Thermal Decomposition of the Solid Phase of Nitromethane: *Ab Initio* Molecular Dynamics Simulations

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The Car-Parrinello molecular dynamics simulations were employed to investigate thermal decomposition of the solid nitromethane. It is found that it undergoes chemical decomposition at about 2200 K under ambient pressure. The initiation of reactions involves both proton transfer and commonly known C–N bond cleavage. About 75 species and 100 elementary reactions were observed with the final products being H_2O, CO_2, N_2, and CNCNC. It represents the first complete simulation of solid-phase explosive reactions reported to date, which is of far-reaching implication for design and development of new energetic materials.

Explosives have been in extensive use for centuries, but their decomposition mechanism is not yet clear. Despite a great deal of research interest in the decomposition behavior, little progress has been made.

Sorescu *et al.* [1,2], Agrawal *et al.* [3], as well as Seminario *et al.* [4], investigated liquid-phase and solid-phase properties of NM at ambient and high pressure. Soulard [5] calculated Hugoniot curves and Wei *et al.* [6] examined the bimolecular and multiple molecular collisions. In order to explore possible decomposition pathways, Manaa *et al.* [7] performed density functional based molecular dynamics simulations to determine the early chemical events of hot and dense NM. Liu *et al.* [8] successfully investigated the compressibility of solid NM in the high-pressure regime. Zeman *et al.* [9] analyzed the possibility of primary fission pathways to explain Walker's observation [10] and provided an explanation about the new aspects of NM initiation reactivity. Although these studies provided useful information about NM under high temperature and pressure, they do not provide direct observation of the decomposition reaction of solid-phase NM.

The question that our study aims to answer is how thermal motion triggers chemical reactions under high temperature that lead to detonation. This is an impossible task for the classical molecular dynamics simulations, due to the limitations of the parameterized potentials.

In the present study, the CPMD methods were used with the plane wave and pseudopotential [11,12]. The total length of simulation was 205 ps, which is considered to be quite long for an *ab initio* simulation. The simulation was carried out by using a time step of 4 a.u. and a fictitious electron mass of 400 a.u. The electronic wave functions are expanded in a plane-wave basis set with the cutoff energy of 70 Ry. The Troullier-Martins norm-conserving

pseudopotential was used in all of these calculations. Temperature control was done through Nose-Hoover thermostats [13] and could be applied to both ions and electrons in the CPMD simulations. The electronic degrees of freedom were also coupled by a coupling frequency of 15 000/cm. Four molecules of NM were included in the simulation box with periodic boundary conditions. An *NVT* ensemble was employed.

In order to investigate the decomposition of NM, the external temperature was gradually increased by an increment of 100 K. The simulation time for each temperature was about 10 ps (100 000 steps). This long simulation time was necessary to avoid sudden and rapid increase of atomic velocity due to fast heating.

NM pyrolysis is a complex phenomenon involving nonlinear processes as demonstrated by the temporal dependence of the thermally decomposed products. The rupture and rearrangement of explosive components take place by the decomposition and combination reactions during the dynamics simulation. It includes four distinct decomposition stages with four NM molecules starting to react with other molecules or molecular fragments at different times. Upon decomposition, the obtained products are smaller and more reactive species, and they interact with each other to form stable intermediates or long-chain products. The resulting overall mechanism for the reactions was composed of 75 species and 100 reactions. Some transient species exist on a time scale of tens of femtoseconds. We will now concentrate on the intermediates (INT) that exist in the system for more than 0.5 ps, which are listed in Table I along with their lifetime. The decomposition mechanism can be explored by studying the transition states and the intermediates.

