Ab initio calculations of the effects of H$^+$ and NH$_4^+$ on the initial decomposition of HMX

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ABSTRACT

In this work, the effects of H$^+$ and NH$_4^+$ on the initial decomposition of HMX were investigated on the basis of the B3P86/6-31G** and B3LYP/6-31G* calculations. Three initial decomposition pathways including the N–NO$_2$ bond fission, HONO elimination and C–N bond dissociation were considered for the complexes formed by HMX with H$^+$ (PHMX1 and PHMX2) or with NH$_4^+$ (AHMX). We found that H$^+$ and NH$_4^+$ did not evidently induce the HMX to trigger the N–NO$_2$ heterolysis because the energy barrier of N–NO$_2$ heterolysis was found to be higher than the bond dissociation energy of N–NO$_2$ homolytic cleavage. Meanwhile, the transition state barriers of the HONO elimination from the complexes were found to be similar to that from the isolated HMX, which means that the HONO elimination reaction of HMX was not affected by the H$^+$ and NH$_4^+$. As for the ring-opening reaction of HMX due to the C–N bond dissociation, the calculated potential energy profile showed that the energy of the complex (AHMX) went uphill along the C–N bond length and no transition state existed on the curve. However, the transition state energy barriers of C–N bond dissociation were calculated to be only 5.0 kcal/mol and 5.5 kcal/mol for the PHMX1 and PHMX2 complexes, respectively, which were much lower than the C–N bond dissociation energy of isolated HMX. Moreover, among the three initial decomposition reactions, the C–N bond dissociation was also the most energetically favorable pathway for the PHMX1 and PHMX2. Our calculation results showed that the H$^+$ can significantly promote the initial thermal decomposition of C–N bond of HMX, which, however, is influenced by NH$_4^+$ slightly.

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1. Introduction

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (cyclotetramethylene tetranitramine, HMX) is one of the most widely used energetic compounds in explosives and solid propellants because of its good performance and security. Many physicochemical properties of HMX have been studied intensively in the past, such as molecular structure [1,2], crystallization [3], crystal phase change [4–6], thermal decomposition behavours [7,8], intermolecular interaction in condensed phase [9,10], sensitivity [11,12], etc. Today, the investigation on HMX is still a subject of interest to both experimentalists and theoreticians [13–15].

It is well known that crystalline HMX can exist in four polymorphic phases, denoted as α-, β-, γ- and δ-HMX. HMX molecule may exhibit several conformations, such as the chair and boat forms. However, the most stable form is the β-HMX at room temperature, whose molecular structure has a chair configuration with a center of inversion (C_i symmetry). Theoretical calculations have shown that the HMX molecules with different configurations appear very similar molecular energy [16,2]. Generally, β-HMX is considered as a model structure to study the thermal decomposition mechanisms that have been intensively studied by several research groups [17,18].

As for the initial decomposition mechanism of HMX, four different unimolecular reaction mechanisms have been proposed: NO$_2$ elimination, HONO elimination, concerted ring scission and dissociation of the ring along the C–N bond [19]. Among these mechanisms, N–NO$_2$ bond homolysis is putatively considered as the most important "first reaction" in the detonation of HMX [20,21]. However, a recent in situ FTIR spectroscopy experiment shows that the C–N bond cleavage and N–NO$_2$ bond cleavage are competitive reactions at 205 °C, but the C–N bond rupture is dominant at higher temperature [22]. In addition, some theoretical calculations point out that the HONO elimination might be energetically favorable for the decomposition of the HMX in condensed phase [23]. Evidently which decomposition mechanism

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is pivotal will be determined by many factors, such as temperature, condensed phase, molecular interaction, etc.

