



# Article Effects of Different Guests on Pyrolysis Mechanism of α-CL-20/Guest at High Temperatures by Reactive Molecular Dynamics Simulations at High Temperatures

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Abstract: The host-guest inclusion strategy has the potential to surpass the limitations of energy density and suboptimal performances of single explosives. The guest molecules can not only enhance the detonation performance of host explosives but also can enhance their stability. Therefore, a deep analysis of the role of guest influence on the pyrolysis decomposition of the host-guest explosive is necessary. The whole decomposition reaction stage of CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH was calculated by ReaxFF-MD. The incorporation of CO<sub>2</sub>, N<sub>2</sub>O and NH<sub>2</sub>OH significantly increase the energy levels of CL-20. However, different guests have little influence on the initial decomposition paths of CL-20. The  $E_{a1}$  and  $E_{a2}$  values of CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH systems are higher than the CL-20/H<sub>2</sub>O system. Clearly, incorporation of CO<sub>2</sub>, N<sub>2</sub>O, NH<sub>2</sub>OH can inhibit the initial decomposition and intermediate decomposition stage of CL-20/H<sub>2</sub>O. Guest molecules become heavily involved in the reaction and influence on the reaction rates.  $k_1$  of CL-20/N<sub>2</sub>O and CL-20/NH<sub>2</sub>OH systems are significantly larger than that of CL-20/H<sub>2</sub>O at high temperatures.  $k_1$ of CL-20/CO<sub>2</sub> system is very complex, which can be affected deeply by temperatures.  $k_2$  of the CL- $20/CO_2$ , CL- $20/N_2O$  systems is significantly smaller than that of CL- $20/H_2O$  at high temperatures. k<sub>2</sub> of CL-20/NH<sub>2</sub>OH system shows little difference at high temperatures. For the CL-20/CO<sub>2</sub> system, the  $k_3$  value of CO<sub>2</sub> is slightly higher than that for CL-20/H<sub>2</sub>O, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH systems, while the  $k_3$  values of N<sub>2</sub> and H<sub>2</sub>O are slightly smaller than that for the CL-20/H<sub>2</sub>O, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH systems. For the CL-20/N<sub>2</sub>O system, the  $k_3$  value of CO<sub>2</sub> is slightly smaller than that for CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/NH<sub>2</sub>OH systems. For the CL-20/NH<sub>2</sub>OH system, the k<sub>3</sub> value of H<sub>2</sub>O is slightly larger than that for CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O systems. These mechanisms revealed that CO2, N2O and NH2OH molecules inhibit the early stages of the initial decomposition of CL-20 and play an important role for the decomposition subsequently.

Keywords: host-guest inclusion strategy; pyrolysis decomposition; ReaxFF-MD; reaction rate

# 1. Introduction

Successful balance between high energy and safety of energetic materials is challenging due to the time-consuming and difficult nature of synthesizing new energetic materials. Host–guest energetic materials, as shown in Figure 1, by embedding hydrogen- [1–3] or nitrogen-containing [4,5] oxidizing small molecules into the crystal lattice voids may achieve the highest possible energy density and the maximum possible chemical stability [6].

2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20), as one of the energetic materials with greatest detonation performances and highest density from synthesized compounds, has been widely studied recently [7]. CL-20 has five polymorphs (namely  $\beta$ ,  $\gamma$ ,  $\varepsilon$ ,  $\zeta$  and  $\delta$ ) and an  $\alpha$ -form hydrate [8], in which the  $\varepsilon$ -CL-20 has the highest density (2.044 g·cm<sup>-3</sup>) [8],  $\beta$ -CL-20 and  $\gamma$ -CL-20 are the dominant configurations of CL-20 molecules found in co-crystals [9]. Thus, many approaches have been used to tune its



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). performance, such as co-crystals [10–13], nanosized particles [14] and so on. The nanoscaling cocrystals demonstrate enhanced stability and high solubility of nano-particles [15]. However, the high production costs and easily phase transition limit the widespread use of CL-20 [16,17]. Fortunately, removal of H<sub>2</sub>O from hydrated  $\alpha$ -CL-20 can retain the stacking model [18]. Then, small molecules are filled in the cavity structure region that removes H<sub>2</sub>O molecules to form  $\alpha$ -CL-20 host–guest explosives [3–5], which also can be regarded as the solvates of CL-20 [19–21]. Bennion J.C. [3] synthesized two polymorphic hydrogen peroxide (HP) solvates of  $\alpha$ -CL-20. Two  $\alpha$ -CL-20/H<sub>2</sub>O<sub>2</sub> host–guest compounds are scarcely changing the lattice volume of the  $\alpha$ -CL-20/H<sub>2</sub>O and improving the energy. Thereafter, researches are focused on adopting a host–guest inclusion strategy to embed a suitable guest within the void by removing the water of  $\alpha$ -CL-20/H<sub>2</sub>O. A series of  $\alpha$ -CL-20-guest energetic materials such as CL-20/CO<sub>2</sub> [4], CL-20/N<sub>2</sub>O [4], CL-20/NH<sub>2</sub>OH [5] have been constructed in this manner.



Constitution coordination

**Figure 1.** (a) 3D energetic host-guest inclusion materials [1]. (b) Illustration of explosive-oxidant self-assembled strategy and its comparison with traditional energetic material [2].

