

Mechanism for Unimolecular Decomposition of HMX (1,3,5,7-Tetranitro-1,3,5,7-tetrazocine), an ab Initio Study

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To improve the mechanistic understanding of the possible decomposition in the gas phase of the energetic material HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), we used ab initio calculations to determine the various unimolecular decomposition channels. We find three distinct mechanisms: (i) homolytic cleavage of N–N bond to form NO_2 ($M = 46$) and HMR ($M = 250$) which subsequently decomposes to form various products; (ii) successive HONO eliminations to give four HONO ($M = 47$) plus a stable intermediate ($M = 108$); (iii) O-migration from one of the NO_2 groups of HMX to neighboring C atom followed by the decomposition of intermediate ($M = 296$) to INT222 (a ring-opened RDX structure) and MN-oring ($M = 74$), which can undergo dissociation to smaller mass fragments. The decomposition scheme for HMX is similar to that for RDX presented earlier (*J. Phys. Chem. A* 2000, 104, 2261), except that concerted decomposition of HMX to four MN ($M = 74$) molecules is not a favorable decomposition pathway, whereas this pathway was found in RDX decomposition (both experimentally and theoretically). The formation of RDR-o in the N–N homolysis pathway 1 or the formation of INT222 in pathways 1 and 3 presents a unified mechanistic scheme for the decomposition of both of these nitramines. The HMX decomposition mechanism correlates with available condensed phase experimental results, but detailed comparison of the predicted gas phase energetics is not possible.

1. Introduction

The cyclic nitramines, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), are important energetic materials with applications ranging from explosives and rocket propellants to automobile air bags. They release large amounts of energy through a bulk decomposition process, which is very complicated involving both unimolecular and bimolecular reactions. Understanding the underlying complex chemical processes is essential to obtain to an improved model for combustion or detonation of these energetic materials.

Unlike RDX, where Zhao et al.¹ studied the gas phase decomposition using IRMPD technique, experimental studies of HMX are limited to condensed phase decomposition.^{2–17} Reported decomposition products vary greatly depending on such experimental conditions as heating rate, sample dimensions, and the composition of the surrounding matrix. This has made unambiguous identification of the primary decomposition products difficult. However, most experiments agree that the final gas phase products from the burning surface are smaller mass fragments such as NO_2 , N_2O , NO , CH_2O , CO , N_2 , HCN , H_2O , H_2 , and CO_2 . In order to determine the initial steps, we focus on the gas phase unimolecular decomposition mechanism of HMX.

2. Current Work

In this paper we present a comprehensive mechanistic study of the thermal decomposition of HMX based on ab initio quantum mechanics, using density functional methodology (DFT-B3LYP). This is a continuation of our previous work¹⁸ on RDX, using exactly the same methods. Section 3 surveys the experimental and theoretical work in the published literature, section 4 outlines the computational methods, and section 5

presents the results. These are compared to experiments in section 6 with concluding remarks in section 7.

3. Literature Survey

3.1. Experimental Studies. Suryanarayana et al.^{2a} studied thermal decomposition of HMX at $T = 230, 254, \text{ and } 280$ °C using mass spectrometry. They proposed a concerted decomposition mechanism of HMX to four methylenenitramine (MN) molecules, which can further decompose to CH_2O and N_2O . In a separate experiment using ion impact fragmentation of HMX, Suryanarayana et al.^{2b} detected mass fragments of 30, 46, 75, 120, 128, 148, 205, and 222 in the mass spectra.

Goshgarian³ detected large molecular masses with $m/e = 222, 175, 148, 128, 120, \text{ and } 81$ in addition to the usual smaller mass fragments in the thermal decomposition of HMX in an on-stream reactor at 240–290 °C. The mass peak at 222 was attributed to a ring open RDX structure, which can subsequently decompose to 175, 148, 128, etc.