The initial stages of decomposition are not typical unimolecular processes of C–N bond scission [14]. During the

simulation, the fast vibrations of the nitro group induced an inversion-type motion along with a stretch in the N–O bond, which led to oxygen transfer from the nitro to the methyl group. The nitrogen atom was combined with one of the hydrogen atoms of the methyl group, forming the transition state (TS) (1) with a four-membered ring, which could undergo further decomposition by ring opening. Therefore, a proton transfer event between two small fragments occurred on a time scale of about 191.8 ps, which yielded CH_2O and HNO. The fragment NO_2 recombines with CH_3 and formed the allotrope CH_3ONO as the simulation continues, which could undergo further decomposition and form the majority of NO at an early time from the reaction of $[CH_3ONO \rightarrow CH_3O + NO]$, which agrees with the mechanism proposed by Zhang and Bauer [15].


$$(1)$$
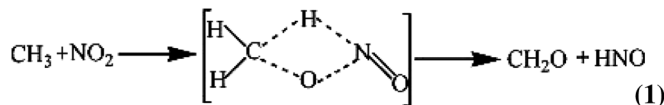
The CH_2O and HNO intermediates could recombine to form an isomer of (1), i.e., (2), which is a structure with a five-membered ring. This species was not very stable and could undergo further dissociations through the breaking of the C–H bond between the C atom and one of the H atoms of H_2CO and the breaking of the N–O bond. The rupture of C–H and N–O bonds in the (2) structure lead to the formation of OCHO, which was decomposed into a smaller and stable CO intermediate and OH radical. The OH radical and NH_2 radical combined to form an NH_2OH fragment, which is shown in the scheme below:


$$NH_2 + OH \longrightarrow NH_2OH \qquad (2)$$
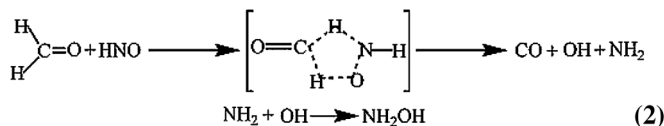
The second NM molecule started to participate in the reactions with the molecular species of the initial decomposition product NH_2OH at about 196.4 ps, forming (3) (shown in the scheme below). During the decomposition of (3), an intermolecular hydrogen transfer occurred. The H atom elimination via a simple rupture of the C–H bond did not involve any intermolecular rearrangement and formed fragment CH_2NO_2 and a relatively unstable NH_3OH intermediate which could further decompose to NH_3 and an OH radical. Afterwards, the unstable intermediate CH_2NO_2 could react with the OH radical to form CH_2NO_2OH that decomposed to CH_2NO and proton abstraction hydrogen peroxide HO_2 through unimolecular decomposition. The CH_2NO, HO_2, and NH_3 joined together to form the transition states (4) with a long-chain structure, as shown in the following scheme. The decomposition of (4) was triggered by the N–O and H–O bond breaking, leading to CH_2NO, NH_4^+, and O_2 molecular fragments. The third incoming NM molecule started to react with the decomposed O_2 molecular species, which was obtained by decomposition of (4).

$$(3)$$

$$(4)$$
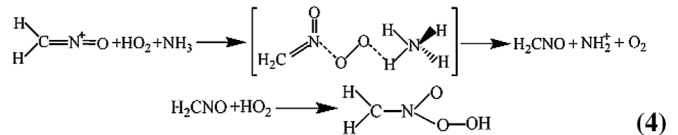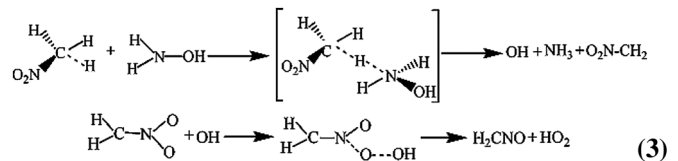
Finally, the fourth NM molecule started to get involved with the NH_3 intermediate to form $NO_2CH_3NH_3$ that reacted with the OH radical and formed a large $NO_2(CH_3)(NH_3)OH$ fragment at 200.1 ps. Then, H_2O_2 underwent a unimolecular decomposition to form two OH radicals. This was the basis for the formation of water molecules, which was considered as a major decomposition product in the thermal decomposition of all energetic materials. It was found that the formation of a water molecule was around 200.2 ps, and it was the most abundant intermediate species in the NM decomposition. It acted as an intermediate transporting hydrogen atom to other fragments that formed new molecular species. The behavior of water suggests that water probably acted as a catalyst in the decomposition process. In our simulations, a number of reactions have been found to occur under the catalysis of water molecules. We expect this phenomenon to be prevalent until chemical equilibrium is reached. The following scheme demonstrates the formation of the first water molecule:
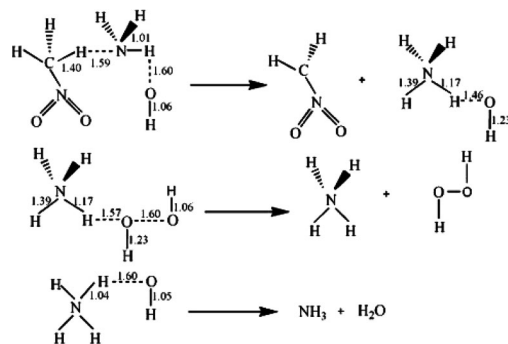
The H_2CNO intermediate, which was generated by the decomposition of (4), could subsequently react with HOCO, forming the transition state (5) with a chain structure. The hydrogen was eliminated from HOCO, leading to the second final decomposition product, i.e., CO_2.


