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Hydrogen Promoted Decomposition of Ammonium Dinitramide: an *ab initio* Molecular Dynamics Study

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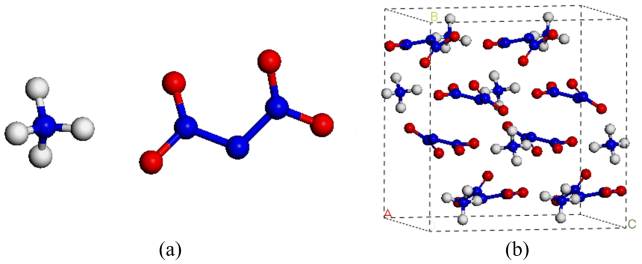
Thermal decomposition of a famous high oxidizer ammonium dinitramide (ADN) under high temperatures (2000 and 3000 K) was studied by using the *ab initio* molecular dynamics method. Two different temperature-dependent initial decomposition mechanisms were observed in the unimolecular decomposition of ADN, which were the intramolecular hydrogen transfer and N−NO_2 cleavage in $N(NO_2)^-$. They were competitive at 2000 K, whereas the former one was predominant at 3000 K. As for the multimolecular decomposition of ADN, four different initial decomposition reactions that were also temperature-dependent were observed. Apart from the aforementioned mechanisms, another two new reactions were the intermolecular hydrogen transfer and direct N−H cleavage in NH_4^+. At the temperature of 2000 K, the N−NO_2 cleavage competed with the rest three hydrogen-related decomposition reactions, while the direct N−H cleavage in NH_4^+ was predominant at 3000 K. After the initial decomposition, it was found that the temperature increase could facilitate the decomposition of ADN, and would not change the key decomposition events. ADN decomposed into small molecules by hydrogen-promoted simple, fast and direct chemical bonds cleavage without forming any large intermediates that may impede the decomposition. The main decomposition products at 2000 and 3000 K were the same, which were NH_3, NO_2, NO, N_2O, N_2, H_2O, and HNO_2.

Key words: Ammonium dinitramide, High temeprature, *ab initio* molecular dynamics, Hydrogen transfer

I. INTRODUCTION

High oxidizer is an important component of solid propellants, and the overall performance of propellants benefits from the outstanding oxidizer with high density, high energy, low toxicity and pollution, and good compatibility. During the past several decades, great efforts have been devoted to designing, synthesizing, and developing novel advanced high oxidizers [1–5]. Among all the high oxidizers, ammonium dinitramide (FIG. 1, ADN, $NH_4{}^+N(NO_2)_2{}^-$) [6, 7] was considered as an outstanding representative with great value for future research and application. ADN, a novel energetic salt shows better energy property than the traditional oxidizer ammonium perchlorate. In order to promote the application of ADN, it is necessary to understand its structure and decomposition behavior under different conditions. In particular, thermal decomposition of solid ADN, including its initiation and combustion mechanisms, is essential for the improvement of the safety profile during its application and disposal, and could also provide valuable guidance regarding the development of energetic salts. Therefore, it is important to clearly understand the thermal decomposition of ADN at different external conditions, and a certain amount of relevant work [8–18] has been



(a) (b)

FIG. 1 A molecule (a) and a 1×1×2 supercell (b) of ADN. Carbon, nitrogen, oxygen, and hydrogen atoms are represented by gray, blue, red, and white spheres, respectively.