In practice, HMX commonly combines other ingredients to produce the explosives and propellants, which have different ingredients interacting with each other. The intermolecular interactions may modulate the properties of HMX. Typically, in the solid propellants containing HMX and ammonium perchlorate (AP), AP can hydrolyze and the H^+ and NH_4^+ will be generated once the propellant adsorbs water. In this case, H^+ and NH_4^+ might affect the properties of HMX during manufacturing and storage of the propellants. To our best knowledge, there are very few reports on the effects of H^+ and NH_4^+ on the initial decomposition of HMX.

In our previous work [24], we reported that the β-HMX can form two complexes with H^+ (see Scheme 1), whose energies are very similar to each other. One (PHMX1) is related to the combination of H^+ with the O-atom of NO_2 group and the other (PHMX1) is formed by the combination of H^+ with the N-atom of HMX ring. In addition, a complex of β-HMX with NH_4^+ (AHMX) having the lowest energy has been optimized by means of DFT calculation. In view of the geometry, it has been found that although the HMX in the complexes still keeps a chair configuration, the geometry of the HMX in the complexes differs significantly from that of β-HMX. The symmetry change in the eight-member ring of HMX results in the rearrangement of the NO_2 groups on the sides of ring. The detailed geometries of the complexes can be seen in our previous work [24].

In this study, we further investigated the three complexes to determine the effects of H^+ and NH_4^+ on the initial decomposition of HMX. The relevant active energies of the thermal decomposition for the complexes are compared with the values of isolated HMX reported in the literatures. Results mainly involve the N–NO_2 heterolytic cleavage, HONO elimination and the dissociation of the ring along the C–N bond for the three complexes.

2. Computational details

The B3LYP function with a moderate basis set (6-31G*) has been utilized to predict the thermal decomposition reactions of HMX [17,19]. In this study, complexes formed through the interaction of HMX with H^+ or NH_4^+ and the transition states were optimized at the B3LYP/6-31G* level of theory. Once convergence, harmonic vibrational frequencies were further calculated to confirm the equilibrium geometries or transition states. The B3LYP/6-31G* calculated zero-point vibrational energy (ZPE) was included in the calculation of active energy. By scanning the N–NO_2 bond length and optimizing the other structure parameters at the same time, the potential energy curves of the N–NO_2 heterolytic cleavage were obtained at the B3P86/6-31G** level of theory in order to make a comparison with the recently calculation results on the N–NO_2 homolytic cleavage [24]. All the calculations were performed using a Gaussian 03 program package [25].