The simulation of  $\alpha$ -CL-20/guest mainly focused on the mechanism of host–guest molecular interaction and the pyrolysis mechanism at high temperatures. The intermolecular interaction is the central scientific issue of energetic cocrystals. Guo [6] had reviewed some typical energetic inclusion compounds and their structures, intermolecular interactions, stabilities, and energy properties. It provides a method to predict appropriate size of guest incorporate into the cavities of the  $\alpha$ -CL-20 crystal. The systematic studies [22–24] on the comparison of interaction between the host–guest energetic complexes are devoted to summarizing the influence of guest on the performance of  $\alpha$ -CL-20. The results would prove fundamental to summarize the properties of guest for  $\alpha$ -CL-20/guest with structural stability. Meanwhile, in order to deeply analyze the role of hydrogen–guest small molecules in the host–guest system, the initial decomposition reactions of ICM-102/HNO<sub>3</sub> [25], ICM-102/H<sub>2</sub>O<sub>2</sub> [26] with pure ICM-102 and CL-20/H<sub>2</sub>O<sub>2</sub> [27] at several high temperatures were systematically studied by molecular dynamics simulations. It was found that the

addition of small guest molecules significantly increased the energy levels of ICM-102 and CL-20 but had little effect on the thermal stability of the host-guest system. The initial reaction path of ICM-102 molecule was not changed by HNO<sub>3</sub> and  $H_2O_2$ , but HNO<sub>3</sub> and  $H_2O_2$  promoted the decomposition of ICM-102 molecule in the subsequent decomposition process. With the increase of temperature, the influence of  $H_2O_2$  on the pyrolysis reaction of CL-20 weakens [28].

All the simulation researches provide information to understand the influence of guest for the host explosives. However, the role of different nitrogen-guest small molecules in the host–guest system has not been studied systematically at different high temperatures. At the same high temperature, when do the different guest molecules participate in the decomposition reaction of host–guest explosive and how do they affect the decomposition process mechanism of host–guest explosive? What is the influence of the same guest on the pyrolysis of the host–guest explosive at different high temperatures? Therefore, detailed studies of the mechanism of the  $\alpha$ -CL-20/nitrogen-guest detonation reaction at different high temperatures are necessary.

ReaxFF-MD [25,27,28] can conduct in-depth and detailed research on the pyrolysis mechanism of host–guest explosive at the microscopic scale and find how guest molecules participate in the pyrolysis reaction of the guest is an important factor affecting the energy release and detonation performance of the host explosives. In this study, we investigated the initial reaction of CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH and compared with the pure CL-20/H<sub>2</sub>O at various temperatures (2500, 2750, 3000, 3250, and 3500 K) by ReaxFF-lg reactive MD simulations (MD/ReaxFF-lg). The initial reaction paths, the change of generated/destroyed chemical bond numbers, the main product compositions, kinetic parameters in the different stages were analyzed. The mechanism for the improvement of the explosive energy and stability by incorporation of CO<sub>2</sub>, N<sub>2</sub>O and NH<sub>2</sub>OH is also discussed.

#### 2. Results and Discussion

# 2.1. Potential Energy (PE) and Total Energy for CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH Systems

The evolution of potential energy (PE) of CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH systems with time at (a) 2500 K, (b) 2750 K, (c) 3000 K, (d) 3500 K is shown in Figure 2. All the PE of CL-20/guest are much larger than that of  $CL-20/H_2O$ . It demonstrates that the addition of small guest molecules significantly increases the energy levels of CL-20 just shown in Figure 3. All the systems exhibit an initial rise in the PE curves at different temperatures which correspond to the endothermic reaction stage. When PE is maximized, the value thereafter decreases, signifying that the reaction becomes exothermic. The maximum value of PE increases in the order incorporation of  $H_2O < NH_2OH <$  $CO_2 < N_2O$  at different temperatures, and the heat release is also increased. That is, the incorporation of guests may have remarkable influence on heat release during the reaction. At a relatively low temperature of 2500 K, the PE curve is smooth. However, when the temperature increases to 2750 K, the PE curve is a little bit steeper. As the temperature increases to, much higher, 3000 K and 3500 K, the PE curve changes little. That is, no obvious heat release occurs during the reaction for much higher temperatures. With the increase of temperature, the PE is observed to be close to equilibrium for much shorter time. Therefore, the higher the temperature, the earlier the complete reaction.

The evolution of potential energy (PE) of (a) CL-20/H<sub>2</sub>O, (b) CL-20/CO<sub>2</sub>, (c) CL-20/N<sub>2</sub>O, (d) CL-20/NH<sub>2</sub>OH system with time at different temperatures is shown in Figure 4. The trend of PE curves for CL-20/H<sub>2</sub>O and CL-20/N<sub>2</sub>O is very similar. The trend of PE curves for CL-20/CO<sub>2</sub> and CL-20/NH<sub>2</sub>OH is very similar. That is, the incorporation of N<sub>2</sub>O may have the same influence on heat release with H<sub>2</sub>O. However, the incorporation of CO<sub>2</sub> may have the same influence on heat release with NH<sub>2</sub>OH.



**Figure 2.** Evolution of potential energy of  $CL-20/H_2O$ ,  $CL-20/CO_2$ ,  $CL-20/N_2O$ ,  $CL-20/NH_2OH$  system with time at (a) 2500 K, (b) 2750 K, (c) 3000 K, (d) 3500 K. Thick trendline corresponds to the actual concentration data of corresponding matching color.



**Figure 3.** Evolution of potential energy of (a)  $CL-20/H_2O$ , (b)  $CL-20/CO_2$ , (c)  $CL-20/N_2O$ , (d)  $CL-20/NH_2OH$  system with time at different temperatures. Thick trendline corresponds to the actual concentration data of corresponding matching color.



**Figure 4.** The total energy of  $CL-20/H_2O$ ,  $CL-20/CO_2$ ,  $CL-20/N_2O$ ,  $CL-20/NH_2OH$  systems with time at 2500 K. Thick trendline corresponds to the actual concentration data of corresponding matching color.