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conducted so far. Specifically, by using thermomicroscopic (TM), thermogravimetric (TG), modulated differential scanning calorimetry (MDSC), and Fourier transform infrared (FTIR) methods, Lobbecke *et al.* [8] studied the thermal decomposition and the associated gas release of ADN at temperature ranging from 20 °C to 275 °C. The results showed that ADN melted at 91.5 °C, followed by the exothermal decomposition finished at 200 °C. The main decomposition products were NH_4NO_3, H_2O and N_2O, meanwhile, other gases like NH_3, NO_2, NO, N_2 and O_2 were also detected. Oxley *et al.* [9] reported that the production of N_2O during ADN decomposition was only attributed to the dinitramide, and the main decomposition paths varied from different temperatures (50−450 °C): (i) T<160 °C, ADN→NH_4^++NO_3^-+N_2O; (ii) T>160 °C, ADN→NH_3+$HN(NO_2)_2$, $HN(NO_2)_2$→N_2O+HNO_3. Furthermore, by utilizing TG and differential scanning calorimetry (DSC) methods with the mass spectrometer (MS) (50−250 °C), Vyazovkin *et al.* [10] demonstrated that N_2O, NO and NO_2 were the main products during the early decomposition stage of ADN, while H_2O, HONO, NH_3 and HNO_3 were produced in the following stages. They proposed two possible main thermal paths were: (i) ADN→NH_4^++N_2O+NO_3^- and (ii) ADN→NH_4^++NO_2+NNO_2^-. However, it should be noted that the proposed reactions in this report were completely different from that in other reports [11], which were (i) ADN→NH_3+$HN(NO_2)_2$; (ii) ADN→NH_3+HNO_3+N_2O. Moreover, Izatoet *et al.* [12] investigated the kinetics of thermal decomposition (30−350 °C) of ADN by employing the TG-DTA-MS-IR method and found that the main gases released were NH_3, H_2O, N_2, NO, N_2O, and NO_2. In addition, Rahm and Brinck studied the thermal decomposition of ADN [16] based on the chemical modeling of molecular clusters, the computed results showed that the decomposition reaction of N-NO_2 breaking could be favored if there is a polarized coordination of $N(NO_2)^-$ by an NH_4^+ and this reaction is the rate-determining step under atmospheric and low-pressure. Furthermore, they also used theoretical methods to investigate the thermal decomposition of dinitraminic acid $HN(NO_2)_2$ [17] (HDN) in gas-phase and $N(NO_2)^-$ [18] in solution, it was found that the decomposition of HDN is initiated by a dissociation and formed NO_2, while two decomposition mechanisms including the direct transformation into nitrate and nitrous oxide and a bond breaking into the NNO_2 radical anion and NO_2 are competitive.

Through the aforementioned studies on the decomposition of ADN in solid phase, several possible decomposition paths were proposed according to the main decomposition products detected. However, the decomposition of ADN is very fast and complex, which sometimes is challenging to be clearly understood through experiments, resulting in the inconsistence proposed mechanisms that have been reported. For instance, the proposed initial decomposition reactions and the detected decomposition products were different in three independent experimental results [9–11], which implies that the decomposition behavior and process of ADN have not been well understood. Besides, the temperature ranges in these studies were limited (30−450 °C). Therefore, it is desirable to carry more studies with expanded temperature ranges, in order to further understand the decomposition chemistry of ADN.

As a high-precision theoretical method, the *ab initio* molecular dynamics (AIMD) method has been successfully employed to investigate the thermal decomposition of several famous CHNO energetic compounds under high temperature or pressure, including hexanitrohexaazaisowurtzitane (CL-20) [19], pentaerythritol tetranitrate (PETN) [20], 1,1-diamino-2,2-dintroethylene (FOX-7) [21], and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) [22]. Through the AIMD method, it is convenient to investigate the key chemical events of decomposition, such as initial decomposition reactions, processes, intermediates, and products. This makes AIMD a promising method that could be employed to study the thermal decomposition of energetic compounds, since the laboratory operating of energetic compounds is usually much more dangerous and challenging than that of other safe compounds. Hence, in the present study, the chemical process of the decomposition of ADN under high temperature was studied systematically with the help of AIMD method. The main purpose of this work is to confirm the possible initial decomposition mechanisms, uncover the decomposition process, and investigate the effects of temperature on the thermal decomposition of ADN.

II. COMPUTATIONAL METHODS

In this study, all AIMD simulations were performed by the CASTEP code [23] using norm-conserving pseudopotentials [24] and a plane-wave expansion of the wave functions. The Perdew-Burke-Ernzerhof (PBE) [25] exchange-correlation function and a single k-point were employed. The Tkatchenoko and Scheffer (TS) [26] was utilized to correct the missing van der Waals (vdW). The ionic temperature was controlled by using a Nosé thermostat [27]. An NVT ensemble was employed. A time step of 1.0 fs was used. Since the simulation of decomposition in the solid-phase at ambient temperature is a very slow process, AIMD simulations in the present study were carried out at a higher temperature (2000 and 3000 K) than the normal decomposition. A plane wave cutoff of 500 eV for AIMD simulations and 830 eV for geometry optimizations were used. The calculated crystal cell parameters (a=7.10 Å, b=11.67 Å, c=5.56 Å) were very close to the experimental results [28] (a=6.96 Å, b=11.79 Å, c=5.61 Å), and the absolute errors were 2.8%, 1.0%, and 0.9%, respectively. Both the unimolecular and multimolecular