Farber and Srivastava⁴ detected several decomposition products at $m/e = 222, 148, 128, 120, 102, 74, 56, 46, 32, 30, 28, \text{ and } 18$. 148 was the major decomposition product of HMX at 175–275 °C. They proposed a homolytic cleavage of the HMX ring to two 148 ($\text{C}_2\text{H}_4\text{N}_4\text{O}_4$) fragments which can form two MN molecules via subsequent decomposition. They also detected peaks at $m/e = 249$ and 250 as a result of the elimination of HNO_2 and NO_2 from HMX. Moreover, the $m/e = 120$ was attributed to reactions of gaseous products with the condensed phase.

Morgan and Bayer⁵ in their pyrolysis study using electron spin resonance (ESR) detected CH_2N and NO_2 radicals as the decomposition products coming from MN intermediates.

In contrast, decomposition of HMX in solution⁶ does not yield any gaseous NO or NO_2 radicals.

From high-temperature pyrolysis studies^{7–9} several plausible schemes were proposed involving the formation of $m/e = 222$, 176, 175, 148, 128, 102, 81, etc. These larger molecular masses can further dissociate to the observed smaller gaseous products.

Using simultaneous thermogravimetric modulated beam mass spectrometry and isotope scrambling experiments, Behrens and Bulusu¹⁰ and Behrens^{11,12} observed gaseous pyrolysis products such as H₂O, HCN, CO, CH₂O, NO, N₂O, CH₃NHCHO, (CH₃)₂NNO, 1-nitroso-3,5,7-trinitro-1,3,5,7-tetrazocine (ONTNTA), and a nonvolatile polyamide residue between 210 and 235 °C. They suggested several different reaction branches to understand the complex decomposition process of HMX in condensed phase. Their results also support the water-catalyzed decomposition of HMX where water is trapped within HMX particles.^{8,9,13}

In the recent CO₂ laser assisted combustion of HMX, Tang et al.^{14,15} detected several larger molecular masses at 97, 81, 70, 54, 47, 45, 43, and 42 as minor species in addition to the usual small mass fragments in the HMX flame structure.¹⁶

Brill¹⁷ suggested two competing global reactions during the thermal decomposition of condensed phase HMX:



However, in laser-assisted self-oscillating burning of HMX, Tang et al.¹⁵ concluded that a multiple step reaction at condensed phase might explain the experimental data more realistically.

Summarizing the wide array of condensed phase experimental observations, there is agreement in identifying the major gaseous products in the HMX flame structure. However, several plausible mechanistic schemes have been proposed for the condensed phase decomposition of HMX. Most experimental studies support the formation of CH₂O, N₂O, HONO, and HCN as the condensed phase decomposition products, which further decompose to the gaseous products in the HMX flame.

3.2. Theoretical Studies. Very few theoretical studies have previously been reported for HMX. A conformational study based on quantum chemistry (DFT at the B3LYP level) was used to derive a force field.¹⁹ Using the force field the effect of hydrostatic pressure on the packing of HMX crystal^{20,21} was studied with molecular dynamics simulations. A quantum mechanics calculation (DFT at the B3LYP level) of the electronic structure was used to predict the nuclear quadrupole interactions in HMX.²²

Melius and Binkley²³ used empirically corrected ab initio quantum mechanics (BAC-MP4) on nitramine-containing systems to estimate the energetics of the reactants, products, and possible intermediates for RDX and HMX, suggesting some possible decomposition mechanisms. Their studies also included the possibility of water-catalyzed decomposition of HMX.