#### 2.2. Initial Decomposition Stage

#### 2.2.1. Initial Reaction Path of CL-20/Nitrogen-Guest

Table 1 shows the initial reaction paths of host–guest molecules and their occurrence frequency for CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH at four high temperatures. There are two main initial decomposition reactions of host CL-20 molecules  $C_6H_6O_{12}N_{12} \rightarrow C_6H_6O_{10}N_{11} + NO_2$  and  $C_6H_6O_{12}N_{12} \rightarrow C_6H_5O_{12}N_{12} + H$ . The frequency of  $C_6H_6O_{12}N_{12} \rightarrow C_6H_6O_{10}N_{11} + NO_2$  is much more than that of  $C_6H_6O_{12}N_{12} \rightarrow C_6H_5O_{12}N_{12} + H$ . As the increase with the temperatures, the frequency of both main initial decomposition reaction improves for CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH. A small part of H<sub>2</sub>O, N<sub>2</sub>O, NH<sub>2</sub>OH is broken to smaller pieces except for CO<sub>2</sub> with no decomposition. At the same high temperature, the frequency of both main initial decomposition reactions is not significantly different for CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/CO<sub>2</sub>, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/N<sub>2</sub>OH. It demonstrates that different guests have little influence on the initial decomposition paths.

Host-Guest Crystal	Temperatures	<b>Initial Reaction Paths</b>	Frequency
CL-20/H <sub>2</sub> O	2500	$\begin{array}{c} C_{6}H_{6}O_{12}N_{12} \rightarrow C_{6}H_{6}O_{10}N_{11} + NO_{2} \\ C_{6}H_{6}O_{12}N_{12} \rightarrow C_{6}H_{5}O_{12}N_{12} + H \\ H_{2}O \rightarrow H + OH \end{array}$	29 21 20
	3000	$\begin{array}{c} C_{6}H_{6}O_{12}N_{12} \rightarrow C_{6}H_{6}O_{10}N_{11} + NO_{2} \\ C_{6}H_{6}O_{12}N_{12} \rightarrow C_{6}H_{5}O_{12}N_{12} + H \\ H_{2}O \rightarrow H + OH \end{array}$	51 31 20
	3500	$\begin{array}{c} C_{6}H_{6}O_{12}N_{12} \rightarrow C_{6}H_{6}O_{10}N_{11} + NO_{2} \\ C_{6}H_{6}O_{12}N_{12} \rightarrow C_{6}H_{5}O_{12}N_{12} + H \\ H_{2}O \rightarrow H + OH \end{array}$	69 41 27
CL-20/CO <sub>2</sub>	2500	$\begin{array}{c} C_{6}H_{6}O_{12}N_{12} \rightarrow C_{6}H_{6}O_{10}N_{11} + NO_{2} \\ C_{6}H_{6}O_{12}N_{12} \rightarrow C_{6}H_{5}O_{12}N_{12} + H \end{array}$	41 25
	3000	$\begin{array}{c} C_6H_6O_{12}N_{12} \rightarrow C_6H_6O_{10}N_{11} + NO_2 \\ C_6H_6O_{12}N_{12} \rightarrow C_6H_5O_{12}N_{12} + H \end{array}$	60 38
	3500	$\begin{array}{c} C_6H_6O_{12}N_{12} \rightarrow C_6H_6O_{10}N_{11} + NO_2 \\ C_6H_6O_{12}N_{12} \rightarrow C_6H_5O_{12}N_{12} + H \end{array}$	65 34

**Table 1.** The initial reaction paths of host–guest molecules and their occurrence frequency for  $CL-20/H_2O$ ,  $CL-20/CO_2$ ,  $CL-20/N_2O$ ,  $CL-20/NH_2OH$  at four high temperatures.

Host-Guest Crystal	Temperatures	Initial Reaction Paths	Frequency
		$C_6H_6O_{12}N_{12} \rightarrow C_6H_6O_{10}N_{11} + NO_2$	30
-	2500	$C_6H_6O_{12}N_{12} \to C_6H_5O_{12}N_{12} + H$	25
		$N_2O \rightarrow N + NO$	5
		$N_2O \rightarrow N_2 + O$	18
	3000	$C_6H_6O_{12}N_{12} \to C_6H_6O_{10}N_{11} + NO_2$	63
CL-20/N <sub>2</sub> O		$C_6H_6O_{12}N_{12} \rightarrow C_6H_5O_{12}N_{12} + H$	31
		$N_2O \rightarrow N + NO$	5
_		$N_2O \rightarrow N_2 + O$	34
	3500	$C_6H_6O_{12}N_{12} \to C_6H_6O_{10}N_{11} + NO_2$	77
		$C_6H_6O_{12}N_{12} \to C_6H_5O_{12}N_{12} + H$	49
		$N_2O \rightarrow N + NO$	11
		$N_2O \rightarrow N_2 + O$	24
	2500	$C_6H_6O_{12}N_{12} \to C_6H_6O_{10}N_{11} + NO_2$	31
		$C_6H_6O_{12}N_{12}\to C_6H_5O_{12}N_{12}+H$	22
		$NH_2OH \rightarrow NH_2 + OH$	8
_		$NH2OH \rightarrow NH_2O + H$	11
	3000	$C_6H_6O_{12}N_{12} \to C_6H_6O_{10}N_{11} + NO_2$	41
		$C_6H_6O_{12}N_{12} \to C_6H_5O_{12}N_{12} + H$	31
$CL_{20}/NH_{20}H$		$NH_2OH \rightarrow NH_2 + OH$	27
CL-20/10112011		$NH_2OH \rightarrow NH_2O + H$	15
	3500	$C_6H_6O_{12}N_{12} \to C_6H_6O_{10}N_{11} + NO_2$	69
		$C_6H_6O_{12}N_{12} C_6H_5O_{12}N_{12} + H$	48
		$C_6H_6O_{10}N_{11} \to C_6H_6O_8N_{10} + NO_2$	6
		$C_6H_5O_{12}N_{12} \to C_6H_5O_{10}N_{11} + NO_2$	7
		$C_6H_6O_{12}N_{12} \rightarrow C_6H_4O_{12}N_{12} + 2H$	5
		$NH_2OH \rightarrow NH_2 + OH$	35
		$NH_2OH \rightarrow NH_2O + H$	20

Table 1. Cont.