3. Results and discussion

3.1. N–NO_2 bond dissociation

The earlier calculation results have shown that the N–NO_2 bond rupture is putatively one of the most important initial reactions for the thermal decomposition of nitramine [19,26–28]. Here, we first considered the N–NO_2 bond dissociation reactions for the HMX and the three complexes (PHMX1, PHMX2 and AHMX) as shown in Scheme 1. The natural bond orbital (NBO) calculations have
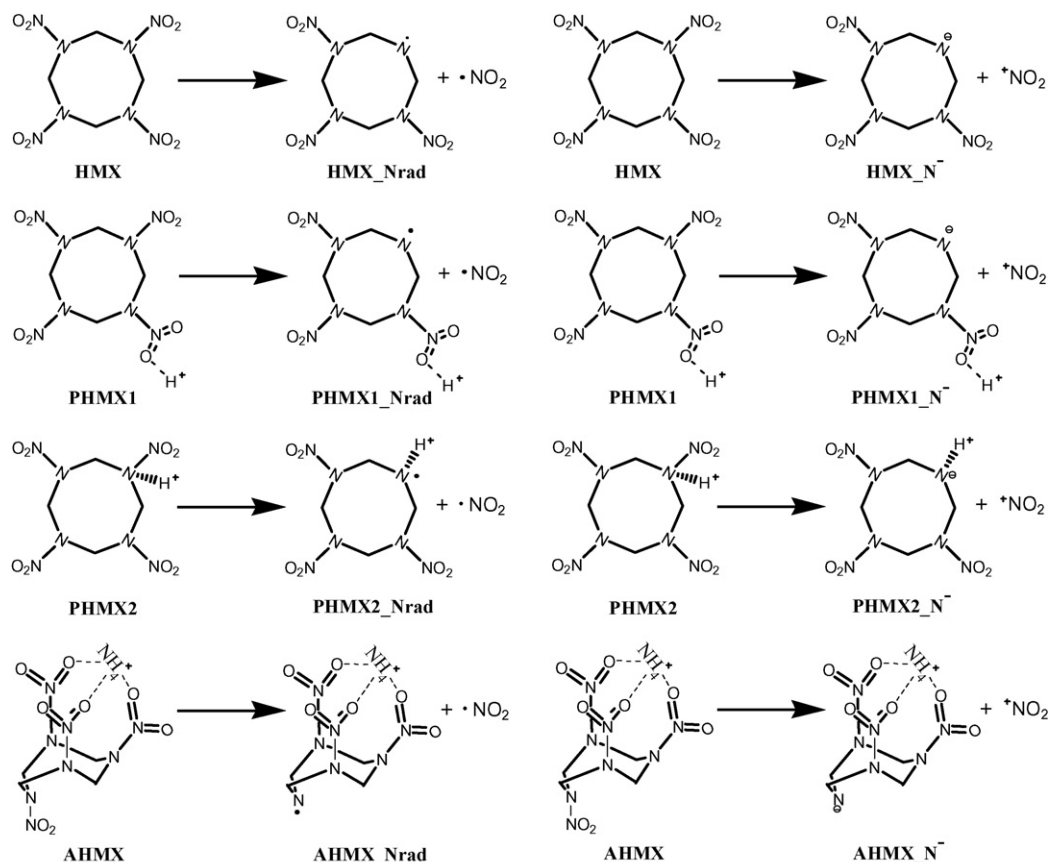
Scheme 1. Homolytic (right) and heterolytic (left) cleavage of the N–NO_2 bond for the HMX and its complexes with H^+ and $NH4^+$, respectively.

revealed that the bond involved in the reactions of Scheme 1 is the least stable among the four $N-NO_2$ bonds for each complexes [24]. Evidently, the rupture of this weakest bond should occur more easily and is generally considered to be responsible for the safety of energetic compounds.

These possible decomposition mechanisms involve the homolytic and heterolytic fissions of the $N-NO_2$ bond. As for the homolysis of the $N-NO_2$ bond, the B3P86/6-31G** calculations show that the weakest $N-NO_2$ bond dissociation energies of the two complexes with H^+ (PHMX1 and PHMX2) decrease about 5 kcal/mol and 20 kcal/mol, respectively, in comparison with that of β-HMX. However, the $N-NO_2$ bond dissociation energy for the complex with NH_4^+ (AHMX) decreases only about 1.7 kcal/mol [24].

In the complexes, because of the combination of H^+ and NH_4^+, the atomic charges occurs redistribution in the HMX molecule. It is unclear that whether the charge redistribution may induce the heterolytic cleavage of the $N-NO_2$ bond. So, we attempted to optimize the transition states of the $N-NO_2$ heterolysis of the complexes but unsuccessfully. On the basis of the B3P86/6-31G** calculations, furthermore, the potential energy curves of the heterolytic fission were obtained from scanning the $N-NO_2$ bond distance while optimizing the other structural parameters.

