDX. Interestingly, the addition of Al_2O_3 also to certain extent increases the formation of these products. With temperature increasing, their formation in the pure RDX accelerates and gradually exceeds that in Al-RDX or Al_2O_3 -RDX. For example, Figure 11 illustrates the evolution of these products at 3000 K. It is observed that, for N_2 , the peak content in the pure RDX is slightly higher with a much faster overall generating rate in contrast to Al-RDX. The paths to final N_2 are listed in Table S3 of SI. It is expected

to consider that the Al nanoparticles possess a moderate N-extraction capability and subsequent bimolecular reactions are restrained due to the interaction between light molecular species and the dispersed Al contained clusters. As to H_2O and CO_2 , the difference in the peak content and the overall generation rate between the pure RDX and Al-RDX becomes much more distinct. The strong O-extraction capability of the Al nanoparticles is responsible for it (Figure 8). This O-extraction by Al clusters severely impedes the subsequent bimolecular reactions in producing O contained H_2O and CO_2 . The weak O-extraction capability of Al_2O_3 nanoparticles is also exhibited by slightly lower peak contents and overall generation rates of H_2O and CO_2 .

Figure 12. Amount of total species in the final equilibrium state.

Besides, we show in Figure 12 the amounts of total species approaching the final equilibrium state at 2500 and 3500 K. The exact values are listed in Table S2 of SI. It shows that Al-RDX produces the smallest amount of species, less than that of pure RDX or Void-RDX, especially when we only take the gaseous species into account. From the perspective of the detonation and combustion

properties of aluminized EMs, the lessened gaseous products disfavor the increases of detonation volume and specific impulse. While, the deficiency in gaseous products can be fully compensated by the much higher heat of reaction.

3.6. Results of Programmed Heating and Adiabatic Simulations.

The NVT simulations with a constant temperature are effective in describing scenarios in which EMs undergo steady detonation or combustion. Nevertheless, this simulation scheme cannot well simulate situations in which EMs are gradually heated at the ignition stage. The programmed heating simulations within the NVT ensemble are feasible. This is because the ignition is essentially a temperature increasing process prior to the steady detonation or combustion, although the practical ignition do not proceed at a constant heating rate. The NVE simulations can also describe the ignition reasonably for EMs in highly confined spaces almost without mass and heat transfer.

Figure 13. Evolution of (a) RDX molecules and temperature, and (b) PE during the programmed heating from 300 to 3500 K. The inset image in (b) is the closeup of PE profile in the first 1 ps.

Hence, we present in Figure 13 the evolution of RDX molecules and the corresponding PE profiles during the programmed heating from 300 to 3500 K within the NVT ensemble. It is found that the decomposition of the pure RDX and Void-RDX starts at ~ 1000 K and accelerates quickly with temperature increasing, while Al-RDX and Al_2O_3 -RDX undergo decomposition once heating starts. The PE profiles show that Al-RDX with a highly active Al content only exhibits a short-time low-peak induction period in the first 1 ps, and subsequently proceeds along a “down-hill” barrier-free exothermic reaction pathway. In contrast, the other three systems go through a long-time relatively high peak induction period in the first ~ 100 ps followed by an exothermic process. Moreover, Al-RDX shows much higher heat of reaction than others. Even though the Al_2O_3 nanoparticles contribute little to the heat of reaction, they do lower the energy needed to ignite, implying a lower ignition temperature. Owing to much stronger subsequent self-catalyzed acceleration in bimolecular decomposition of RDX in the pure RDX and Void-RDX, the RDX molecules in the four systems fully decompose almost at the same time. As aforementioned, the initial barrier-free or low-barrier Al-involved reactions and the subsequent restraint of bimolecular reactions by the Al contained clusters are responsible for the decomposition behaviors of Al-RDX and Al_2O_3 -RDX. All these results are in good accordance with the results presented formerly.