# 2.2.2. Effect of Nitrogen-Guest on the k1

There are three stages for the evolution of the thermal decomposition of CL-20/nitrogenguest. Firstly, the initial decomposition stage is characterized by rate constant  $k_1$  and activation energy  $E_{a1}$ . Then, the intermediate decomposition stage is characterized by rate constant  $k_2$  and activation energy  $E_{a2}$ . Finally, the final product evolution stage is characterized by rate constant  $k_3$  and activation energy  $E_{a3}$ .

During the initial decomposition stage, the reaction rate was calculated by the change of the number of CL-20 molecules. The decay of the number of CL-20 molecules with time follows first-order decay exponential function [29]:  $N(t) = N_0 \times \exp[-k_1(t - t_0)]$ , where  $N_0$  is the initial number of CL-20 molecules,  $t_0$  is the time when CL-20 started to decompose, and  $k_1$  is the initial decomposition stage rate constant (Table 2).

Table 2. Reaction rate constant  $k_1$  in the initial endothermic reaction stage.

Host-Guest Crystal	T/K	$k_1/ps^{-1}$
	2500	1.417
	2750	1.918
CL-20/H <sub>2</sub> O	3000	2.388
	3250	2.932
	3500	3.476
	2500	1.179
	2750	1.745
CL-20/CO <sub>2</sub>	3000	2.131
	3250	3.075
	3500	3.984

ost–Guest Crystal	T/K	$k_1/ps^{-1}$
	2500	1.848
	2750	2.344
CL-20/N <sub>2</sub> O	3000	2.839
_	3250	4.357
	3500	5.653
	2500	1.434
	2750	2.163
CL-20/NH <sub>2</sub> OH	3000	2.851
-	3250	3.985
	3500	4.944

Table 2. Cont.

The logarithm of  $k_1$  plotted against the inverse temperature (1/*T*) at 2500, 2750, 3000, 3250, and 3500 K is shown in Figure 5. The  $E_{a1}$  values of the CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH systems are 64.90, 87.12, 81.93 and 90.12 kJ·mol<sup>-1</sup>, respectively. Clearly, incorporation of CO<sub>2</sub>, N<sub>2</sub>O, NH<sub>2</sub>OH impede the initial decomposition. This indicates that nitrogen-guest can inhibit the trigger decomposition of CL-20/H<sub>2</sub>O.



**Figure 5.** The logarithm of reaction rate  $(\ln(k_1/s^{-1}))$  against inverse temperature (1/T) in the exothermic decomposition stage at different temperatures. Thick trendline corresponds to the actual concentration data of corresponding matching color.

In addition,  $k_1$  of CL-20/N<sub>2</sub>O system is significantly larger than that of CL-20/H<sub>2</sub>O at high temperatures. This indicates that N<sub>2</sub>O significantly accelerates the reaction rate in the initial decomposition stage at high temperatures.  $k_1$  of CL-20/NH<sub>2</sub>OH system is significantly larger than that of CL-20/H<sub>2</sub>O at relatively higher temperatures (3500 K, 3250 K, 3000 K, 2750 K). As the temperature decreased to 2500 K, the difference between  $k_1$  of the CL-20/NH<sub>2</sub>OH and CL-20/N<sub>2</sub>O systems almost disappears. This indicates that NH<sub>2</sub>OH significantly accelerates the reaction rate in the initial decomposition stage at relatively higher temperature.  $k_1$  of CL-20/CO<sub>2</sub> system is much complex. At higher temperatures,  $k_1$  of CL-20/CO<sub>2</sub> is much larger than that of CL-20/H<sub>2</sub>O. However,  $k_1$  of CL-20/CO<sub>2</sub> is much smaller than that of CL-20/H<sub>2</sub>O at relatively lower temperatures. This indicates the temperature has significant influence on the initial decomposition rate for CL-20/CO<sub>2</sub>.