4. Computational Methods

We optimized the geometries of the reactants, products, intermediates, and transition states (TS) at the B3LYP flavor of density functional theory. This includes the generalized gradient approximation (Becke 1988 non local gradient correction), exact exchange using the Becke three-parameter exchange functional,²⁴ and the nonlocal correlation functional of Lee, Yang, and Parr.²⁵ We used the 6-31G(d) basis set, which is consistent with our earlier investigations on RDX. This level of theory is expected to predict the energetics of large molecular systems like RDX to within a few kcal/mol.^{26,27}

All stationary points have been positively identified as local minima [all curvatures positive from diagonalizing the Hessian,

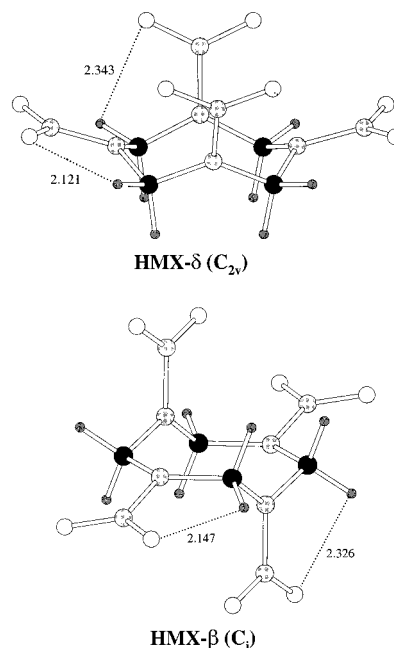


Figure 1. Optimized geometries of HMX in δ and β form.

(NIMAG) = 0] or as transition states TS [exactly one negative curvature, NIMAG = 1]. Vibrational frequencies were calculated at all stationary points to obtain zero point energies (ZPE) and thermodynamic parameters (entropy and enthalpy as a function of temperature). All calculations were carried out with Jaguar quantum chemistry program package.²⁸

5. Results

Figure 1 shows the optimized geometry of HMX for delta (a boatlike conformation) and beta (a chairlike conformation). The optimized structures of the decomposition products are shown in Figure 2 while the various TS are presented in Figure 3. Table 1 gives the relative energies of two possible initial decomposition processes:

- (i) N–N homolysis and
- (ii) HONO elimination.

The vibrational frequencies of all the stable intermediates and some important products are given in Table 2 while the frequencies for all the TS are given in Table 3.

The potential energy profile of the unimolecular decomposition mechanism is illustrated in Figures 4, 5, and 6. These various results for HMX and the analogous results for RDX¹⁸ are combined into a generalized decomposition scheme for RDX and HMX in Figure 7.

The optimized geometries (XYZ coordinates) of all the reactants, products, intermediates, and TS are included as supplementary information (Tables S1–S12).

Here and in the Discussion, the energies are corrected for ZPE. Where this correction is *not* made, we will indicate so by adding “no ZPE”.

5.1. Conformations of HMX. Crystalline HMX can exist in four polymorphic phases: α , β , γ , and δ . The β form, stable at room temperature, has a monoclinic structure with two chairlike molecules of C_1 symmetry per unit cell.²⁹ The δ HMX crystal, stable in the temperature range 103–162 °C, has C_2 symmetry and crystallizes in orthorhombic symmetry with eight boatlike molecules per unit cell.³⁰ The molecular structures of the α and γ forms of HMX are quite similar to that of δ form, but the precise 2-fold symmetry axis of δ is missing.^{31,32} In addition, the γ form is a hydrate.