$$(5)$$
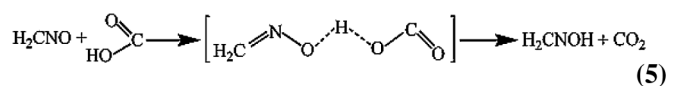
The relatively unstable fragment CHONH reacted with the OH radical, forming INT9 in Table I. In addition, the intermediates NO_2 and INT2 could be obtained simultaneously by breaking the C–N bond from fragment

TABLE I.   The various stable INTs and their lifetimes.

	Intermediates (INTs)	Lifetime (ps)		Intermediates (INTs)	Lifetime (ps)
1	$H_2N^+{=}C{-}N{-}OH$ (with H, H on C and N)	0.51	12	$HO{-}N{=}C{-}N{-}C$ with O and OH (H, H)	1.9
2	$H_2N{=}CH_2$ (H,H on N; H,H on C)	0.55	13	$H{-}\bar{C}{=}N^+{=}O$	2.3
3	$\bar{N}{=}C{=}N{-}C{=}N^+$ with O (H,H)	0.56	14	$H_2\bar{C}{-}N^+{=}O$ with $O{-}OH$	2.5
4	$O{=}C{=}N{-}O{-}OH$ (H,H)	0.59	15	$H_2C{=}O$	3.4
5	$H_2N^+{=}C{-}N^+{=}O$ (H on C, H on N)	0.61	16	$H{-}O{-}N{=}C$	4.5
6	$C{-}N{=}O$	0.9	17	$H_2N{-}C{=}N{-}O{-}H$ (H on C)	6.4
7	$H_2N^+{=}C{-}OH$ (H)	1.1	18	$H{-}N{=}C{=}O$	8.5
8	$H{-}N{=}C{=}N{-}C{=}N{-}O{-}H$ (H on C)	1.1	19	$H{-}N{=}C{=}N{-}H$	10.2
9	$H{-}N{=}C{-}N{-}O{-}H$ with H (H on C)	1.2	20	$\bar{N}{=}C{=}N^+{-}O{-}H$ (H)	10.9
10	$H{-}N{=}C{=}N{-}C{=}N{-}O{-}H$ (H)	1.3	21	$\bar{N}{=}C{=}N^+{-}N{=}C{=}N{-}H$ (H)	76.8
11	ring structure with N, C, O, N (H, H)	1.6	22	$H_2N^+{=}C$ with N–N ring and C, N	86.1

$NH_2(CH_2)NO_2$. The intermediate HNO got involved with the fragment NH_2CH_3 to form NO. The complex (6) was formed from the OH radical and was catalyzed by water, and it decomposed into fragments CHONH and CH_2NO, which could be further decomposed through H–O bond breaking and rupture of C–N and C–H bonds forming stable intermediates, such as OH radical, CHO, NH_2, and intermediate INT13, which are considered to play an important role during the course of the decomposition by acting as a catalyst that hydrogen transfer involving the catalyst controls; i.e., INT13 is a virtually linear structure