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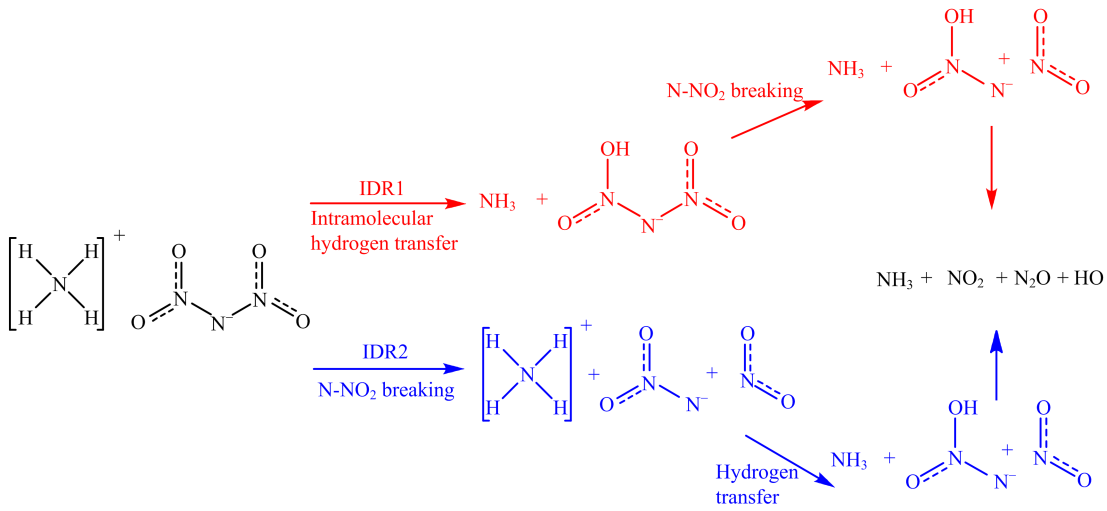

FIG. 2 Two different initial decomposition reactions of unimolecular ADN at 2000 and 3000 K.

decomposition simulations were performed after 5 ps of equilibration at 300 K. The unimolecular decompositions of isolated ADN were investigated by using NVT ensemble dynamics with a 15.0 Å cubic periodic cell, which is large enough to prevent interactions between periodic images. In order to provide appropriate statistical sampling and acquire more reliable MD results, 10 independent simulations were carried out at 2000 and 3000 K for 5 ps, respectively. The multimolecular decomposition simulations at 2000 and 3000 K were performed on a 1×1×2 supercell (8 molecules, FIG. 1(b)). The initial positions of the simulation supercell were taken from the experimental result of X-ray crystal structure [28]. The Bong-lengths criteria was employed to identify the changes in geometry in the simulations.

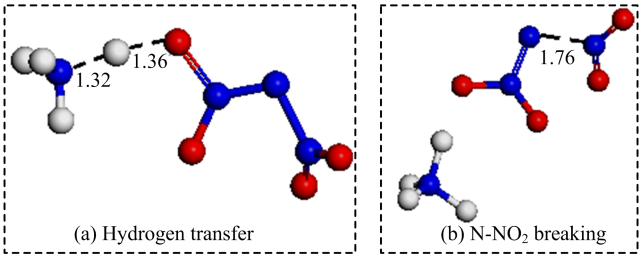

FIG. 3 The snapshots of two different initial decomposition reactions of unimolecular ADN at 2000 and 3000 K. Carbon, nitrogen, oxygen, and hydrogen atoms are represented by gray, blue, red, and white spheres, respectively.