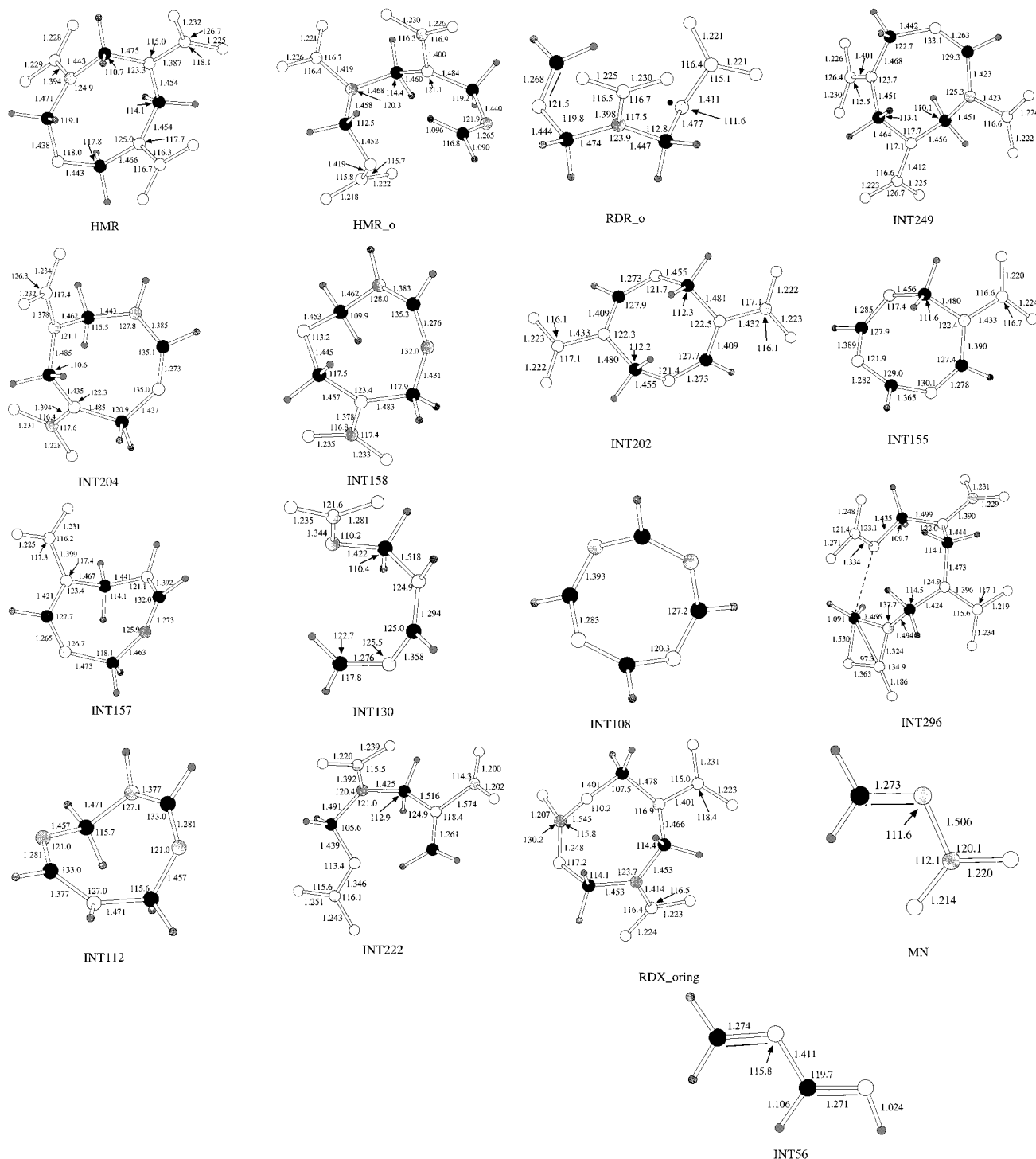


Figure 2. Optimized structures of the intermediates and some important products in the unimolecular decomposition of HMX. The large solid, dark gray, and light gray circles represent the C, N, and O, respectively, and the small gray circle represents H atoms.

Thus, considering the various polymorphic forms of HMX, we find two primary molecular conformations, chair (β) and boat (δ), as shown in Figure 1. The β form is 2.5 kcal/mol *more* stable than the δ form (2.0 kcal/mol including ZPE) at the B3LYP/6-31G(d) level of theory. This compares well with the energy differences of 2.1 kcal/mol predicted at the B3LYP/6-311G(d,p) level, 3.5 ± 1.0 kcal/mol at the B3LYP/6-311G(d,p)//MP2/6-311G(d,p) level. Indeed using the classical force field,¹⁹ the energy difference is 2.6 kcal/mol.