Fig. 1 shows three plots of energy as a function of the $N-NO_2$ bond length for the complexes. It can be seen that the energies continue to go uphill as the $N-NO_2$ bond length increases. Like the $N-NO_2$ homolysis for isolated HMX [19]. The $N-NO_2$ heterolysis for the three complexes is an endothermic and reversible process. For the PHMX1 and AHMX, the energies (BDE) of $N-NO_2$ homolysis were calculated to be 40.5 kcal/mol and 43.8 kcal/mol, respectively [24]. Clearly, the energies of $N-NO_2$ heterolysis are much higher than those of $N-NO_2$ homolysis for the two complexes, which implies that the $N-NO_2$ heterolytic reaction is very unlikely for the PHMX1 and AHMX. As for the PHMX2, the energy of the $N-NO_2$ heterolysis is about 35–38 kcal/mol, which is only about 10 kcal/mol higher than that of $N-NO_2$ homolysis (25.9 kcal/mol). On the other hand, this heterolysis energy for PHMX2 is lower than the BDE of $N-NO_2$ homolysis for isolated HMX. For the above reason, it cannot be completely excluded that the HMX occurs the $N-NO_2$ heterolysis once the N-atom of HMX ring combines with H^+ to form the complex PHMX2.

The results presented here indicate that H^+ and NH_4^+ cannot significantly induce the $N-NO_2$ bond to dissociate heterolytically.

Scheme 2. HONO elimination for the HMX and its complexes with H^+ and $NH4^+$, respectively.

In all cases, the heterolysis of $N-NO_2$ is more unfavorable in energy than the homolysis of $N-NO_2$. H^+ has a great impact on the $N-NO_2$ homolytic decomposition but NH_4^+ has negligible influence.

3.2. HONO elimination

HONO elimination is considered as a competitive reaction channel with respect to the $N-NO_2$ bond dissociation for the HMX decomposition, especially in the condensed phase [23], because the calculated energy barrier of the HONO elimination is 44.6–45.0 kcal/mol, which is very close to the BDE of the $N-NO_2$ bond. Formation of HONO can take place by means of the intramolecular elimination reaction, where the hydrogen atom transfers from the CH_2 group to the NO_2 group (Scheme 2). To investigate the influence of H^+ and NH_4^+ on the process of HONO formation, we optimized the HONO elimination transition states for the complexes PHMX1, PHMX2 and AHMX at the B3LYP/6-31G* level of theory. These transition states were verified to have only one imaginary frequency (shown in Table 1), the vibrational mode of which connects the reactant and product. The structures of these three transition states (TS_1, TS_2 and TS_3) are given in Fig. 2 and the corresponding energy barriers are provided in Table 1.

In view of the structure, a significant difference in the active N–N, H–C and H–O bond distances can be found in the three transition sates (TS_1, TS_2 and TS_3). For example, the N–N bond lengths of the TS_1, TS_2 and TS_3 are 1.987 Å, 2.253 Å and 2.088 Å, respectively. However, it can be seen from Table 1 that the three transition states have very similar activation energy: the energy discrepancy
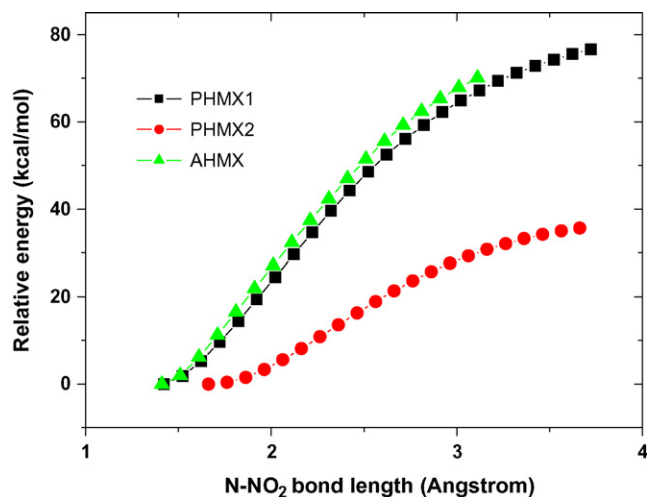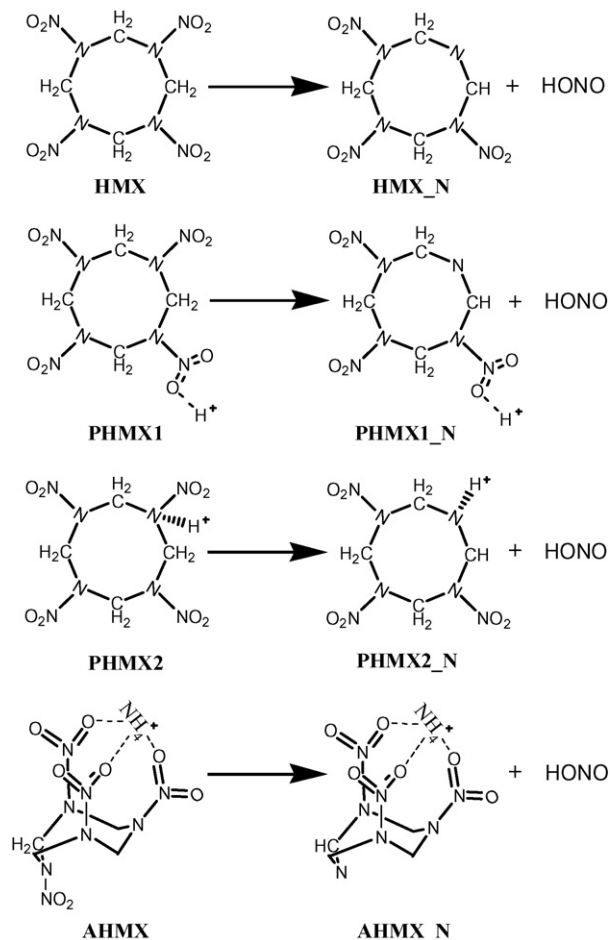