# 2.3. Intermediate Decomposition Stage

#### 2.3.1. Effect of Nitrogen-Guest on the Main Intermediate Products

Figure 6 shows the evolution curves of the main intermediate products and host-guest molecules at different temperatures. For CL-20/H<sub>2</sub>O at 2500 K, the number curve of host CL-20 fluctuates slightly, but the overall level remains horizontal before 0.5 ps. The  $NO_2$ fragments appears immediately at about 0ps. However, the number curve of guest H<sub>2</sub>O fluctuates slightly, but the overall level remains horizontal before 0.9 ps. This demonstrates that the initial decomposition of  $CL-20/H_2O$  may have broken the  $C-NO_2$  bonds of host CL-20 to form NO<sub>2</sub>. During 0.5 ps~1 ps, the number of host CL-20 decreases sharply and disappears at 1ps, while the number of NO<sub>2</sub> fragments increases rapidly. During 0.9 ps~1 ps, the number of guest  $H_2O$  decreases, while the number of guest  $H_2O$  reaches the minimum value. It demonstrates that guest H<sub>2</sub>O begins to participate the decomposition reaction deeply. The results of the trend are consistent with those of PE before 1ps for endothermic decomposition stage. During 0.5 ps~1 ps, the number of guest NO<sub>2</sub> increases sharply, while the number of guest  $NO_2$  reaches the maximum value. Due to the participation of  $H_2O$ , the pyrolysis products begin to diversify. The  $NO_3$  and NO fragments begin to appear. All the curves for  $NO_3$  and NO fragments are similarity at the high temperatures. However, the amount of  $NO_3$  and NO fragments would improve as the increase of temperatures. As the temperature increased, the variation curves of the main intermediate produces and host-guest molecules for CL-20/H2O remains the same approximately. However, the reaction rates  $(k_2)$  are significantly different. The influence of high temperature on  $k_2$  will be analyzed in the following section.



Figure 6. Cont.





**Figure 6.** Evolution curves of the main intermediate products and host–guest molecules at different temperatures (**a**–**l**). Thick trendline corresponds to the actual concentration data of corresponding matching color.

For CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH at high temperatures, the evolution tendency of the main intermediate products and host molecules is similar with that for CL-20/H<sub>2</sub>O at 2500 K. The variation curves of the guest are quite different.

Figures 7–9 show the evolution curves of the host and guest molecules for  $CL-20/H_2O$ , CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH at 2500 K, 3000 K, 3500 K. All the host CL-20 variation tendency are similarity. The influence of different guest on  $k_2$  is not significant at 2500 K. With higher temperature, the  $k_2$  significantly larger. The guest H<sub>2</sub>O and CO<sub>2</sub>, they are the main decomposition products. The variation tendency can divide into four stages: firstly, the tendency of guest is a level for little changeable. Secondly, it decreases for guest decomposition quickly. Then, it increases quickly as the main products. Finally, it reaches horizontal for the completely decomposition. There are two differences for the variation tendency: the first is that  $H_2O$  and  $CO_2$  start to decrease at different times. The longer time to stay at the first stage for  $CO_2$  shows that  $CO_2$  may be more stability than  $H_2O$ , and the second is that the minimum values of  $H_2O$  and  $CO_2$  are different. It a greater intensity in pyrolysis reaction for  $H_2O$  than that of  $CO_2$ . As the increase of temperatures, the shorter time to stay the first stage and the smaller minimum for  $CO_2$  and  $H_2O$ . It displays that the more intense in pyrolysis reaction at higher temperatures. For N<sub>2</sub>O, NH<sub>2</sub>OH just as the role for guest, the variation tendency slowly decreases and then sharply decreases until disappears. However, the reaction rates  $(k_2)$  for CO<sub>2</sub>, N<sub>2</sub>O, NH<sub>2</sub>OH are significantly different at different temperatures.



**Figure 7.** Evolution curves of the host and guest molecules for CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH at 2500 K. Thick trendline corresponds to the actual concentration data of corresponding matching color.



**Figure 8.** Evolution curves of the host and guest molecules for CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH at 3000 K. Thick trendline corresponds to the actual concentration data of corresponding matching color.



**Figure 9.** Evolution curves of the host and guest molecules for CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH at 3500 K. Thick trendline corresponds to the actual concentration data of corresponding matching color.

#### 2.3.2. Effect of Nitrogen-Guest on the k<sub>2</sub>

After the PE reached the maximum value, the intermediate exothermic decomposition indicates the chemical reaction stage. The intermediate decomposition stage rate constant  $k_2$  can be obtained by fitting the PE curves with a first order decay exponential function [30]:  $U(t) = U_{\infty} + \Delta U_{exo} \exp[-k_2(t - t_{max})]$ , where U(t) is the potential energy value at time t,  $U_{\infty}$  is the asymptotic value of PE,  $\Delta U_{exo}$  is the reaction heat, and its size is the difference between the maximum potential energy  $U_{max}$  and  $U_{\infty}$ .

The chemical reaction rate constants obtained by fitting equation at different temperatures are shown in Table 3. The value of  $\Delta U_{exo}$  has little change with a gradually increase of  $U_{\infty}$  and  $k_2$  as temperature increases. This indicates that temperature has a limited effect on the exothermic reaction [31].

Host–Guest Crystal	T/K	$U_{\rm max}$	$u_{\infty}$	$\Delta U_{exo}$	$k_2/\mathrm{ps}^{-1}$
	2500	-1,424,794	-1,650,929	226,135	0.1523
	2750	-1,413,953	-1,636,452	222,499	0.2251
CL-20/H <sub>2</sub> O	3000	-1,403,193	-1,621,948	218,755	0.2963
	3250	-1,397,567	-1,606,748	209,181	0.38057
	3500	-1,384,266	-1,591,748	207,482	0.46484
	2500	-1,398,845	-1,630,254	231,409	0.11404
	2750	-1,389,461	-1,617,052	227,591	0.17252
CL-20/CO <sub>2</sub>	3000	-1,379,278	-1,603,764	224,486	0.23059
	3250	-1,3694,15	-1,589,817	220,402	0.30645
	3500	-1,359,754	-1,575,870	216,116	0.38217
	2500	-1,381,272	-1,616,532	235,260	0.12789
	2750	-1,372,536	-1,602,557	230,021	0.19377
CL-20/N2O	3000	-1,363,624	-1,588,473	224,849	0.25909
	3250	-1,354,660	-1,572,699	218,039	0.35959
	3500	-1,345,497	-1,556,825	211,328	0.46010
CL-20/NH <sub>2</sub> OH	2500	-1,403,762	-1,639,940	236,178	0.14567
	2750	-1,395,173	-1,625,769	230,596	0.21743
	3000	-1,385,384	-1,611,798	226,414	0.28695
	3250	-1,377,669	-1,595,917	218,248	0.378106
	3500	-1,369,830	-1,580,037	210,207	0.47146

Table 3. Partial parameters of PE curve attenuation process.

