

# Mechanism of the Improvement of the Energy of Host–Guest Explosives by Incorporation of Small Guest Molecules: HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> Promoted C–N Bond Cleavage of the Ring of ICM-102

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## Research Article

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# Abstract

Host–guest materials exhibit great potential applications as an insensitive high-energy-density explosive and low characteristic signal solid propellant. To investigate the mechanism of the improvement of the energy of host–guest explosives by guest molecules, ReaxFF-Ig reactive molecular dynamics simulations were performed to calculate the thermal decomposition reactions of the host–guest explosives systems ICM-102/HNO<sub>3</sub>, ICM-102/H<sub>2</sub>O<sub>2</sub>, and pure ICM-102 under different constant high temperatures and different heating rates. Incorporation of guest molecules significantly increased the energy level of the host–guest system. However, the initial reaction path of the ICM-102 molecule was not changed by the guest molecules. The guest molecules did not initially participate in the host molecule reaction. After a period of time, the H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub> guest molecules promoted cleavage of the C–N bond of the ICM-102 ring. Stronger oxidation and higher oxygen content resulted in the guest molecules more obviously accelerating destruction of the ICM-102 ring structure. The guest molecules accelerated the initial endothermic reaction of ICM-102, but they played a more important role in the intermediate exothermic reaction stage: incorporation of guest molecules (HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>) greatly improved the heat release and exothermic reaction rate. Although the energies of the host–guest systems were clearly improved by incorporation of guest molecules, the guest molecules had little effect on the thermal stabilities of the systems.

## 1. Introduction

Synthesis of new high-performance energetic materials is always a goal of researchers. In recent years, a series of new host–guest energetic materials have been obtained through the host–guest inclusion strategy, such as CL-20/H<sub>2</sub>O<sub>2</sub> and the HGI- 1/2/3 series<sup>2</sup>, which are composed of an insensitive high-energy-density explosive ICM-102<sup>3, 4</sup>. The usual way is to embed the guest oxidizing small molecules in the lattice voids of the high energy explosive. The relative position relationship between the voids and the host explosive molecules determines the ratio of host/guest molecules. Generally, a hydrogen bond will form between a H atom of the guest molecule and an O atom (or another atom) of the host explosive to maintain the stability of the host– guest structure.

There are significant differences in the energy densities, detonation performance, and other aspects of host–guest systems obtained by adding different guest molecules<sup>5</sup>. For instance, Xu et al.<sup>6</sup> compared the calculated detonation velocity/pressure values of HNIW/N<sub>2</sub>O and HNIW/CO<sub>2</sub>, and the results all showed that the detonation velocity/pressure of HNIW/N<sub>2</sub>O was superior to that of HNIW/CO<sub>2</sub>. For guest molecules, the difference in the elemental composition leads to a different influence on the reaction mechanism of the host explosive. However, at present, it is difficult to obtain the mechanisms of different guest molecules participating in and influencing the reactions of the host explosives through macroscale experimental characterization methods. In addition, the mechanisms of the improvement of the energies of the host– guest explosives by guest molecules are also of interest.

In recent years, molecular dynamics (MD) simulations based on the ReaxFF<sup>7</sup> reactive force field have provided a good choice to investigate the chemical reaction mechanisms of energetic materials under

extreme conditions. Since Strachan et al. used ReaxFF to calculate the chemical reactions of RDX explosives under shock<sup>8</sup> and high temperatures<sup>9</sup>, the ReaxFF MD method has been used to investigate explosive reactions. Furman et al.<sup>10</sup> used the ReaxFF-Ig<sup>11</sup> reactive force field and added the long-range interactions between molecules to clarify the difference in the activation energies between gas phase and condensed phase TNT explosives from the reaction mechanism for the first time. Guo et al.<sup>12</sup> used the ReaxFF-Ig force field to explain why addition of TNT molecules results in a decrease in the sensitivity of the co-crystal explosive CL-20/TNT from the perspective of the microchemical reaction. Research on single-compound explosives<sup>13, 14, 15</sup> and co-crystal explosives<sup>16, 17</sup> has been extensive; however, there are few studies related to the reaction mechanisms of host-guest explosives<sup>18</sup> under extreme conditions. In addition, it is still unclear how different guest molecules affect the reaction mechanism and thermal reaction kinetic parameters of the host molecules.