Fig. 1. Potential energy curves of heterolytic cleavage of the $N-NO_2$ bond for the complexes: PHMX1, PHMX2 and AHMX, calculated at the B3P86/6-31G** level of theory.

Table 1
Energies of the stable structures and transition states for the initial decomposition of the HMX and complexes with H^{+} and NH4^{+}, calculated at the B3LYP/6-31G* level of theory

| Structure	Total energy (a.u.)	ZPE[a] (kcal/mol)	V_i (cm^{-1})[b]	Activation energy (kcal/mol)
HMX	–	–		0
TS (HONO elimination)	–	–	–	44.6–45.0[c]
TS (C–N scission)	–	–	–	55.3[c]
PHMX1	−1196.85939	127.8		0
TS$_1$	−1196.78336	123.0	1582.4	42.9
TS$_4$	−1196.84855	126.2	95.6	5.0
PHMX2	−1196.86047	128.0		0
TS$_2$	−1196.78556	123.4	1647.6	42.4
TS$_5$	−1196.84969	126.7	144.1	5.5
AHMX	−1253.49671	153.9		0
TS$_3$	−1253.41774	148.8	1587.8	44.2

[a] Zero-point energy.
[b] Imaginary vibration frequency.
[c] Ref. [17].

of the TS$_1$ and TS$_2$ is only 0.5 kcal/mol and the TS$_3$ has the activation energy of 1.3–1.8 kcal/mol higher than TS$_1$ and TS$_2$. In addition, the activation energies of the HONO elimination for the three complexes are found to be very close to that for the HMX [17]. The small activation energy difference indicates that the H^{+}

and NH4^{+} might not evidently affect the probability of the HONO elimination of HMX.