The logarithm of  $k_2$  plotted against the inverse temperature (1/*T*) at 2500, 2750, 3000, 3250, and 3500 K is shown in Figure 10. The  $E_{a2}$  values of the CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH systems are 80.76, 87.58, 92.73 and 84.88 kJ·mol<sup>-1</sup>, respectively. Clearly, incorporation of CO<sub>2</sub>, N<sub>2</sub>O, NH<sub>2</sub>OH can inhibit the intermediate decomposition of CL-20/H<sub>2</sub>O.



**Figure 10.** The logarithm of reaction rate  $(\ln(k_1/s^{-1}))$  against inverse temperature (1/T) in the exothermic decomposition stage at different temperatures. Thick trendline corresponds to the actual concentration data of corresponding matching color.

The pre-exponential factor derived from the pyrolysis simulations of the CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH systems are 29.65, 29.68, 30.03, 29.80. Assuming unimolecular decomposition, transition state theory leads to A = (k<sub>B</sub>T/h)exp( $\Delta$ S/R) where  $\Delta$ S<sub>(CL-20/H2O)</sub> = -17.47 J·mol<sup>-1</sup>·K<sup>-1</sup>,  $\Delta$ S<sub>(CL-20/CO2)</sub> = -17.23 J·mol<sup>-1</sup>·K<sup>-1</sup>,  $\Delta$ S<sub>(CL-20/N2O)</sub> = -14.32 J·mol<sup>-1</sup>·K<sup>-1</sup>,  $\Delta$ S<sub>(CL-20/NH2OH)</sub> = -16.23 J·mol<sup>-1</sup>·K<sup>-1</sup>. This negative activation of entropy is consistent with the TST for multimolecular reactions, suggesting that the reaction involves a multimolecular transition state [32]. The decrease of entropy at the transition state because of the embedding of nitrogen-containing guests.

In addition,  $k_2$  of CL-20/CO<sub>2</sub> system is significantly smaller than that of CL-20/H<sub>2</sub>O at high temperatures. This indicates that  $CO_2$  significantly inhibits the reaction in the intermediate decomposition stage at high temperatures. k<sub>2</sub> of CL-20/N<sub>2</sub>O system is significantly smaller than that of  $CL-20/H_2O$  at relatively lower temperatures (2500 K and 2750 K). As the temperature increased to 3500 K, the difference between  $k_2$  of the CL-20/H<sub>2</sub>O and CL-20/N<sub>2</sub>O systems almost disappears. This indicates that N<sub>2</sub>O significantly restrains the reaction in the intermediate decomposition stage at relatively low temperature. With increasing temperature,  $N_2O$  has increasingly less effect on the reaction rate. However,  $k_1$  of CL-20/N<sub>2</sub>O indicates that N<sub>2</sub>O significantly accelerates the reaction in the initial decomposition stage at high temperatures. The conclusion is contrary to that for ICM-102/HNO<sub>3</sub> [27]. This maybe caused by the hydrogen content for nitrogen-guest.  $k_2$  of CL-20/H<sub>2</sub>O and CL-20/NH<sub>2</sub>OH systems are little difference at high temperatures, NH<sub>2</sub>OH has little effect on the reaction rate at high temperatures. The opposite effect of  $CL-20/H_2O_2$  [33] maybe due to the difference of hydrogen content in the guest. The influence of  $CO_2$  and  $N_2O$  on the decomposition reaction of host explosive may be the little interaction between  $CO_2$ ,  $N_2O$  and CL-20 [27]. However, the influence of  $H_2O_2$  on the decomposition reaction of host explosive may be the significant interaction between  $H_2O_2$ and CL-20 [27].

# 2.4. Final Product Evolution Stage

2.4.1. Effect of Nitrogen-Guest on the Final Products

To clarify the effect of  $CO_2$ ,  $N_2O$  and  $NH_2OH$  molecules on the main products, the population of  $CO_2$ ,  $N_2$ ,  $H_2O$  after the complete decomposition reaction for  $CL-20/H_2O$ ,  $CL-20/CO_2$ ,  $CL-20/N_2O$ ,  $CL-20/NH_2OH$  at 2500 K, 3000 K and 3500 K are shown at Figures 11–13.



**Figure 11.** The population of CO<sub>2</sub> after the complete decomposition reaction for CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH at 2500 K, 3000 K and 3500 K.



**Figure 12.** The population of N<sub>2</sub> after the complete decomposition reaction for CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH at 2500 K, 3000 K and 3500 K.



**Figure 13.** The population of  $H_2O$  after the complete decomposition reaction for CL-20/ $H_2O$ , CL-20/ $CO_2$ , CL-20/ $N_2O$ , CL-20/ $N_2O$  at 2500 K, 3000 K and 3500 K.