III. RESULTS AND DISCUSSION

A. Unimolecular decomposition

From ten independent simulations at 2000 and 3000 K, two different initial decomposition reactions (IDR, FIG. 2) were observed, and the corresponding snapshots were shown in FIG. 3. As described, at 2000 K, ADN decomposed through intramolecular hydrogen transfer (IDR1) [9, 11] and N−NO_2 cleavage in $N(NO_2)^-$ (IDR2) [10, 16–18], which were ADN→NH_3+$HN(NO_2)_2$, and ADN→NH_4^++NO_2+N_2O_2, respectively. The observed number of times, *i.e.* the occurred number of times in 10 independent simulations, of two different decomposition reactions of unimolecular ADN at 2000 and 3000 K were counted. It can be found that the observed number of times for the two paths (IDR1, IDR2) were equal (5 times) at 2000 K, while the number of times for IDR1 increased to 7 at 3000 K while for IDR2 decreased to 3, indicating that these two reactions are competitive at 2000 K, and IDR1 became predominant along with the temperature increases. For further decomposition based on IDR1, the N−NO_2 bond cleavage of $HN(NO_2)_2$ would generate NO_2+HONNO (FIG. 2), and the subsequent decomposition of HONNO would produce N_2O through one of the following reactions: (i) HONNO→HO+N_2O or (ii) H+HONNO →H_2O+N_2O (H from N−H bond cleavage). The former reaction path was predominant at 3000 K, while the later one was mostly observed at 2000 K. This may be due to that N−OH cleavage was easier to occur at higher temperature, and the hydrogen was necessary for the promotion of the HONNO decomposition at low temperature. As for the further decomposition based on IDR2, one H in NH_4^+ would transfer into N_2O_2 forming HONNO (FIG. 2), and the HONNO would decompose into N_2O via the similar path of IDR1. In all, the main initial decomposition reaction should be: ADN→NH_3+N_2O+NO_2+OH. The production of OH and NH_3 could release H and O, and the active H could interact with N or O to capture O in N_2O and NO_2, thus generating N_2 and NO: H+N_2O→N_2+OH and H+NO_2→NO+OH. Meanwhile, the active O played a role in the oxidization of

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TABLE I The main unimolecular decomposition products of ADN at 2000 and 3000 K.

MD	2000 K	3000 K
1	N_2O+NO+NO_2+H_2+2H	N_2+2NO_2+H_2+2H
2	N_2O+NO+NO_2+H_2+2H	N_2+NO_2+NO+H_2O+2H
3	N_2O+2NO+HO+H_2+H	N_2+2NO+H_2+2H+O_2
4	NO_2+NO+N_2+HO+H_2+H	N_2+2NO+2H_2+2O
5	N_2+2NO+O_2+H_2+2H	N_2+2NO+H_2+H_2O+O
6	N_2+2NO+H_2+2H+2O	N_2+NO+H_2+O_2+2H+O
7	N_2O+NO+NO_2+H_2+2H	N_2+2NO+H_2+2O+2H
8	N_2+2NO+HO+H_2+H+O	N_2+2NO+H_2+O_2+2H
9	NO_2+NO+N_2+O+H_2+2H	N_2+2NO+H_2+O_2+2H
10	NO_2+NO+N_2+HO+H_2+H	N_2+2NO+2H_2+O_2

NH_x(x=1−3) into NO or NO_2. The isolated H and O could also self-bond into H_2 and O_2, respectively. The final decomposition products simulated via AIMD are listed in Table I. The main decomposition products were similar in independent simulations at 2000 and 3000 K, which were NO_2, NO, N_2O, N_2, H_2, O_2, H_2O, H, and O. These gas products from our AIMD simulation were consistent with that obtained from previous experimental investigations [8–12, 16]. The decomposition of ADN experienced a faster and deeper process when at 3000 K than that at 2000 K, as NO and N_2 was more commonly observed in all ten simulations at 3000 K. Besides, the observation of NO_3^- was attributed to the reactions of NO_2+OH→NO_3^-+H, and NO_2+N_2O_2→NO_3^-+N_2O, which has been reported in previous experimental studies [9, 10]. The unstable NO_3^- would quickly interreact with H or NH_4^+ to form HNO_3 that has also been reported as the initial decomposition product [9, 11], which could further transform into other N_xO_y.