In this study, the MD method based on ReaxFF-Ig was used to calculate the thermal decomposition reactions of the host-guest explosive systems ICM-102/HNO<sub>3</sub> and ICM-102/H<sub>2</sub>O<sub>2</sub>, and pure ICM-102 under different constant temperatures (2500, 2750, 3000, 3250, and 3500 K) and programmed heating (heating rates of 50 and 100 K/ps). The mechanisms of the energy improvement of the host-guest explosives by the guest molecules are discussed in detail. The initial reaction paths between the host and guest molecules in the systems are clarified. The effect of the guest molecules on the kinetic parameters in the endothermic/exothermic reaction stage of thermal decomposition of the host-guest systems was investigated, and the effect of the guest molecules on formation of the main final small molecules products was analyzed.

## 2. Computational Methods

### 2.1 Computational Model

The initial ICM-102/H<sub>2</sub>O<sub>2</sub> and ICM-102/HNO<sub>3</sub> unit cell structures were obtained from the Cambridge Crystallographic Data Centre (CCDC, CCDC numbers 1831628 and 1887848). Both of the unit cells contain eight ICM-102 molecules, and the difference is the number of guest molecules: ICM-102/HNO<sub>3</sub> contains eight HNO<sub>3</sub> molecules and ICM-102/H<sub>2</sub>O<sub>2</sub> contains four H<sub>2</sub>O<sub>2</sub> molecules. We enlarged the unit cells along the *a*, *b*, and *c* axes to construct a 3 × 3 × 2 ICM-102/HNO<sub>3</sub> supercell containing 3600 atoms and a 2 × 2 × 4 ICM-102/H<sub>2</sub>O<sub>2</sub> supercell containing 2880 atoms (Figure 1). The pure ICM-102 supercell for calculation comparison was obtained by removing the HNO<sub>3</sub> molecules. Each of the three supercells was relaxed for sufficient time to guarantee that the molecules were in reasonable positions at relatively low energies before formal calculation.

Figure 1. Initial unit cell structures. The C, H, N, and O atoms of the host ICM-102 molecules are gray, white, blue, and red, respectively. The H, N, and O atoms of the guest molecules are green, cyan, and pink, respectively. The same representations will be used hereafter.

### 2.2 Simulation Method

All of the simulations were performed with the LAMMPS MD simulator based on the ReaxFF-Ig reactive force field. First, the equilibrium structures of the supercells at 0 K were obtained by energy minimization with the conjugate gradient algorithm. The initial velocities were assigned to the atoms according to the Maxwell–Boltzmann distribution at 298 K. The Berendsen thermostat was used to relax the supercells with the canonical ensemble (NVT) at 298 K for 10 ps. The equilibrium supercell structures were then obtained by an isobaric–isothermal (NPT) MD simulation at 0 Pa and 298 K for 10 ps. The structures of all of the molecules remained intact during the whole relaxation simulations. NVT MD simulations with the Berendsen thermostat were performed to heat the supercell systems to the target temperatures (2500, 2750, 3000, 3250, and 3500 K) until the potential energy (PE) stabilized or to heat the systems from 300 to 3000 K in 54 ps (heating rate  $\sim 50$  K/ps) or 27 ps (heating rate  $\sim 100$  K/ps). The time step was 0.1 fs, and periodic boundary conditions were applied. The atom trajectories, molecular species, and bonds between the atoms were recorded every 50 fs. We used a bond order  $\geq 0.3$  to judge formation of chemical bonds<sup>19, 20</sup>.

It has been reported that the ReaxFF-Ig force field can effectively describe the reactions of ICM-102<sup>21, 22</sup>. To verify the applicability of the ReaxFF-Ig force field for ICM-102/HNO<sub>3</sub> and ICM-102/H<sub>2</sub>O<sub>2</sub>, we compared the cell parameters after relaxation at 298 K and 0 Pa with the initial parameters from the CCDC. A comparison of the lattice parameters and densities of ICM-102/HNO<sub>3</sub> and ICM-102/H<sub>2</sub>O<sub>2</sub> is given in Table 1. The lattice parameters after relaxation by the ReaxFF-Ig were not considerably different from the initial parameters in the CCDC database, which shows that the ReaxFF-Ig force field can describe ICM-102/HNO<sub>3</sub> and ICM-102/H<sub>2</sub>O<sub>2</sub>.