The population of CO<sub>2</sub> for CL-20/NH<sub>2</sub>OH and CL-20/H<sub>2</sub>O are nearly equivalent at high temperatures. The population of CO<sub>2</sub> for CL-20/N<sub>2</sub>O is the lowest, while the population of CO<sub>2</sub> for CL-20/H<sub>2</sub>O is largest at 2500 K. As the temperature increase, the more population of CO<sub>2</sub> for CL-20/N<sub>2</sub>O grows acutely. However, the population of CO<sub>2</sub> for CL-20/NH<sub>2</sub>OH decrease acutely. It demonstrates that the CO<sub>2</sub>-produced mechanism for a N<sub>2</sub>O guest is different with CO<sub>2</sub> and NH<sub>2</sub>OH guests. The populations of N<sub>2</sub> for CL-20/NH<sub>2</sub>OH and CL-20/H<sub>2</sub>O are nearly equivalent at high temperatures. As the temperature increases, the more the population of CO<sub>2</sub> for CL-20/CO<sub>2</sub>, CL-20/NH<sub>2</sub>OH and CL-20/H<sub>2</sub>O are nearly equivalent at high temperatures. As the temperature increases, the more the populations of CO<sub>2</sub> for CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O guests. The populations of H<sub>2</sub>O for CL-20/CO<sub>2</sub> and N<sub>2</sub>O guests. The populations of H<sub>2</sub>O for CL-20/NH<sub>2</sub>OH and CL-20/H<sub>2</sub>O are nearly equivalent at high temperatures. The varying tendency of population for the three main products shows that the influence of guest NH<sub>2</sub>OH and H<sub>2</sub>O, CO<sub>2</sub> and N<sub>2</sub>O are much same to each other. This may be caused by the hydrogen for two guest groups.

### 2.4.2. Effect of Nitrogen-Guest on the k<sub>3</sub>

The final products of thermal decomposition of CL-20/guest are N<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O. The formation rates  $k_3$  can be obtained by fitting the variation trend of the final products with the exponential function [34]:  $C(t) = C_{\infty} \{1 - \exp[-k_3(t - t_i)]\}$ , 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.

Comparison of the  $k_3$  values of CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> for the (a) CL-20/H<sub>2</sub>O, (b) CL-20/CO<sub>2</sub>, (c) CL-20/N<sub>2</sub>O, (d) CL-20/NH<sub>2</sub>OH at different temperatures is shown in Figure 14. All the  $k_3$  values of CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> are increased as the temperature improvement. This may be due to the facilitation on production the three main products. The  $k_3$  value of H<sub>2</sub>O is larger than that of N<sub>2</sub>, while the  $k_3$  value of N<sub>2</sub> is larger than that of CO<sub>2</sub> for CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH. This demonstrates that the production of H<sub>2</sub>O is the easiest and the production of CO<sub>2</sub> is the most difficult.



**Figure 14.** Comparison of the  $k_3$  values of CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> for (a) CL-20/H<sub>2</sub>O, (b) CL-20/CO<sub>2</sub>, (c) CL-20/N<sub>2</sub>O, (d) CL-20/NH<sub>2</sub>OH at different temperatures. Thick trendline corresponds to the actual concentration data of corresponding matching color.

Comparison of the  $k_3$  values of CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> for the CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH at different temperatures is shown in Figure 15. For the CL-20/CO<sub>2</sub> system, the  $k_3$  value of CO<sub>2</sub> is slightly higher than that for CL-20/H<sub>2</sub>O, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH systems, while the  $k_3$  values of N<sub>2</sub> and H<sub>2</sub>O are slight smaller than that for CL-20/H<sub>2</sub>O, CL-20/N<sub>2</sub>O, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH systems. This indicates that CO<sub>2</sub> restrains the formation of H<sub>2</sub>O and N<sub>2</sub> molecules. For the CL-20/N<sub>2</sub>O system, the  $k_3$  value of CO<sub>2</sub> is slightly smaller than that for CL-20/H<sub>2</sub>O, CL-20/H<sub>2</sub>O, CL-20/H<sub>2</sub>O, CL-20/N<sub>2</sub>O systems. This indicates that N<sub>2</sub>O restrains the formation of CO<sub>2</sub>. For the CL-20/NH<sub>2</sub>OH systems, the  $k_3$  value of H<sub>2</sub>O is slightly larger than that for CL-20/H<sub>2</sub>O, CL-20/NH<sub>2</sub>OH system, the  $k_3$  value of H<sub>2</sub>O is slightly larger than that for CL-20/H<sub>2</sub>O, CL-20/N<sub>2</sub>O systems. This indicates that NH<sub>2</sub>OH accelerates the formation of H<sub>2</sub>O.



**Figure 15.** Comparison of the  $k_3$  values of CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> for CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH at different temperatures. Thick trendline corresponds to the actual concentration data of corresponding matching color.

#### 3. Discussion

We have performed MD/ReaxFF-lg simulations to investigate the thermal decomposition reaction of the CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH systems at different temperatures. In this work, guest is not only enhanced the safety but also improved its detonation performance.

During the thermal decomposition reaction of CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH systems at different temperatures, the initial reaction path is not significantly influenced by the incorporation of CO<sub>2</sub>, N<sub>2</sub>O, NH<sub>2</sub>OH: C<sub>6</sub>H<sub>6</sub>O<sub>12</sub>N<sub>12</sub>  $\rightarrow$  C<sub>6</sub>H<sub>6</sub>O<sub>10</sub>N<sub>11</sub> + NO<sub>2</sub> and  $C_6H_6O_{12}N_{12} \rightarrow C_6H_5O_{12}N_{12}$  + H. At the same high temperature, the frequencies of both two main initial decomposition reaction are not significantly different for CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH. As for the increase with the temperatures, the frequency of both main initial decomposition reactions improve for CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O, CL-20/NH<sub>2</sub>OH. The nitrogen guest can inhibit the trigger decomposition for the larger  $E_{a1}$  and  $E_{a2}$  values. Embedding N<sub>2</sub>O and NH<sub>2</sub>OH can significantly accelerate the reaction in the initial decomposition rates at high temperatures for the larger  $k_1$  at high temperatures. However, incorporation of CO<sub>2</sub>, higher temperature has a significant influence on the initial decomposition for the complex  $k_1$ . Embedding CO<sub>2</sub> and N<sub>2</sub>O significantly inhibits the reaction in the intermediate decomposition stage at high temperatures for the smaller  $k_2$  at high temperatures. Incorporation of NH<sub>2</sub>OH has little effect on the reaction rate at high temperatures, with a small difference of  $k_2$ . All the  $k_3$ values of  $CO_2$ ,  $H_2O$  and  $N_2$  are increased as the temperature improves. Guest  $CO_2$  restrains the formation of  $H_2O$  and  $N_2$  molecules for the higher  $k_3$  value. Guest  $N_2O$  restrains the formation of CO<sub>2</sub> for the higher  $k_3$  value. Guest NH<sub>2</sub>OH accelerates the formation of H<sub>2</sub>O