B. Multimolecular decomposition

In this section, AIMD method was also employed to investigate the multimolecular thermal decomposition of ADN at 2000 and 3000 K, respectively. As described in FIG. 4, the energy changes at 3000 K were more obvious and faster than those at 2000 K, indicating that the decomposition at 3000 K were more drastic than that at 2000 K. Notably, the multimolecular thermal decomposition of ADN at 2000 and 3000 K were found to be more complicated than the unimolecular decomposition. In addition to the proposed two reactions of IDR1 and IDR2, another two initial decomposition mechanisms were also involved in decomposing eight ADN molecules at 2000 and 3000 K, which were the intermolecular hydrogen transfer (IDR3): the H in NH_4^+ of one ADN molecule transfers into the O in $N(NO_2)_2^-$ of another ADN molecule, and the pure N−H bond breaking (IDR4): NH_4^+→NH_3+H. The generated H in IDR4 would not suffer the intramolecular or the intermolecular transfer into $N(NO_2)_2^-$, but would react with other intermediates to promote the decomposition. Table II listed the observed number of times of the four different initial multimolecular decomposition reactions of ADN at 2000 and 3000 K. The IDR1, IDR2, IDR3 and IDR4 were observed for 1, 4, 2 and 1 number of times at 2000 K, respectively, and the number of times were changed to 3, 1, 2 and 2 when at 3000 K, indicating that N−NO_2 cleavage (IDR2) and intramolecular hydrogen transfer (IDR1) are the dominating initial decomposition mechanisms at 2000 and 3000 K, respectively. The hydrogen-related reactions (IDR1, IDR3 and IDR4) were competitive with the N-NO_2 breaking (both are 4 number of times) at 2000 K, whereas they became preponderant at 3000 K (number of times: 7 *vs.* 1). Since Rahm and Brinck [16] ever reported that IDR2 could be favored if there is an polarized coordination of $N(NO_2)^-$ by an NH_4^+, it may be inferred this polarization effect reduces with the increasing of temperature, making IDR2 to be disfavored at higher temperature to some degree. These observations of multimolecular decomposition were similar to those of unimolecular decomposition of ADN. Further, after the initial decomposition, ADN would decompose into small products such as N_2 and H_2O by hydrogen-promoted simple, fast and direct N−O, N−N, N−H and O−H cleavage and recombination (FIG. 6) without forming any long catenulate, big nitrogen-rich or carbon inter-

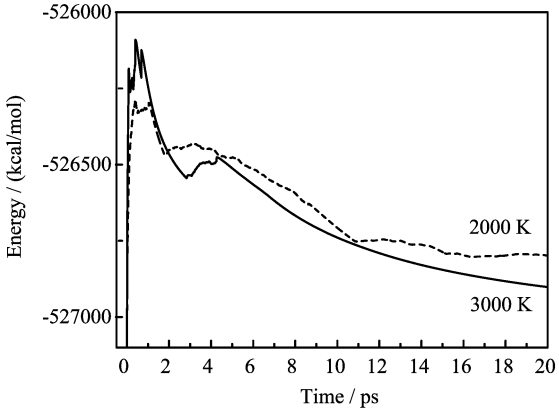

FIG. 4 The time dependence of the total energy of multimolecular ADN at 2000 and 3000 K.

TABLE II The observed number of times of four different initial decomposition reactions of multimolecular ADN at 2000 and 3000 K.

T/K	IDR1[a]	IDR2[b]	IDR3[a]	IDR4[c]
2000	1	4	2	1
3000	3	1	2	2

[a] Intramolecular hydrogen transfer.
[b] N−NO_2 breaking.
[c] N−H breaking

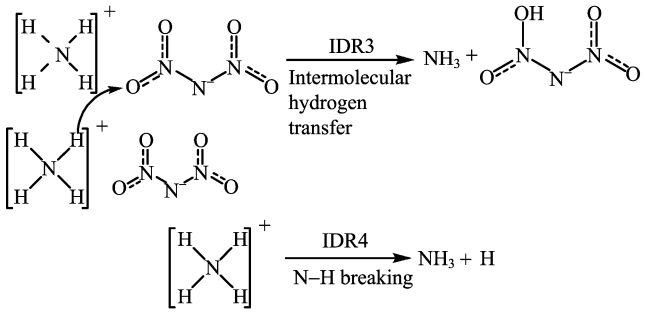

FIG. 5 Two new initial decomposition reactions of multimolecular ADN at 2000 and 3000 K.