Comparing the activation energies of the HONO elimination with the BDE of the N–NO$_2$ bond for the initial decomposition of the three complexes, we can find that the N–NO$_2$ BDEs for PHMX1
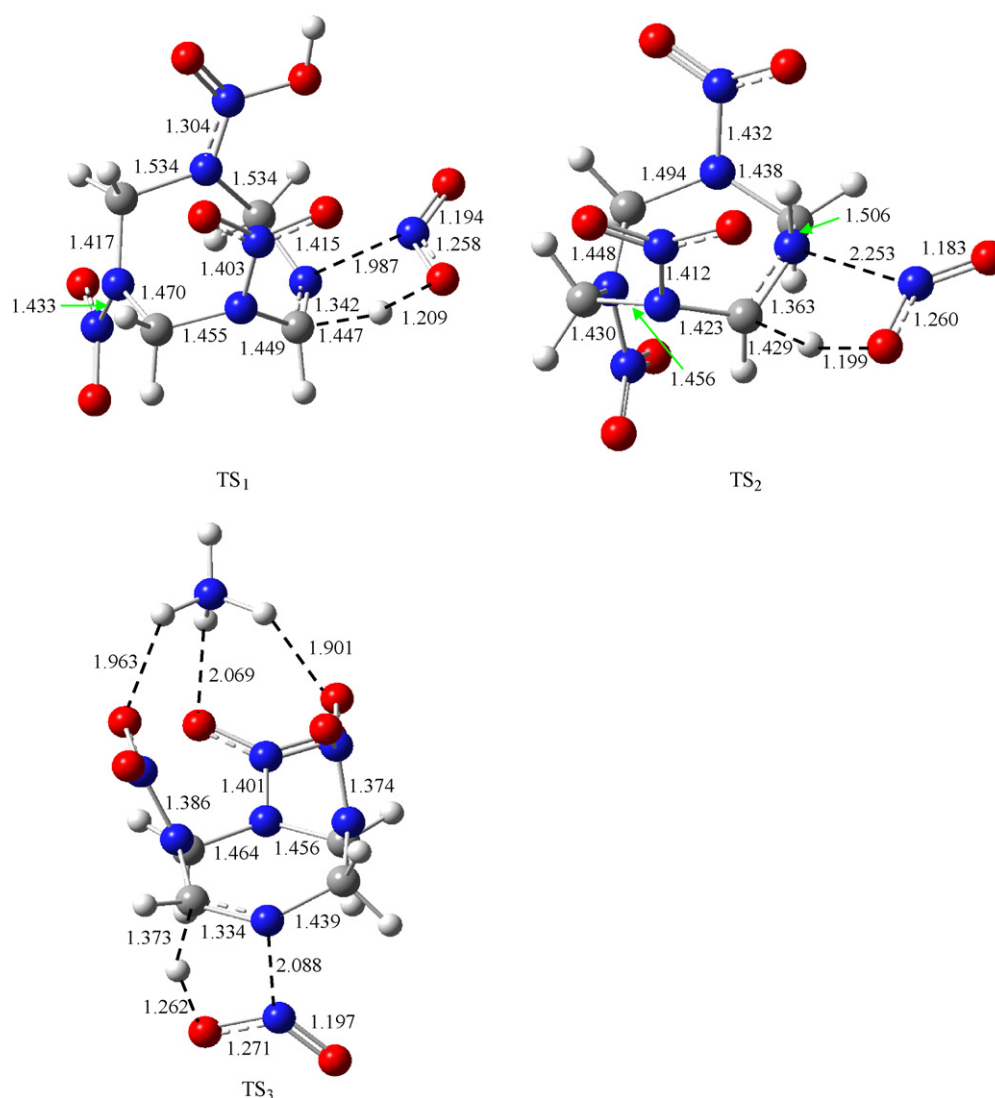
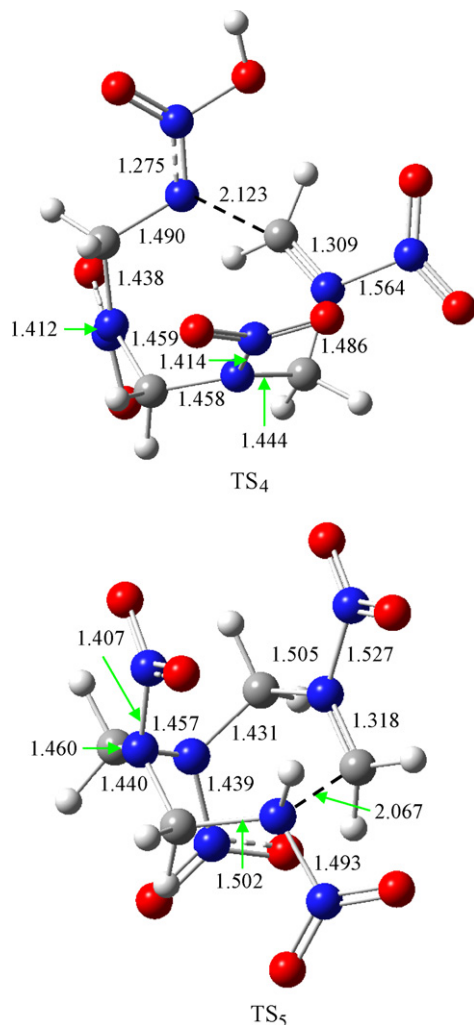