For the adiabatic simulations, the evolutions of the RDX molecules, PE, and temperature are presented in Figure 14. The most outstanding characteristics of these profiles are that the decomposition rate is entirely dictated by the energy release rate, which in essence determines the temperature increase rate for an adiabatic system. The Al-RDX with a highly active Al content is endowed with the highest rates of overall energy release, temperature increase, and decomposition. Comparatively, the less active Al_2O_3 nanoparticle also displays much higher catalyzing activity than the void contained RDX. It is worthwhile to point out that the preheating at 1500 K prior to the NVE

adiabatic simulations has somewhat activated (ignited) the energetic systems, we thus cannot see the PE peaks as those in the other simulation schemes. Nevertheless, the remarkably slow rates of energy release and temperature increase within the first 50-60 ps are distinctly exhibited by the PE (Figure 14b) and temperature (Figure 14c) evolution profiles of the pure RDX system. We have also examined the evolutions of the populations and reactions of the key intermediates and final products under programmed heating and adiabatic heating conditions, with similar mechanisms found. That is, similar to the RDX decomposition, their reaction rates are also determined by the energy release rates, which are eventually governed by the reaction kinetics depicted in Section 3.1.

Figure 14. Evolution of (a) RDX molecules, (b) PE, and (c) temperature within the NVE ensemble. The evolution is preceded by a preheating of 2 ps at 1500 K within the NVT ensemble.

4. CONCLUSIONS

Summarily, based on reactive force field molecular dynamics simulations, we have explored the thermal decomposition of four representative RDX-based energetic systems under three heating

schemes. The energetics, kinetics and key products have been analyzed, in virtue of which the catalysis activity of Al and Al₂O₃ nanoparticles on the thermal decomposition of RDX has well been understood. The following conclusions can be drawn.

(1) The thermal decomposition of pure RDX proceeds through the early unimolecular reactions followed by the later bimolecular reactions. For both RDX and aluminized RDX materials, bimolecular reactions are the dominant pathway in terms of the number of reactions. In addition, the stable intermediates like CH₂O and unstable radicals like HO, CN, CHN, CHON, NO₂, NO, H, and O play an essential role in facilitating the bimolecular decomposition.

(2) The overall RDX decomposition rates of Al-RDX and Al₂O₃-RDX are higher than those of Void-RDX and pure RDX at lower temperatures; while a reversal is observed at higher temperatures.

(3) The highly active Al nanoparticles can significantly increase the heat of reaction relative to the pure RDX; whereas Al₂O₃ nanoparticles cannot. The presence of the Al nanoparticles can greatly reduce the induction time and the energy required to activate the exothermic reactions, and Al₂O₃ nanoparticles can also demonstrate such catalysis capability.

(4) The size of the largest cluster decreases with temperature increasing, whereas the number of Al contained clusters increases. Generally, the number of Al contained clusters in Al-RDX is one order of magnitude higher than that of Al₂O₃-RDX. Additionally, the highly active Al nanoparticles display a strong O-extraction capability coupled by a moderate capability to react with C/H/N atoms; whereas Al₂O₃ exhibits a much weaker such capability.

(5) The case of decomposition under the programmed heating condition is similar to that under the constant-temperature heating condition; as to the case of the adiabatic heating condition, the Al-RDX system always exhibits the fastest decomposition, energy release and temperature increase, followed by Al₂O₃-RDX, Void-RDX and pure RDX. In other words, the catalysis of the Al and Al₂O₃

nanoparticles becomes more remarkable under the programmed heating and adiabatic heating conditions.

■ ASSOCIATED CONTENT

Supporting Information

Moment at which RDX molecules undergo 50 % and 100 % decomposition and total number (N) of molecules of the four models approaching the final equilibrium state at 2500 and 3500 K, videos of RDX on the surfaces of Al and Al₂O₃, and high frequent reactions leading to the final generation of N₂. This material is 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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■ REFERENCES

- (1) DeLuca, L. T., Overview of Al-Based Nanoenergetic Ingredients for Solid Rocket Propulsion. *Defence Technol.* **2018**, *14*, 357-365.
- (2) Elbasuney, S.; Fahd, A.; Mostafa, H. E., Combustion Characteristics of Extruded Double Base Propellant Based on Ammonium Perchlorate/Aluminum Binary Mixture. *Fuel* **2017**, *208*, 296-304.
- (3) Huang, Y.; Risha, G. A.; Yang, V.; Yetter, R. A., Combustion of Bimodal Nano/Micron-Sized Aluminum Particle Dust in Air. *Proc. Combust. Inst.* **2007**, *31*, 2001-2009.
- (4) Lewis, W. K.; Rumchik, C. G.; Broughton, P. B.; Lindsay, C. M., Time-Resolved Spectroscopic Studies of Aluminized Explosives: Chemical Dynamics and Apparent Temperatures. *J. Appl. Phys.* **2012**, *111*, 014903.
- (5) Rezaei, A. H.; Keshavarz, M. H.; Tehrani, M. K.; Reza Darbani, S. M.; Farhadian, A. H.; Mousavi, S. J.; Mousaviazar, A., Approach for Determination of Detonation Performance and Aluminum Percentage of Aluminized-Based Explosives by Laser-Induced Breakdown Spectroscopy. *Appl. Opt.* **2016**, *55*, 3233-3240.
- (6) Türker, L., Thermobaric and Enhanced Blast Explosives (TBX and EBX). *Defence Technol.* **2016**, *12*, 423-445.