Table 1. Comparison of the lattice parameters and densities of ICM-102/HNO<sub>3</sub> and ICM-102/H<sub>2</sub>O<sub>2</sub>.

crystal	method	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	$\rho/\text{g}\cdot\text{cm}^{-3}$
ICM-102/HNO <sub>3</sub>	from CCDC	33.717	35.607	27.022	1.954
	ReaxFF-Ig	34.051	35.960	27.290	1.902
ICM-102/H <sub>2</sub> O <sub>2</sub>	from CCDC	28.256	29.392	29.660	1.913
	ReaxFF-Ig	28.267	29.404	29.672	1.911

### 2.3 Calculation Methods of the Kinetic Parameters in Different Reaction Stages

The thermal decomposition reaction of explosives can be divided into three stages:

The initial decomposition stage, intermediate decomposition stage, and final product evolution stage<sup>23</sup>. Through fitting the calculation results, the reaction rates/product formation rate constants and activation energies in the different stages were obtained to characterize the kinetic parameters of the thermal decomposition reaction at high temperatures.

The initial decomposition stage is an endothermic process, and it can also be called the endothermic reaction stage. The ICM-102 molecules decompose and absorb heat in this stage, so we used the change

of the number of ICM-102 molecules to calculate the reaction rate in this stage. The change of the number of ICM-102 molecules with time was fitted by a first-order decay exponential function:

$$N(t) = N_0 \times \exp[-k_1(t - t_0)] \quad (1)$$

where  $N_0$  is the initial number of ICM-102 molecules,  $t_0$  is the time when ICM-102 starts to decompose, and  $k_1$  is the initial decomposition stage rate constant.

The intermediate exothermic stage of the thermal decomposition reaction then occurs. In this stage, the molecules in the system react violently and rapidly release a large amount of heat, so the heat release rate of the system is used to express the reaction rate in this stage. The PE curves were fitted by a first-order decay exponential function:

$$U(t) = U_\infty(T) + \Delta Q(T) \times \exp[-k_2(t - t_{\max})] \quad (2)$$

where  $U_\infty(T)$  is the asymptotic value of PE ( $\text{kcal} \cdot \text{mol}^{-1}$ ),  $\Delta Q(T)$  is the system heat released ( $\text{kcal} \cdot \text{mol}^{-1}$ ),  $k_2$  is the intermediate decomposition stage rate constant, and  $t_{\max}$  is the time of the maximum PE.

Finally, the changes of the numbers of main final products  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  at different temperatures were fitted by

$$C(t) = C_\infty \{1 - \exp[-k_3(t - t_i)]\} \quad (3)$$

where  $C_\infty$  is the asymptotic number of the product,  $k_3$  is the formation rate constant of the product, and  $t_i$  is the time of appearance of the product.

## 3. Results And Discussion

### 3.1 Improvement of the energy of host–guest systems by small guest molecules

The improvement of the energy level of the system is reflected in the heat release, detonation pressure/velocity, and other properties. In the three systems, the number of ICM-102 molecules was not exactly the same. To facilitate comparison between the different systems, we divided the value of the heat release by the total number of ICM-102 molecules in the system to obtain the average heat release of each ICM-102 molecule. A comparison of the average heat release of each ICM-102 molecule in the pure ICM-102, ICM-102/ $\text{H}_2\text{O}_2$ , and ICM-102/ $\text{HNO}_3$  systems at different temperatures is shown in Figure 2.

Incorporation of the different guest molecules increased the heat release of the system. Moreover, the  $\text{HNO}_3$  guest molecule with stronger oxidation ability and higher O atom content than  $\text{H}_2\text{O}_2$  more significantly increased the heat release of the host–guest system. A comparison of the heat release (at 3000 K) and detonation pressure/velocity<sup>2</sup> values of the different host–guest systems are shown in Figure 3. With increasing oxygen balance (OB) value of the system, both the heat release and detonation pressure values of the system greatly increased. Incorporation of  $\text{H}_2\text{O}_2$  did not improve the detonation velocity. Except for the  $\text{H}_2\text{O}_2$  guest molecule, the detonation velocity was positively correlated with the OB value.