It is conceivable that flexible cyclic nitramines like HMX might exhibit some additional metastable nonsymmetric low-energy conformations, besides the chair and boat forms. How-

ever, such low-energy conformers would have little impact on the mechanism of thermal decomposition. In this work, we perform all our calculations on the β conformation, the most stable form and the one exhibited in the crystal at room temperature.

5.2. Initiation of Decomposition. Three distinct initial decomposition channels have been identified for RDX in our earlier study:²³

- (1) concerted ring breaking,
- (2) homolysis of N–NO₂ bond, and
- (3) HONO elimination.

Since the molecular structure of HMX has NO₂ groups with two different orientations (two equatorial and two axial, see

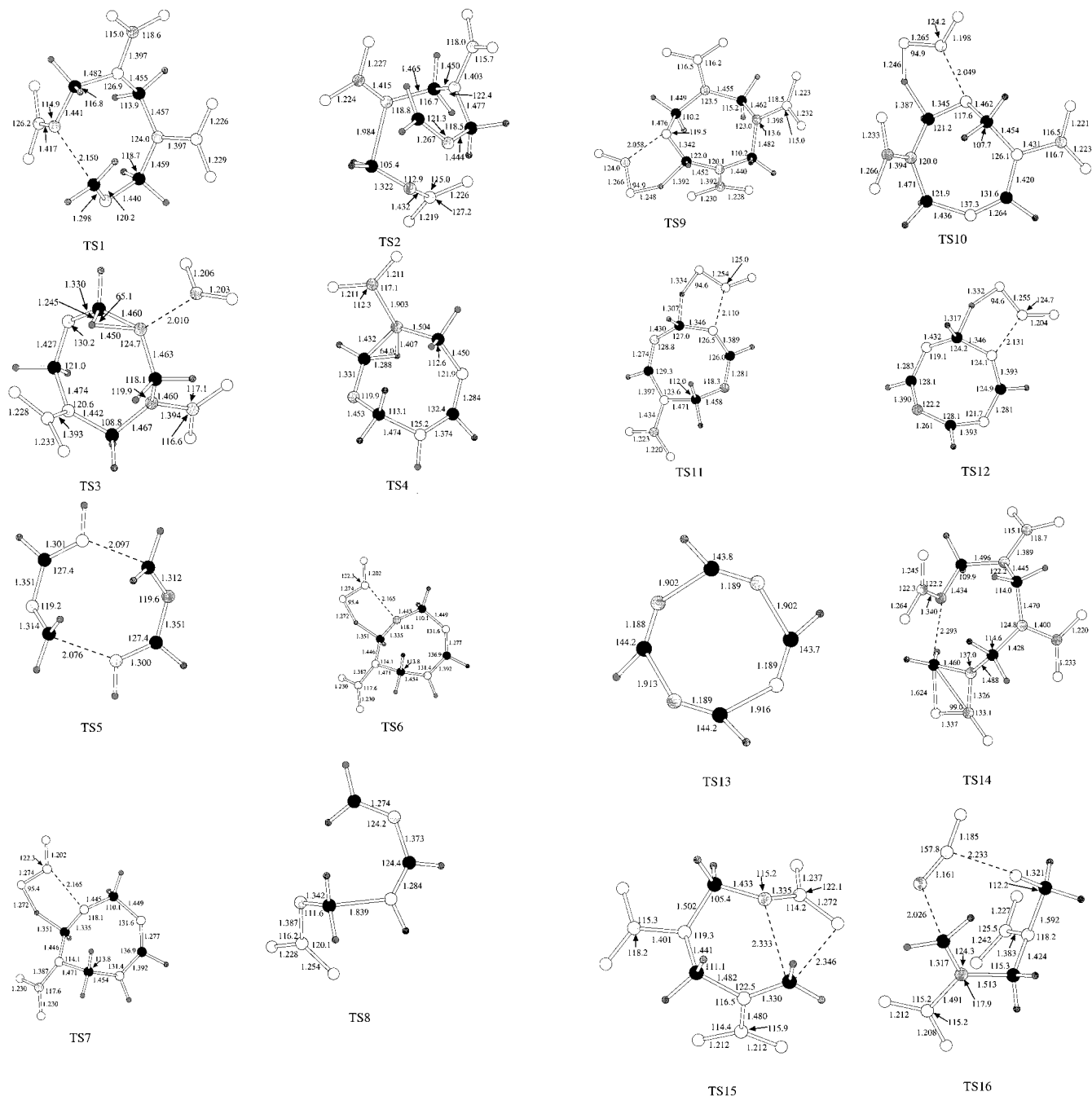


Figure 3. Optimized structures of the transition states in the unimolecular decomposition of HMX. Symbols stand for C, N, O and H atoms, respectively, as described in Figure 2.

TABLE 1: Relative Energies^a for Two Competitive Initial Decomposition Processes in HMX

| | β -HMX | δ -HMX |
|---------------------------------|--------------|---------------|
| N-NO ₂ bond cleavage | | |
| eq HMR radical | 43.6 | 45.6 |
| ax HMR radical | 46.5 | 45.4 |
| HONO elimination TS | 49.0 | 50.6 |

^a Without ZPE correction.

Figure 1), it is likely that there will be preferential elimination of one NO₂ group over the other. We explored these possibilities, with the results summarized in Table 1.

The concerted ring scission involves breaking alternate C-N bonds and multiple possibilities do not exist.

Table 1 clearly shows that removal of NO₂ from equatorial position generates the most stable C₄H₈N₇O₆ (HMR) radical. 43.6 kcal/mol energy is required to remove one equatorial NO₂ whereas 46.5 kcal/mol is required for removing the axial NO₂ from β HMX. In δ HMX, dissociation energy of both sets of N-NO₂ bonds are roughly equal. Thus, in β HMX the N-N homolytic pathway can initiate by the preferential elimination of an equatorial NO₂ group.

The concerted HONO elimination involves breaking of both N-NO₂ and C-H bonds. The short nonbonded N-O...H-C distance plays an important role in HONO elimination. The N-O...H-C distance is smaller for equatorial NO₂ groups in both β and δ HMX as shown in Figure 1. Because of weak equatorial NO₂ bond and closer nonbonded O...H distance, the concerted HONO elimination will preferentially occur from

TABLE 3 (Continued)