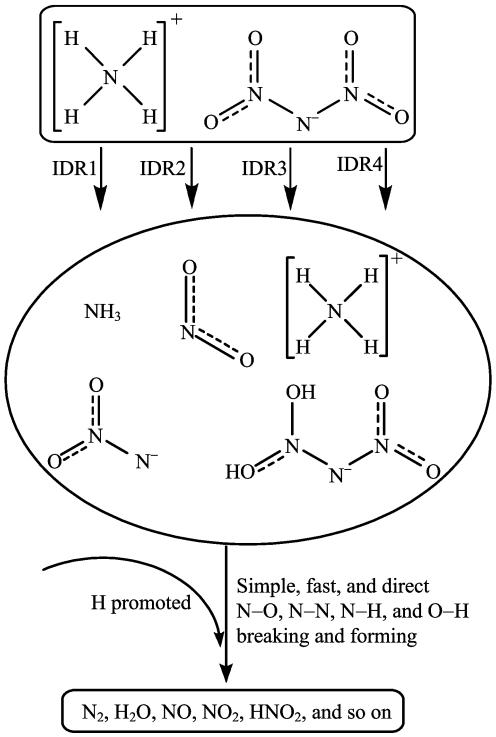

FIG. 6 The total decomposition process of multimolecular ADN at 2000 K.

mediates both at 2000 and 3000 K, which was in line with the thermal decomposition of some organic energetic compounds including nitromethane [29], 1,3,5-triamino-2,4,6-trinitrobenzene [30], and 3,6-di(azido)-1,2,4,5-tetrazine [31]. The hydrogen-promoted decomposition reactions would be elaborated in the following section. In addition, it was found that the subsequent key events of ADN decomposition at 2000 and 3000 K were similar, and the only difference was the faster decomposition rate when at 3000 K. Therefore, the following discussions were mainly focused on the decomposition process at 2000 K.

As described in FIG. 7 for the radial distribution function (RDF) of multimolecular ADN at 2000 K, the peak at about 0.75 Å was corresponding to the H−H bond, indicating the formation of H_2 [11], while the

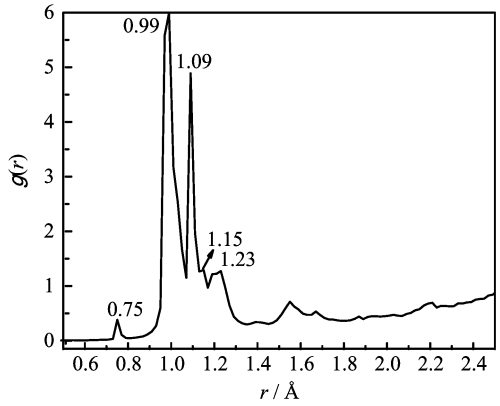

FIG. 7 The radial distribution function of multimolecular ADN at 2000 K.

peak at about 0.99 Å was associated with the O−H bond, suggesting the generation of H_2O or OH. In addition, the peak at ∼1.09 Å was related to the N≡N bond, indicating the formation of N_2. The peak at ∼1.15 Å could be assigned to the N=O and N−H bonds, which indicated the generation of NO and NH_3. The peak at ∼1.23 Å was related to the N−O bond in NO_2. It is worthy to point that the two strongest peaks at 0.99 and 1.09 Å indicated that the H_2O and N_2 were two main decomposition products. The RDF of multimolecular ADN at 3000 K showed similar manner to that at 2000 K, meaning that they underwent similar procedure.

FIG. 8 described the time dependence of the number of four main bonds (N−H, N−O, N−N and O−H bond) in the system at 2000 K. Firstly, the number of N−H bond decreased fast to zero in 6.0 ps, and fluctuated at around 0−5. Therefore, the changing process of the weak N−H bond would be: NH_4^+ decomposed into NH_3, and H easily left N to promote the further decomposition via capturing O in N−O bond to form OH and H_2O, while the rest N would combine with either N or O atoms. Secondly, the number of N−O bond decreased gradually because of the generation of N_2O, NO, N_2 and H_2O. Thirdly, the number of N−N bond deceased in the first 3.0 ps which may be due to the cleavage of N−N bond in $N(NO_2)^-$, whereas the gradual increase of the number of N−N bond in the following 17.0 ps was because of the formation of N_2. Finally, the number of O−H bond increased along with the decomposition process of ADN, which was due to the formation of H_2O. FIG. 9 depicted the time dependence of the number of ADN molecule and the main decomposition products (NH_3, NO_2, NO, N_2O, N_2, HNO_2, and H_2O) in the system at 2000 K. All eight ADN molecules decomposed in about 0.6 ps, accompanied by the release of NH_3 [8–12], followed by its transformation into other compounds in about 6.0 ps. The formation of NO_2 occurred at very early stage at about 0.02 ps via the reaction: $N(NO_2)_2^- \rightarrow NO_2$+N-$NO_2$. Subsequently,