- (7) Peuker, J. M.; Krier, H.; Glumac, N., Particle Size and Gas Environment Effects on Blast and Overpressure Enhancement in Aluminized Explosives. *Proc. Combust. Inst.* **2013**, *34*, 2205-2212.
- (8) Culick, F. E. C., Stability of Longitudinal Oscillations with Pressure and Velocity Coupling in a Solid Propellant Rocket. *Combust. Sci. Technol.* **1970**, *2*, 179-201.
- (9) Blomshield, F.; Stalnaker, R.; Beckstead, M., Combustion Instability Additive Investigation. In *35th Joint Propulsion Conference and Exhibit*, American Institute of Aeronautics and Astronautics: 1999.
- (10) Sundaram, D.; Yang, V.; Yetter, R. A., Metal-Based Nanoenergetic Materials: Synthesis, Properties, and Applications. *Prog. Energ. Combust. Sci.* **2017**, *61*, 293-365.
- (11) Sergienko, A. V.; Popenko, E. M.; Slyusarsky, K. V.; Larionov, K. B.; Dzidziguri, E. L.; Kondratyeva, E. S.; Gromov, A. A., Burning Characteristics of the HMX/CL-20/AP/Polyvinyltetrazole Binder/Al Solid Propellants Loaded with Nanometals. *Propellants, Explos., Pyrotech.* **2018**, *43*, 1-8.
- (12) Yuan, J.; Liu, J.; Zhou, Y.; Wang, J.; Xv, T., Aluminum Agglomeration of AP/HTPB Composite Propellant. *Acta Astronaut.* **2018**, *156*, 14-21.
- (13) Yan, Q.-L.; Zhao, F.-Q.; Kuo, K. K.; Zhang, X.-H.; Zeman, S.; DeLuca, L. T., Catalytic Effects of Nano Additives on Decomposition and Combustion of RDX-, HMX-, and AP-Based Energetic Compositions. *Prog. Energ. Combust. Sci.* **2016**, *57*, 75-136.
- (14) Zhu, Y. L.; Huang, H.; Ren, H.; Jiao, Q. J., Influence of Aluminum Particle Size on Thermal Decomposition of RDX. *J. Energ. Mater.* **2013**, *31*, 178-191.
- (15) Irikura, K. K., Aminoxyl (Nitroxyl) Radicals in the Early Decomposition of the Nitramine RDX. *J. Phys. Chem. A* **2013**, *117*, 2233-2241.
- (16) Losada, M.; Chaudhuri, S., Transport in Aluminized RDX under Shock Compression Explored Using Molecular Dynamics Simulations. *J. Phys. Conf. Ser.* **2014**, *500*, 162002.
- (17) Liu, R.; Yang, L.; Zhou, Z.; Zhang, T., Thermal Stability and Sensitivity of RDX-Based Aluminized Explosives. *J. Therm. Anal. Calorim.* **2014**, *115*, 1939-1948.
- (18) Xiao, L.; Zhang, Y.; Wang, X.; Hao, G.; Liu, J.; Ke, X.; Chen, T.; Jiang, W., Preparation of a Superfine RDX/Al Composite as an Energetic Material by Mechanical Ball-Milling Method and the Study of Its Thermal Properties. *RSC Adv.* **2018**, *8*, 38047-38055.