molecules for the higher  $k_3$  value. The influence of guest NH<sub>2</sub>OH and H<sub>2</sub>O, N<sub>2</sub>O and CO<sub>2</sub> on decomposition products may be similar for the same amount products.

The results of this study revealed that the guest CO<sub>2</sub>, N<sub>2</sub>O and NH<sub>2</sub>OH played a certain inhibitory role during the early stages of the host CL-20 thermal decomposition reaction. The study provided a theoretical basis for the synthesis of new energetic materials with host-guest inclusion strategy.

#### 4. Computational Methods

The initial unit cell structures of CL-20/H<sub>2</sub>O, CL-20/CO<sub>2</sub>, CL-20/N<sub>2</sub>O and CL-20/NH<sub>2</sub>OH were obtained from the Cambridge Crystallographic Data Centre. In the unit cell, there are eight CL-20 molecules and four guest molecules (H<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub>O and NH<sub>2</sub>OH) (Figure 16). We enlarged the unit cell 48 times along both the *a*, the *b* and *c* axes to construct a  $6 \times 4 \times 2$  supercell containing 48 unit cells ((a) contain 384 of CL-20 and 384 of guest. The supercell of (b), (c), (d) contains 384 of CL-20 and 192 of guest).



**Figure 16.** (a)  $\alpha$ -CL-20/H<sub>2</sub>O,  $6 \times 4 \times 2 \alpha$ -CL-20/H<sub>2</sub>O supercell, (b)  $\alpha$ -CL-20/CO<sub>2</sub>,  $6 \times 4 \times 2 \alpha$ -CL-20/CO<sub>2</sub> supercell, (c)  $\alpha$ -CL-20/N<sub>2</sub>O,  $6 \times 4 \times 2 \alpha$ -CL-20/N<sub>2</sub>O supercell, (d)  $\alpha$ -CL-20/NH<sub>2</sub>OH,  $6 \times 4 \times 2 \alpha$ -CL-20/NH<sub>2</sub>OH supercell. The blue atoms represent nitrogen, the red atoms represent oxygen, the white atoms represent hydrogen, the gray atoms represent carbon. The supercell of (a) contains 384 of CL-20 and 384 of guest. The supercell of (b–d) contains 384 of CL-20 and 192 of guest.

First, the canonical ensemble (NVT) and the Berendsen thermostat were applied to the molecular dynamics (MD) simulation with a total time of 10 ps at 1 K, which further relaxed the  $\alpha$ -CL-20/guest supercell. Then, ReaxFF-lg isobaric-isothermal MD (NPT-MD) simulations were performed for 5 ps at 300 K controlled by the Berendsen thermostat based on the relax supercell. Finally, the target temperatures (2500, 2750, 3000, 3250, and 3500 K) are all direct heat from 300 K with NVT-MD simulations. The five different high temperatures are selected to accurately calculate the reaction rate constant and energy barrier. The damping constant is set to 0.25 fs. Komeiji demonstrated that 0.25 fs is enough for calculation accuracy of bonds and angles in molecular dynamics simulations. NVT-MD simulations of the supercell system with the Berendsen thermostat were performed until the potential energy (PE) stabilized. An analysis of the fragments was performed with a 0.3 bond order cutoff value for each atom pair to identify the chemical species [35,36]. The information of the dynamic trajectory was recorded every 20 fs, which was used to analyze the evolution details of  $\alpha$ -CL-20/guest in the pyrolysis process.

To verify the suitability of the ReaxFF-lg force field for the CL-20/guest system, we compared the lattice parameters and density of relaxed CL-20/guest at 298 K and 0 Pa with the initial structure from the CCDC (Table 4). The cell parameters and density of relaxed CL-20/guest calculated by MD/ReaxFF-lg agreed well with the initial structure values for the error value < 5%. This preliminarily indicated that ReaxFF-lg can describe the decomposition of CL-20/guest system.

Crystal	Method	a/Å	b/Å	c/Å	$ ho/{ m g}\cdot{ m cm}^{-3}$
CL-20/H <sub>2</sub> O	from CCDC	9.477	13.139	23.380	2.081
	ReaxFF-lg	9.370	12.993	23.119	2.153
CL-20/CO <sub>2</sub>	from CCDC	9.673	13.203	23.553	2.033
	ReaxFF-lg	9.467	13.167	23.489	2.049
CL-20/N <sub>2</sub> O	from CCDC	9.577	13.256	23.625	2.038
	ReaxFF-lg	9.427	13.049	23.256	2.137
CL-20/NH <sub>2</sub> OH	from CCDC	9.789	13.123	23.509	2.000
	ReaxFF-lg	9.602	12.873	23.059	2.119

Table 4. Comparison of lattice parameters and density of CL-20/guest.

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