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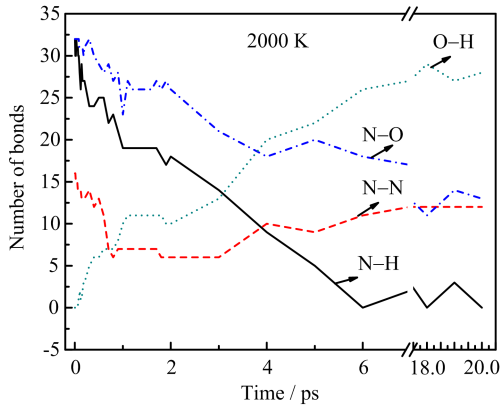

FIG. 8 The time dependence of the number of main chemical bonds in the system at 2000 K.

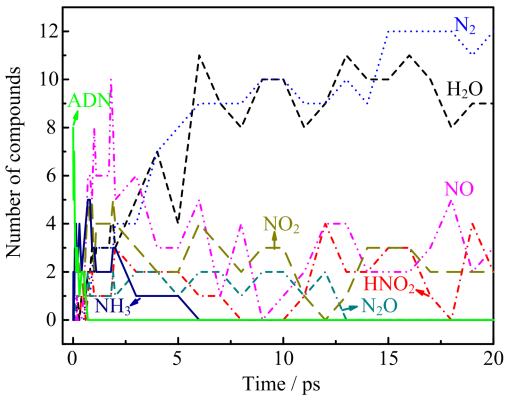

FIG. 9 The time dependence of the number of the ADN molecule and main decomposition products in the system at 2000 K.

NO_2 would further react with H to form NO at about 0.18 ps via the reaction: NO_2+H→NO+OH. The N-NO_2 would react with H to release N_2O at about 0.09 ps through the reaction: N-NO_2+H→N_2O+OH. The N_2O is an active intermediate which would become N_2 in about 13 ps. N_2 formed at about 0.6 ps by the reaction: H+N_2O→OH+N_2. The active OH would combine with H to produce H_2O: OH+H→H_2O. The increasing amount of N_2 and H_2O were formed along with the composition process of ADN, and the existence of NO and NO_2 at the end of the decomposition was because of the high oxygen balance of ADN. Interestingly, HNO_2 involved in the reaction [10] is a relatively stable product: HO+NO↔HNO_2. The unstable HNO_3 [9, 10] was observed a few times by the reaction: HO+NO_2↔HNO_3, and would decompose quickly. Moreover, other unstable intermediates including O_2 [8], O_3 and H_2O_2 were also observed. The unseen of NH_4NO_3 may be because its unstable salt form under extreme high-temperature (2000 and 3000 K in this study). Additionally, the main decomposition products of ADN were NH_3, NO_2, NO, N_2O, N_2, H_2O, and HNO_2, which is consistent with the previous experimental results [8–11].

IV. CONCLUSION

In this study, the AIMD method was employed to study the thermal decomposition of a famous new high oxidizer ADN under high temperature (2000 and 3000 K). The results showed that two different initial decomposition mechanisms were involved during the unimolecular decomposition of ADN, which were the intramolecular hydrogen transfer and N−NO_2 breaking in $N(NO_2)^-$. The two mechanisms competed at 2000 K, and the former one was predominant at 3000 K, indicating that the initial decomposition mechanism was temperature dependent. For the multimolecular decomposition of ADN, another two new reactions were involved, which were the intermolecular hydrogen transfer and directly N−H breaking in NH_4^+. At 2000 K, the N−NO_2 cleavage competed with the other three hydrogen-related decomposition reactions, whereas hydrogen-related decomposition reactions was dominating at 3000 K, indicating that the initial decomposition reactions of multimolecular ADN were also temperature dependent. After the initial decomposition, the temperature increase from 2000 K to 3000 K could facilitate the further decomposition, while did not change the key decomposition events. ADN decomposed into small products like N_2 and H_2O by hydrogen-promoted simple, fast and direct N−O, N−N, N−H and O−H cleavage without reforming any long or big intermediates that may impede the decomposition. The main decomposition products at 2000 and 3000 K were both NH_3, NO_2, NO, N_2O, N_2, H_2O and HNO_2. Our study provided another potential method for understanding the chemical process of ADN and other energetic high oxidizer with similar structure to ADN under high temperatures.

V. ACKNOWLEDGEMENTS

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