- (19) Maiz, L.; Trzciński, W. A., Detonation Characteristics of New Aluminized Enhanced Blast Composites. *Propellants, Explos., Pyrotech.* **2018**, *43*, 650-656.
- (20) Gromov, A. A.; Nalivaiko, A. Y.; Tarasov, V. P.; Zmanovsky, S. V.; Arnautov, A. N.; Sergienko, A. V.; Larionov, K. B., Chapter 5 - Aluminum Powders for Energetics: Properties and Oxidation Behavior. In *Nanomaterials in Rocket Propulsion Systems*, Yan, Q.-L.; He, G.-Q.; Liu, P.-J.; Gozin, M., Eds. Elsevier: 2019; pp 151-173.
- (21) Kim, B.; Kim, M.; Yoh, J. J., Shock to Detonation Transition Analysis Using Experiments and Models. *Proc. Combust. Inst.* **2017**, *36*, 2699-2707.
- (22) Gottfried, J. L.; Bukowski, E. J., Laser-Shocked Energetic Materials with Metal Additives: Evaluation of Chemistry and Detonation Performance. *Appl. Opt.* **2017**, *56*, B47-B57.
- (23) Hou, C.; Geng, X.; An, C.; Wang, J.; Xu, W.; Li, X., Preparation of Al Nanoparticles and Their Influence on the Thermal Decomposition of RDX. *Cent. Eur. J. Energ. Mat.* **2013**, *10*, 123-133.
- (24) Schweigert, I. V., Ab Initio Molecular Dynamics of High-Temperature Unimolecular Dissociation of Gas-Phase RDX and Its Dissociation Products. *J. Phys. Chem. A* **2015**, *119*, 2747-2759.
- (25) Kuklja, M. M., Thermal Decomposition of Solid Cyclotrimethylene Trinitramine. *J. Phys. Chem. B* **2001**, *105*, 10159-10162.
- (26) Umezawa, N.; Kalia, R. K.; Nakano, A.; Vashista, P.; Shimojo, F., 1,3,5-Trinitro-1,3,5-Triazine Decomposition and Chemisorption on Al(111) Surface: First-Principles Molecular Dynamics Study. *J. Chem. Phys.* **2007**, *126*, 234702.
- (27) Guadarrama-Pérez, C.; Martínez de La Hoz, J. M.; Balbuena, P. B., Theoretical Infrared and Terahertz Spectra of an RDX/Aluminum Complex. *J. Phys. Chem. A* **2010**, *114*, 2284-2292.
- (28) Martínez de la Hoz, J. M.; Balbuena, P. B., Vibrational Spectra of an RDX Film over an Aluminum Substrate from Molecular Dynamics Simulations and Density Functional Theory. *J. Mol. Model.* **2013**, *19*, 2773-2778.
- (29) Ye, C.; Ju, X.; Zhao, F.; Xu, S., Adsorption and Decomposition Mechanism of 1,1-Diamino-2,2-Dinitroethylene on Al(111) Surface by Periodic Dft Calculations. *Chin. J. Chem.* **2012**, *30*, 2539-2548.
- (30) Ye, C.-C.; Zhao, F.-Q.; Xu, S.-Y.; Ju, X.-H., Adsorption and Decomposition Mechanism of Hexogen (RDX) on