Fig. 2. Transition states of HONO elimination for the complexes: PHMX1, PHMX2 and AHMX, optimized at the B3LYP/6-31G* level of theory; bond length unit: Å.

and PHMX2 are 2.5 kcal/mol and 16.5 kcal/mol lower than the corresponding activation energies of the TS_1 and TS2, respectively. Clearly, the homolytic cleavage of the $N–NO_2$ is energetically favorable as compared to the HONO elimination when H^+ combines with the N-atom of HMX ring. However, this is not the case when H^+ combines with the O-atom of the NO_2 group. For the AHMX, the $N–NO_2$ BDE is still similar to the activation energy of the TS_3, which means that the NH_4^+ does not change the competitive relationship between $N–NO_2$ homolysis and HONO elimination during the thermal decomposition of HMX.

3.3. C–N bond scission

Experimental investigation has shown that the major products in the thermal decomposition of HMX are CH_2O and N_2O [29]. In order to understand the process of the CH_2O and N_2O formation, several plausible mechanisms has been proposed, among which oxygen migration leading to a 10-member cyclic oxy-ring molecule and subsequent decomposition was studied intensively in the past. This molecular rearrangement is generally considered as the result of the C–N bond scission. Chakraborty et al. [17] once optimized a transition state concerning the C–N bond breakage, which separates the HMX and a ring-opened biradical intermediate. The transition state has an energy barrier of 55.3 kcal/mol as compared to HMX.
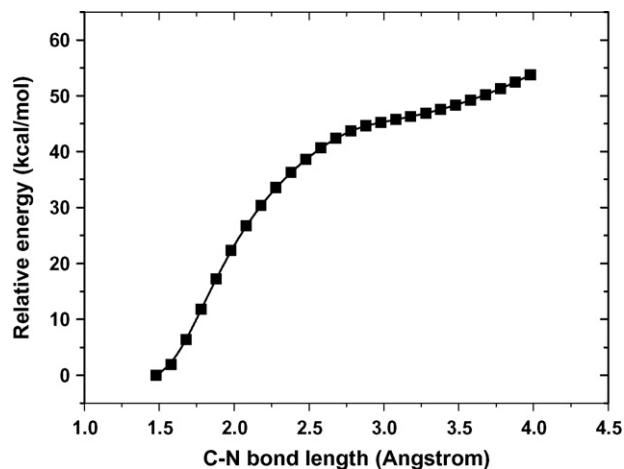
To understand the effects of H^+ and NH_4^+ on the ring-opening reaction of HMX, we examined the transition states resulted from the breakage of the neighboring C–N bond. This C–N bond has the longest bond length and smallest bond order in comparison with the other C–N bonds [24]. Two transition states, TS_4 and TS_5 for the PHMX1 and PHMX2, respectively, shown in Fig. 3, were optimized at the B3LYP/6-31G* level of theory, but the transition state for AHMX was not obtained by the same computation method. The breaking C–N bonds for TS_4 and TS_5 are 2.123 Å and 2.067 Å, respectively, and they are shorter than the corresponding value of the transition state for HMX (2.293 Å) [17]. The calculated imaginary vibration frequency (see Table 1) shows that via the transition states (TS_4 and TS_5), a product can be generated via ring-opening reaction as the C–N bond stretches.