(H–C–N $\sim 135.9°$, O–N–C $\sim 154.4°$). Then, the relative stable intermediate INT13 was formed via (6).

$$HO^- + H_2O + \;\; \rightarrow \;\; [\ldots] \rightarrow HO^- + H_2O + HCO + NH_2 + HCNO \quad (6)$$
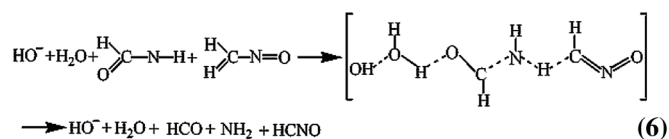
INT18 in Table I, HNCO, an important fragment, which consists of the most reactive species H and NCO, acted as a hydrogen-containing catalyst for one decomposition path-
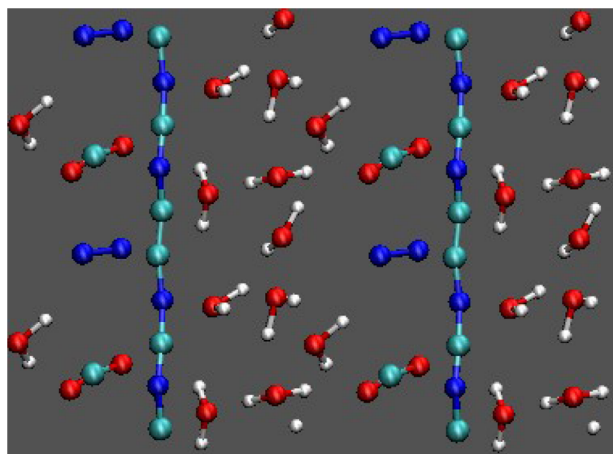
FIG. 1 (color online). The snapshots of CPMD simulation of the solid NM decomposition reaction at 195 ps with an amplified simulation cell $(2 \times 2 \times 2)$ by the periodic boundary conditions where the molecules are shown in "ball and stick" representation, the red, white, blue, and cyan balls refer to oxygen, hydrogen, nitrogen, and carbon atoms, respectively, and the final products are H_2O, CO_2, N_2, and CNCNC.

way involving hydrogen transfers. It appears that the hydrogen-transfer reaction involves transfer of hydrogen to other molecular fragments rather than the abstraction of a hydrogen atom during decomposition. INT18 was similar to INT13 and was considered as a possible trigger of chain processes. Because our simulated system is so small that only 4 molecules were included in the unit cell, the complete chain process is not observed.

As the simulation continued, the number of molecular fragments decreased. The main fragments were NT19, INT20, INT21, and INT22. When the reactive species were nearly all consumed, these molecular fragments alternately appeared, and their lifetime was quite long. Eventually, the system reached a steady state, and the final products are H_2O, CO_2, and N_2 along with INT22 made up of C and N elements only, which is shown in Fig. 1.

In conclusion, the pyrolysis behavior of solid NM has been investigated by conducting quantum-based CPMD simulations. The thermal decomposition is mainly related to molecular collisions, chemical bond forming and breaking, which occur in short range. We believe this small system will capture some features of this type of reactions and their intermediates and products. By monitoring the generation and consumption of reactive fragments, we found that the chemical reactions of solid NM are quite complicated. About 75 species and 100 elementary reactions were observed with the final products being $6H_2O$, CO_2, N_2, and CNCNC in a single unit cell. Some very interesting intermediates were observed which may be valuable for future studies of explosive reactions of NM. It is noteworthy that the commonly known C–N bond cleavage was not the predominant mechanism of decomposition; instead, the C–N bond is alternately broken

and reformed as the decomposition continues. The H_2O molecule acted as an intermediate species transporting hydrogen atom to other molecules and was found to behave as a catalyst in the decomposition. Because the small simulation cell size limits the extension of the reaction, we did not observe the complete chain process. An ongoing work of our group is to study supercells at varying reaction conditions. To the best of our knowledge, this study represents the first complete explosive reaction by a theoretical study. The present work is the first step in our continuous efforts towards systematic studies of chemical reactions of energetic materials.

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