### 3.2 Mechanisms of the energy improvement of the host–guest explosives by the guest molecules

By processing the calculation results from LAMMPS by Python scripts, the primary reactions of the pure ICM-102, ICM-102/H<sub>2</sub>O<sub>2</sub>, and ICM-102/HNO<sub>3</sub> systems were obtained, so as to determine the main initial reaction path in each system. Most of the reactions in the thermal decomposition process are reversible. We selected the primary reactions where the difference between the forward and reverse reaction frequencies was greater than or equal to 5. The primary reactions of the pure ICM-102, ICM-102/H<sub>2</sub>O<sub>2</sub>, ICM-102/HNO<sub>3</sub> systems, their lifetimes, and their occurrence frequencies in the first 10 ps at 3000 K are given in Table 2. To distinguish the same elements from the two components in the host–guest system, the elements in the guest molecules are placed in parentheses in Table 2. From the table, incorporation of the H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub> guest molecules did not change the initial reaction path of ICM-102, which is consistent with the observed atomic trajectory. During the thermal decomposition reactions of the three systems, the intramolecular hydrogen transfer reaction of ICM-102 occurred first. The dimerization reaction between two ICM-102 molecules also occurred early. A schematic diagram of the initial reaction pathway in the three systems is shown in Figure 4. In the host–guest systems, the H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub> guest molecules combined with the ICM-102 molecules. The H atoms of the amino groups of the ICM-102 molecules were attracted by the O atoms of the guest molecules, and the guest molecules then broke the bonds to form H<sub>2</sub>O molecules (this is the earliest formation path of water molecules). Subsequently, the main processes were reactions between small molecules.

Table 2. Primary reactions of the pure ICM-102, ICM-102/H<sub>2</sub>O<sub>2</sub>, and ICM-102/HNO<sub>3</sub> systems at 3000 K.

system	frequencies	reaction time/ps	primary reactions
pure ICM-102	6	0.00-0.95	$C_4H_6N_6O_4 + C_4H_6N_6O_4 \rightarrow C_8H_{12}N_{12}O_8$
	9	0.00-1.70	$C_4H_6N_6O_4 \rightarrow C_4H_5N_6O_3 + HO$
	6	1.10-8.95	$HO + HNO \rightarrow NO + H_2O$
	6	1.25-9.25	$H_3NO \rightarrow HO + H_2N$
	7	1.45-9.85	$H_4NO \rightarrow HO + H_3N$
	6	2.55-8.90	$CN_3 \rightarrow N_2 + CN$
	6	3.55-9.95	$H_4NO \rightarrow H_2O + H_2N$
ICM-102/H <sub>2</sub> O <sub>2</sub>	8	0.00-0.85	$C_4H_6N_6O_4 + C_4H_6N_6O_4 \rightarrow C_8H_{12}N_{12}O_8$
	5	0.00-1.00	$C_4H_6N_6O_4 + (H_2O_2) \rightarrow C_4H_6N_6O_4-(H_2O_2)$
	9	0.05-0.45	$C_4H_6N_6O_4 + (HO) \rightarrow C_4H_5N_6O_4 + H-(HO)$
	6	0.05-0.95	$C_4H_5N_6O_3 + (H_2O_2) \rightarrow C_4H_5N_6O_3-(H_2O_2)$
	10	0.05-1.15	$C_4H_6N_6O_4-(HO) \rightarrow C_4H_5N_6O_4 + H-(HO)$
	9	0.05-3.75	$C_4H_6N_6O_4 \rightarrow C_4H_5N_6O_3 + HO$
	6	1.95-9.65	$H-(O) + H_2O \rightarrow H_3O-(O)$
	11	2.15-9.95	$HNO_2 \rightarrow NO + HO$
	6	2.55-8.00	$HO + H_2-(O) \rightarrow H_2O + H-(O)$
	7	2.75-9.15	$CN_3 \rightarrow N_2 + CN$
ICM-102/HNO <sub>3</sub>	6	0.00-0.75	$C_4H_6N_6O_4 + C_4H_6N_6O_4 \rightarrow C_8H_{12}N_{12}O_8$
	5	0.00-0.45	$C_4H_6N_6O_4 + (HNO_3) \rightarrow C_4H_6N_6O_4-(HO) + (NO_2)$
	22	0.00-8.95	$(HNO_3) \rightarrow (NO_2) + (HO)$
	5	0.05-4.90	$H-(HNO_3) \rightarrow (NO_2) + H-(HO)$
	7	0.10-0.70	$C_4H_6N_6O_4 \rightarrow C_4H_5N_6O_3 + HO$
	7	0.30-9.90	$H-(NO_2) \rightarrow (NO) + H-(O)$
	5	0.45-7.15	$(NO_2) + HO \rightarrow HO-(NO_2)$
	5	1.45-9.45	$H_3O-(O) \rightarrow HO + H_2-(O)$
	7	1.70-9.90	$HN_2O \rightarrow N_2 + HO$
	7	2.40-9.00	$HNO_2 \rightarrow NO + HO$