| | | | | | | | | | | | | | | |
|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| TS11 | | | | | | | | | | | | | | |
| -1436 | 38 | 68 | 96 | 118 | 144 | 168 | 205 | 237 | 303 | 323 | 395 | 420 | 458 | 486 |
| 511 | 524 | 576 | 659 | 669 | 739 | 772 | 789 | 805 | 875 | 907 | 944 | 966 | 987 | 999 |
| 1020 | 1061 | 1139 | 1245 | 1266 | 1317 | 1325 | 1337 | 1344 | 1399 | 1402 | 1445 | 1481 | 1525 | 1593 |
| 1663 | 1697 | 1728 | 1770 | 3060 | 3066 | 3167 | 3192 | 3218 | | | | | | |
| TS12 | | | | | | | | | | | | | | |
| -1441 | 84 | 119 | 160 | 202 | 236 | 285 | 315 | 351 | 410 | 484 | 502 | 567 | 680 | 728 |
| 735 | 799 | 846 | 957 | 964 | 995 | 1002 | 1014 | 1026 | 1044 | 1097 | 1237 | 1328 | 1332 | 1392 |
| 1410 | 1423 | 1481 | 1571 | 1645 | 1687 | 1695 | 1764 | 3057 | 3137 | 3143 | 3181 | | | |
| TS13 | | | | | | | | | | | | | | |
| -740 | 94 | 100 | 134 | 156 | 158 | 164 | 183 | 192 | 291 | 517 | 523 | 525 | 576 | 794 |
| 802 | 807 | 813 | 1041 | 1103 | 1109 | 1124 | 1817 | 1991 | 1994 | 2035 | 3298 | 3300 | 3304 | 3306 |
| TS14 | | | | | | | | | | | | | | |
| -251 | 38 | 61 | 73 | 90 | 98 | 110 | 115 | 129 | 148 | 160 | 191 | 195 | 239 | 241 |
| 288 | 358 | 365 | 379 | 389 | 414 | 436 | 474 | 594 | 595 | 636 | 648 | 660 | 698 | 705 |
| 719 | 751 | 753 | 760 | 795 | 831 | 861 | 878 | 933 | 933 | 943 | 1043 | 1052 | 1092 | 1102 |
| 1114 | 1132 | 1180 | 1211 | 1221 | 1225 | 1285 | 1295 | 1301 | 1314 | 1337 | 1357 | 1389 | 1398 | 1410 |
| 1436 | 1443 | 1456 | 1478 | 1499 | 1509 | 1537 | 1650 | 1681 | 1786 | 3074 | 3095 | 3104 | 3124 | 3157 |
| 3165 | 3186 | 3305 | | | | | | | | | | | | |
| TS15 | | | | | | | | | | | | | | |
| -379 | 46 | 65 | 69 | 81 | 108 | 127 | 196 | 239 | 267 | 325 | 341 | 364 | 397 | 433 |
| 443 | 566 | 586 | 609 | 658 | 687 | 709 | 752 | 757 | 765 | 784 | 830 | 839 | 918 | 932 |
| 944 | 990 | 1070 | 1127 | 1173 | 1210 | 1224 | 1264 | 1297 | 1314 | 1331 | 1346 | 1371 | 1416 | 1431 |
| 1475 | 1506 | 1530 | 1535 | 1665 | 1756 | 3033 | 3071 | 3136 | 3204 | 3246 | 3362 | | | |
| TS16 | | | | | | | | | | | | | | |
| -333 | 46 | 58 | 66 | 83 | 99 | 109 | 143 | 182 | 227 | 237 | 289 | 318 | 334 | 374 |
| 397 | 427 | 453 | 536 | 564 | 576 | 598 | 625 | 682 | 727 | 761 | 772 | 816 | 849 | 910 |
| 973 | 1035 | 1081 | 1125 | 1205 | 1257 | 1260 | 1303 | 1307 | 1328 | 1342 | 1352 | 1376 | 1411 | 1427 |
| 1475 | 1536 | 1549 | 1630 | 1763 | 2151 | 2910 | 3017 | 3022 | 3125 | 3196 | 3275 | | | |

^a All frequencies are in cm^{-1} , and the negative numbers indicate imaginary frequencies.

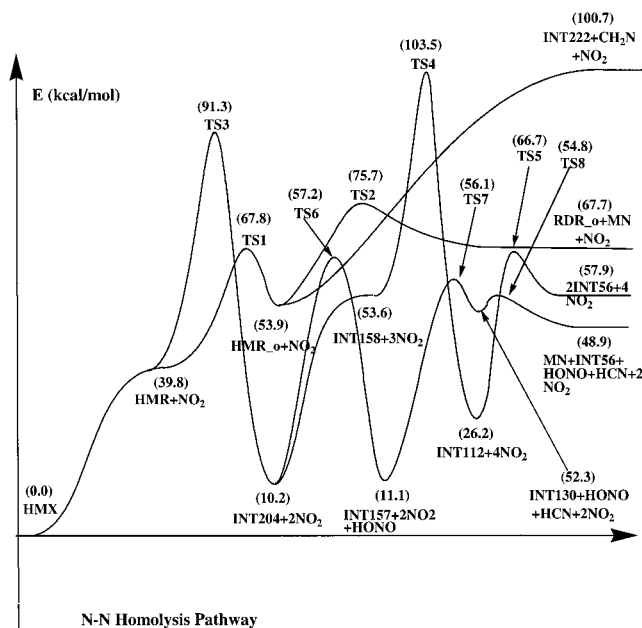


Figure 4. Potential energy profile for N–N homolysis from HMX and further decomposition of the intermediate radicals.

equatorial NO_2 . The HONO elimination from δ HMX is 1.6 kcal/mol higher than from β HMX.