The energies of the TS_4 and TS_5 are provided in Table 1. Interestingly, the calculated activation energies for the TS_4 and TS_5 are only 5.0 kcal/mol and 5.5 kcal/mol for the PHMX1 and PHMX2, respectively. Apparently, these activation energies are much lower than the $N–NO_2$ BDE and the energy barrier for HONO elimination. Meanwhile, they are also much lower than the activation energy of the C–N bond scission for isolated HMX (55.3 kcal/mol) [17]. Such small activation energy indicates that the C–N bond scission of HMX ring is very likely to occur when H^+ interacts with HMX to form the complexes. Theoretically, to our best knowledge, it is the first time to find the significant influence of H^+ on the C–N bond scission.

As for AHMX, because the transition state of the C–N bond rupture could not be obtained successfully by the B3LYP/6-31G* calculation, we scanned the C–N bond distance in order to further evaluate the effect of NH_4^+ on the ring-opening reaction of HMX. The potential energy of AHMX versus C–N bond length was plotted and the curve is presented in Fig. 4. It can be seen that the energy of AHMX increases with the increase in the C–N bond length. No first saddle point is found on the curve in the range from 1.5 to 4.0 Å. The potential energy profile becomes relatively flat when the C–N bond length is greater than 2.7 Å. The energy has been larger than 45 kcal/mol in the flat region. As the C–N bond length further increases, the energy still goes up and can get the barrier value of the transition state for the C–N bond rupture of HMX. It is clear that NH_4^+ may not decrease the energy barrier of the ring-open of HMX, which is quite dissimilar to the case of H^+. The effect of NH_4^+ on the ring-opening of HMX should mainly contribute to the changes in the geometry (e.g., disappearance of transition state, etc.) during the process of the C–N bond rupture.

Fig. 3. Transition states of the C–N bond scission for the complexes: PHMX1 and PHMX2, optimized at the B3LYP/6-31G* level of theory; bond length unit: Å.

Fig. 4. Potential energy curve of the C–N bond scission for the AHMX complex, calculated at the B3LYP/6-31G* level of theory.

4. Conclusion

In this work, three complexes (PHMX1, PHMX2 and AHMX), which were formed by the combination of HMX with H^+ and NH_4^+, respectively, were studied to evaluate the effects of H^+ and NH_4^+ on the initial decomposition of HMX. Three possible initial decomposition pathways of the complexes have been discussed, including the $N–NO_2$ bond fission, HONO elimination and the C–N bond dissociation of the HMX ring. Our calculation results show that the BDEs of the $N–NO_2$ homolytic cleavage are lower than the energy barriers of the $N–NO_2$ heterolysis for the complexes. H^+ and NH_4^+ cannot evidently induce the HMX to initiate the $N–NO_2$ heterolysis. As for the HONO elimination, the transition state barriers for the complexes are found to be close to that for isolated HMX. The HONO elimination of HMX is not obviously affected by the H^+ and NH_4^+. For the C–N bond scission of HMX, the calculated potential energy profile shows that NH_4^+ cannot decrease the energy barrier, but can result in the change in the geometry during the process of the C–N bond scission. When H^+ interacts with HMX to form the complexes, the transition state energies of the C–N bond scission are only 5.0 kcal/mol and 5.5 kcal/mol for the PHMX1 and PHMX2, respectively, much lower than the value for the isolated HMX. In this case, the C–N bond scission of HMX ring is found to be the most energetically favorable pathway by the comparison of the three initial decomposition pathways of HMX. In a word, the present results mean that H^+ may decrease the safety of HMX, but NH_4^+ has little influence.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmgm.2008.06.007.

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