To further analyze the reaction mechanism of ICM-102 decomposition, we calculated the cumulative sums of the net generated bonds at different times, and then divided the cumulative sums by the total number of ICM-102 molecules in the initial system (144 for the pure ICM-102 and ICM-102/HNO<sub>3</sub> systems, and 128 for the ICM-102/H<sub>2</sub>O<sub>2</sub> system). Normalization was performed to facilitate direct comparison of the different systems. Regarding the structure of ICM-102, the cleavage degree of the C–N bond was used to indicate the destruction degree of its ring structure. The changes of the cumulative sums of net broken C–N, H–N, and N–O bonds with time in the pure ICM-102, ICM-102/H<sub>2</sub>O<sub>2</sub>, and ICM-102/HNO<sub>3</sub> systems at

3000 K are shown in Figure 5. C–N cleavage was the fastest and occurred the most in the ICM-102/HNO<sub>3</sub> system, indicating that incorporation of the HNO<sub>3</sub> guest molecule significantly accelerated thermal decomposition of the ICM-102 molecule. In the ICM-102/H<sub>2</sub>O<sub>2</sub> system, the promoting effect of the guest H<sub>2</sub>O<sub>2</sub> molecule on C–N bond cleavage was not obvious before about 4 ps, and the speed of C–N bond cleavage in the system was even slower than that in the pure ICM-102. After 4 ps, the C–N bonds in the ICM-102/H<sub>2</sub>O<sub>2</sub> system were rapidly broken, and the number of cleaved C–N bonds was also greater than that in the pure ICM-102 system. For the H–N bonds, the cleavage speed was also fastest in the ICM-102/HNO<sub>3</sub> system. The promoting effect of the guest H<sub>2</sub>O<sub>2</sub> molecule on H–N bond cleavage was mainly reflected before 6 ps. For cleavage of the N–O bond, the difference among the three systems was not obvious.

ICM-102 molecules contain three different types of C–N bonds: C–NO<sub>2</sub>, C–NH<sub>2</sub>, and C–N in the ring. To determine the influence of the guest molecules on the different types of C–N bonds, these three types of C–N bonds were distinguished and counted separately (Figure 6). Before about 3 ps, the numbers of broken C–N bonds in the rings of the two host–guest systems were less than that in the pure ICM-102 system. After 3 ps, the numbers of broken C–N bonds in both the host–guest systems exceeded that in the pure ICM-102 system, indicating that the HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> guest molecules promoted C–N bond cleavage in the ring after about 3 ps. Generation of C–O bonds in the host–guest systems also exceeded that in the pure ICM-102 system after about 3 ps at 3000 K. This indicates that after 3 ps, the O atoms of the guest molecules mostly connected with C atoms of the ICM-102 ring, promoting C–N bond cleavage. However, the number of C–NO<sub>2</sub> bond was relatively small and similar for the different systems. The number of C–NH<sub>2</sub> bonds in the pure ICM-102 system was always greater than those in the host–guest systems.