- Al(111) Surface by Periodic DFT Calculations. *J. Mol. Model.* **2013**, *19*, 2451-2458.
- (31) Wu, Y.-Y.; Zhao, F.-Q.; Xu, S.-Y.; Ju, X.-H., A Density Functional Theory Study of Adsorption and Dissociation of Isopropyl Nitrate on an Al(111) Surface. *Can. J. Chem.* **2014**, *93*, 362-367.
- (32) Zhou, S.-Q.; Ju, X.-H.; Gu, X.; Zhao, F.-Q.; Yi, J.-H., Adsorption of 2,4,6-Trinitrotoluene on Al(111) Ultrathin Film: Periodic DFT Calculations. *Struct. Chem.* **2012**, *23*, 921-930.
- (33) Mei, Z.; An, Q.; Zhao, F.-Q.; Xu, S.-Y.; Ju, X.-H., Reactive molecular dynamics simulation of thermal decomposition for nano-aluminized explosives. *Phys. Chem. Chem. Phys.* **2018**, *20*, 29341-29350.
- (34) Plimpton, S., Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comput. Phys.* **1995**, *117*, 1-19.
- (35) van Duin, A. C. T.; Dasgupta, S.; Lorant, F.; Goddard, W. A., Reaxff: A Reactive Force Field for Hydrocarbons. *J. Phys. Chem. A* **2001**, *105*, 9396-9409.
- (36) Senftle, T. P., et al., The ReaxFF Reactive Force-Field: Development, Applications and Future Directions. *npj Comput. Mater.* **2016**, *2*, 15011.
- (37) Wang, N.; Peng, J.; Pang, A.; He, T.; Du, F.; Jaramillo-Botero, A., Thermodynamic Simulation of the RDX–Aluminum Interface Using ReaxFF Molecular Dynamics. *J. Phys. Chem. C* **2017**, *121*, 14597-14610.
- (38) Wood, M. A.; van Duin, A. C. T.; Strachan, A., Coupled Thermal and Electromagnetic Induced Decomposition in the Molecular Explosive α -HMX; a Reactive Molecular Dynamics Study. *J. Phys. Chem. A* **2014**, *118*, 885-895.
- (39) Hong, S.; van Duin, A. C. T., Molecular Dynamics Simulations of the Oxidation of Aluminum Nanoparticles Using the Reaxff Reactive Force Field. *J. Phys. Chem. C* **2015**, *119*, 17876-17886.
- (40) Jaramillo-Botero, A.; Naserifar, S.; Goddard, W. A., General Multiobjective Force Field Optimization Framework, with Application to Reactive Force Fields for Silicon Carbide. *J. Chem. Theory Comput.* **2014**, *10*, 1426-1439.
- (41) Wang, N.; Cheng, J.; Li, H.; Du, F.; Li, C.; Hu, J.; Peng, J., Dynamic Evolution of Aluminum Nanoparticle Impacted by RDX Slab. *Chem. Phys. Lett.* **2018**, *695*, 79-86.
- (42) Stukowski, A., Visualization and Analysis of Atomistic Simulation Data with OVITO—the Open Visualization Tool. *Modelling and Simulation in Materials Science and Engineering* **2009**, *18*, 015012.
- (43) Dreizin, E. L., Metal-Based Reactive Nanomaterials. *Prog. Energ. Combust. Sci.* **2009**, *35*, 141-167.
- (44) Levitas, V. I.; Asay, B. W.; Son, S. F.; Pantoya, M., Melt Dispersion Mechanism for Fast Reaction of Nanothermites. *Appl. Phys. Lett.* **2006**, *89*, 071909.
- (45) Levitas, V. I., Burn Time of Aluminum Nanoparticles: Strong Effect of the Heating Rate and Melt-Dispersion Mechanism. *Combust. Flame* **2009**, *156*, 543-546.
- (46) Wang, F.; Chen, L.; Geng, D.; Wu, J.; Lu, J.; Wang, C., Thermal Decomposition Mechanism of CL-20 at Different Temperatures by ReaxFF Reactive Molecular Dynamics Simulations. *J. Phys. Chem. A* **2018**, *122*, 3971-3979.
- (47) Rom, N.; Zybin, S. V.; van Duin, A. C. T.; Goddard, W. A.; Zeiri, Y.; Katz, G.; Kosloff, R., Density-Dependent Liquid Nitromethane Decomposition: Molecular Dynamics Simulations Based on Reaxff. *J. Phys. Chem. A* **2011**, *115*, 10181-10202.
- (48) Wen, Y.; Xue, X.; Long, X.; Zhang, C., Cluster Evolution at Early Stages of 1,3,5-Triamino-2,4,6-Trinitrobenzene under Various Heating Conditions: A Molecular Reactive Force Field Study. *J. Phys. Chem. A* **2016**, *120*, 3929-3937.
- (49) Zhang, C.; Wen, Y.; Xue, X.; Liu, J.; Ma, Y.; He, X.; Long, X., Sequential Molecular Dynamics Simulations: A Strategy for Complex Chemical Reactions and a Case Study on the Graphitization of Cooked 1,3,5-Triamino-2,4,6-Trinitrobenzene. *J. Phys. Chem. C* **2016**, *120*, 25237-25245.
- (50) Jiao, Q.-J.; Zhu, Y.-L.; Xing, J.-C.; Ren, H.; Huang, H., Thermal Decomposition of RDX/AP by TG–DSC–MS–FTIR. *J. Therm. Anal. Calorim.* **2014**, *116*, 1125-1131.
- (51) Zhang, C.; Peng, Q.; Wang, L.; Wang, X., Thermal Sensitivity of HMX Crystals and HMX-Based Explosives Treated under Various Conditions. *Propellants, Explos., Pyrotech.* **2010**, *35*, 561-566.
- (52) Sharia, O.; Kuklja, M. M., Rapid Materials Degradation Induced by Surfaces and Voids: Ab Initio Modeling of B-Octatetramethylene Tetranitramine. *J. Am. Chem. Soc.* **2012**, *134*, 11815-11820.
- (53) Sharia, O.; Tsyshevsky, R.; Kuklja, M. M., Surface-Accelerated Decomposition of δ -HMX. *J. Phys. Chem. Lett.* **2013**, *4*, 730-734.
- (54) Manner, V. W.; Pemberton, S. J.; Gunderson, J. A.; Herrera, T. J.; Lloyd, J. M.; Salazar, P. J.; Rae, P.; Tappan,