### 3.3 Effect of the different guest molecules on the reaction kinetic parameters

The change of the number of ICM-102 molecules with time in the pure ICM-102 system at 3000 K is shown in Figure 7. The fitted curves are basically consistent with the curves of the molecular numbers, indicating that the decrease of the number of ICM-102 molecules conforms to a first-order decay exponential function. In the ICM-102/HNO<sub>3</sub> and ICM-102/H<sub>2</sub>O<sub>2</sub> host–guest systems, the changes of the number of ICM-102 molecules with time are shown in Figures S1 and S2. The logarithm of  $k_1$  plotted against the inverse temperature ( $1/T$ ) at 2500, 2750, 3000, 3250, and 3500 K for the three systems is shown in Figure 8. The initial thermal decomposition processes agree with the Arrhenius law. The fitted initial decomposition activation energy ( $E_{a1}$ ) values of the pure ICM-102, ICM-102/H<sub>2</sub>O<sub>2</sub>, and ICM-102/HNO<sub>3</sub> systems are 131.6, 136.7, and 137.8 kJ·mol<sup>-1</sup>, respectively. Incorporation of guest molecules increased the decomposition rate of ICM-102 in the initial endothermic stage, and the  $E_{a1}$  values of the different systems were not very different in the endothermic stage.

According to Equation (2), the PE curves were fitted to obtain the exothermic stage reaction rates ( $k_2$ ) at different temperatures. The evolution of the PE with time and the fitted curves for the pure ICM-102, ICM-102/H<sub>2</sub>O<sub>2</sub>, ICM-102/HNO<sub>3</sub> systems at 3000 K are shown in Figure 9. The fitted curves are basically consistent with the PE curves, indicating that the intermediate decomposition conforms to a first-order reaction rate equation. The logarithm of  $k_2$  plotted against the inverse temperature ( $1/T$ ) at 2500, 2750, 3000, 3250, and 3500 K for the three systems is shown in Figure 10. The intermediate decomposition

processes agree with the Arrhenius law. The fitted intermediate decomposition activation energy ( $E_a$ ) values of the pure ICM-102, ICM-102/H<sub>2</sub>O<sub>2</sub>, and ICM-102/HNO<sub>3</sub> systems are 113.6, 116.8, and 118.3 kJ•mol<sup>-1</sup>, respectively. Incorporation of the guest molecules greatly improved the reaction rate of the system in the exothermic stage, and HNO<sub>3</sub> had a more obvious promoting effect on the energy release of the system.

By analyzing the calculated products, we found that the main final molecular products were CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, and N<sub>2</sub>. A comparison of the numbers of CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, and N<sub>2</sub> molecules in the pure ICM-102, ICM-102/H<sub>2</sub>O<sub>2</sub>, and ICM-102/HNO<sub>3</sub> systems at 3000 K is shown in Figure 11. The order of the CO<sub>2</sub> and H<sub>2</sub>O molecule numbers in the three systems was ICM-102/HNO<sub>3</sub> > ICM-102/H<sub>2</sub>O<sub>2</sub> > pure ICM-102. The guest oxidizing small molecules had a significant promoting effect on formation of CO<sub>2</sub> and H<sub>2</sub>O. In addition, the promoting effect was greater for higher oxygen content of the guest molecule. However, the number of H<sub>2</sub> molecules in the pure ICM-102 system was slightly greater than those in the two host–guest systems. This is because incorporation of guest molecules increases the oxygen balance of the system, leading to a decrease in the amount of incomplete reaction products (such as hydrogen gas) in the system. The number of N<sub>2</sub> molecules in the ICM-102/HNO<sub>3</sub> system was significantly higher than those in the other two systems. This is because the HNO<sub>3</sub> guest molecule contains nitrogen, and more N<sub>2</sub> is generated during the reaction.

H<sub>2</sub> was generated in a small amount compared with CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub>. The H<sub>2</sub> formation rates of the three systems were similar, so fitting analysis of the H<sub>2</sub> formation rate was not performed. A comparison of the H<sub>2</sub>O formation rates in the pure ICM-102, ICM-102/H<sub>2</sub>O<sub>2</sub>, and ICM-102/HNO<sub>3</sub> systems at different temperatures is shown in Figure 12. At different temperatures, the order of the H<sub>2</sub>O formation rates in the three systems was ICM-102/H<sub>2</sub>O<sub>2</sub> > ICM-102/HNO<sub>3</sub> > pure ICM-102. Moreover, the H<sub>2</sub>O<sub>2</sub> guest molecule accelerated H<sub>2</sub>O formation much more than the HNO<sub>3</sub> guest molecule.