- B. C., The Role of Aluminum in the Detonation and Post-Detonation Expansion of Selected Cast HMX-Based Explosives. *Propellants, Explos., Pyrotech.* **2012**, *37*, 198-206.
- (55) Vadhe, P. P.; Pawar, R. B.; Sinha, R. K.; Asthana, S. N.; Subhananda Rao, A., Cast Aluminized Explosives (Review). *Combust., Explos. Shock Waves* **2008**, *44*, 461-477.
- (56) Xue, X.; Ma, Y.; Zeng, Q.; Zhang, C., Initial Decay Mechanism of the Heated CL-20/HMX Cocrystal: A Case of the Cocrystal Mediating the Thermal Stability of the Two Pure Components. *J. Phys. Chem. C* **2017**, *121*, 4899-4908.
- (57) Xue, X.; Wen, Y.; Long, X.; Li, J.; Zhang, C., Influence of Dislocations on the Shock Sensitivity of RDX: Molecular Dynamics Simulations by Reactive Force Field. *J. Phys. Chem. C* **2015**, *119*, 13735-13742.
- (58) Zhou, T.-T.; Huang, F.-L., Effects of Defects on Thermal Decomposition of HMX Via ReaxFF Molecular Dynamics Simulations. *J. Phys. Chem. B* **2011**, *115*, 278-287.
- (59) Huang, H.; Jiao, Q.; Li, J.; Zhu, X.; Zang, C., Effect of Aluminium Particle Size on the Thermal Decomposition of RDX. *Chin. J. Explos. Propellants* **2011**, *34*, 85-90.
- (60) Miao, M.; Dreger, Z. A.; Patterson, J. E.; Gupta, Y. M., Shock Wave Induced Decomposition of RDX: Quantum Chemistry Calculations. *J. Phys. Chem. A* **2008**, *112*, 7383-7390.
- (61) Chakraborty, D.; Muller, R. P.; Dasgupta, S.; Goddard, W. A., The Mechanism for Unimolecular Decomposition of RDX (1,3,5-Trinitro-1,3,5-Triazine), an Ab Initio Study. *J. Phys. Chem. A* **2000**, *104*, 2261-2272.
- (62) Wu, C. J.; Fried, L. E., Ab Initio Study of RDX Decomposition Mechanisms. *J. Phys. Chem. A* **1997**, *101*, 8675-8679.
- (63) Irikura, K. K.; Johnson, R. D., Is NO₃ Formed During the Decomposition of Nitramine Explosives? *J. Phys. Chem. A* **2006**, *110*, 13974-13978.
- (64) Zhang, L.; Zybin, S. V.; van Duin, A. C. T.; Dasgupta, S.; Goddard, W. A.; Kober, E. M., Carbon Cluster Formation During Thermal Decomposition of Octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetrazocine and 1,3,5-Triamino-2,4,6-Trinitrobenzene High Explosives from ReaxFF Reactive Molecular Dynamics Simulations. *J. Phys. Chem. A* **2009**, *113*, 10619-10640.
- (65) Strachan, A.; van Duin, A. C. T.; Chakraborty, D.; Dasgupta, S.; Goddard, W. A., Shock Waves in High-Energy Materials: The Initial Chemical Events in Nitramine RDX. *Phys. Rev. Lett.* **2003**, *91*, 098301.
- (66) Miao, X.; Xu, H.; Zhao, X.; Pei, Q.; Pang, W.; Wang, G., Safety of Nano-Al/RDX Mixtures. *Chin. J. Explos. Propellants* **2015**, *38*, 69-73.

TOC Graphic