A comparison of the N<sub>2</sub> and CO<sub>2</sub> formation rates in the pure ICM-102, ICM-102/H<sub>2</sub>O<sub>2</sub>, and ICM-102/HNO<sub>3</sub> systems at different temperatures is shown in Figure 13. The promoting effect of the HNO<sub>3</sub> guest molecule on N<sub>2</sub> formation was obvious at all of the temperatures. However, H<sub>2</sub>O<sub>2</sub> had little effect on the formation rate of N<sub>2</sub> at low temperature. At relatively high temperatures (3000 K and above), the promoting effect of H<sub>2</sub>O<sub>2</sub> on N<sub>2</sub> formation was obvious. For CO<sub>2</sub> molecules, the two host–guest systems showed an obvious promoting effect on its formation at different temperatures, and the promoting effect was greater for higher temperature.

### **3.4 Effect of guest molecules on the thermal stabilities of the host–guest systems**

The pure ICM-102, ICM-102/H<sub>2</sub>O<sub>2</sub>, and ICM-102/HNO<sub>3</sub> systems were heated from 300 to 3000 K at different heating rates. The evolution of the PE with time in the pure ICM-102, ICM-102/H<sub>2</sub>O<sub>2</sub>, and ICM-102/HNO<sub>3</sub> systems at heating rates of 100 and 50 K/ps is shown in Figures 14 and Figure S3. The temperature of the system continuously increased under the programmed heating, and the PE value also constantly increased. The PE values of the three systems all increased to a maximum. The PE then started to decrease, which means that the system began to decompose and release heat. By comparing the results

under programmed heating at different heating rates, we found that the system started to decompose at lower temperature for lower heating rate. Incorporation of guest molecules did not significantly change the time when the system began to decompose because the decomposition times in the different systems were almost the same. Therefore, we believe that the different guest molecules had little effect on the thermal stability of the system.

## 4. Conclusions

ReaxFF-Ig MD simulations have been performed to investigate the mechanism of the improvement of the energy of host–guest explosives by guest molecules under different constant high temperatures and different heating rate. The effects of different guest molecules on the initial reaction mechanisms and reaction stages of the systems were analyzed in detail.

Incorporation of guest molecules significantly increased the energy levels of the host–guest systems. However, the initial reaction paths of the ICM-102 molecule in the different systems were similar. The guest molecules did not initially participate in the host molecule reaction. After a period of time, the H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub> guest molecules promoted cleavage of the C–N bond of the ICM-102 ring. Destruction of the ICM-102 ring structure was more obviously accelerated for the guest molecule with stronger oxidation ability and higher oxygen content. At different high temperatures, the intramolecular hydrogen transfer reaction and dimerization reaction between ICM-102 molecules occurred first, and then the guest molecules combined with ICM-102 molecules. Combined with analysis of kinetic parameters, the guest molecules accelerated the initial endothermic reaction of ICM-102, but they played a more important role in the intermediate exothermic reaction stage: incorporation of guest molecules (HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>) greatly improved the heat release in the system and the chemical reaction rate in the exothermic reaction stage. The promoting effect of more oxidizing HNO<sub>3</sub> was greater than that of H<sub>2</sub>O<sub>2</sub>. Although the number and formation rate of the main final products N<sub>2</sub>, H<sub>2</sub>O, and CO<sub>2</sub> improved, the guest molecules HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> had a more obvious promoting effect on formation of N<sub>2</sub> and H<sub>2</sub>O, respectively. Incorporation of guest molecules had little effect on the thermal stabilities of the systems.

The rule of the influence of different guest molecules on the thermal reaction could guide selection of guest molecules in synthesis of host–guest materials.

## Declarations

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### Author Contributions

Y.X. wrote the main manuscript text. L.C., J.L. and J.W. conceived the theory and designed the calculations. K.Y. and D.G. developed all the used reactive molecular dynamics methods. All authors reviewed the manuscript.

## Additional Information

Competing Interests: The authors declare no competing interests.

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