5.3. Reaction Path 1. Homolytic N–N Bond Fission plus Subsequent Decomposition. **5.3.1. N–NO₂ Homolysis To Form HMR.** N–NO₂ bond breaking is most likely a barrierless low-energy decomposition pathway for both RDX and HMX. As discussed above, elimination of NO_2 will occur preferentially from the equatorial position. We calculate a N–N bond dissociation energy of 39.8 kcal/mol (including ZPE) for HMX. This is in very good agreement with our earlier calculated N–N bond dissociation energy of 39.0 kcal/mol for RDX.¹⁸

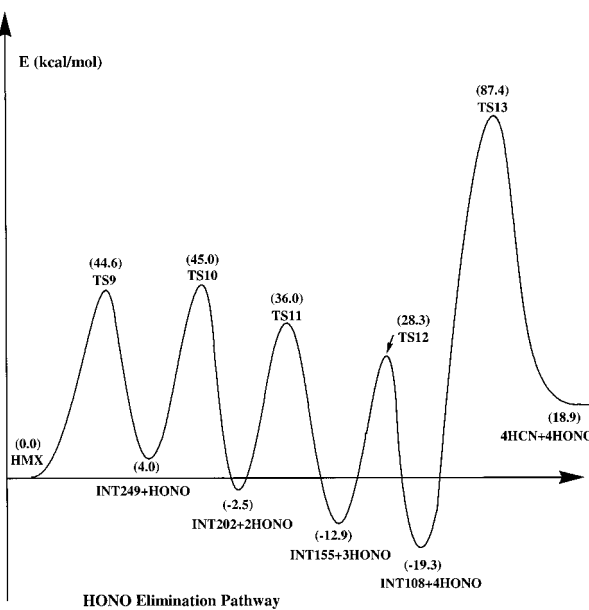


Figure 5. Potential energy profile for HONO elimination from HMX and following decompositions.

In their BAC-MP4 study, Melius and Binkley estimated a dissociation energy of ~ 48 kcal/mol for the N–NO₂ bond.²³ Their estimation was based on the assumption that the N–N bond strength in RDX and HMX should be very similar to that of some smaller nitramines, such as methylenenitramine. However, the N–N bond in both RDX and HMX is somewhat weaker than that of some related nitramines.²⁷ The estimated N–N bond dissociation energies [at the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) level with scaled HF/6-31G(d) ZPE correction] in related nitramines are 46 (dimethylnitramine), 48 (1-nitropiperidine), and 49 (1-nitro-1,3,5-triazine), where in each

the decomposition of RDX, is the ring-opened structure of RDX radical (RDR).¹⁸ Possible decomposition of RDR-o to various smaller mass fragments was discussed in detail in our earlier RDX study.¹⁸

Alternatively, HMR-o can eliminate one CH₂N radical to form INT222 + CH₂N. We scanned the reaction path of CH₂N elimination and did not find any appreciable barrier. Since the elimination of CH₂N proceeds via a simple homolytic cleavage of the C–N bond and does not involve any intramolecular rearrangement, absence of reaction barrier is understandable. INT222 has the same molecular weight and stoichiometry of RDX. It is actually a ring-opened biradical structure of RDX resulting from the rupture of one of the ring CN bonds.

INT222 is 56.0 kcal/mol higher in energy than RDX. Formation of INT222 from RDX thus occurs through a barrierless dissociation of one of the ring C–N bonds. C–N bond energies of some related compounds like nitromethane and dimethylnitramine at similar B3LYP level of theory with variety of basis sets range between 52 and 55 kcal/mol.³⁴ The simultaneous breaking of three CN bonds in RDX, leading to the formation of three MN molecules, required ~59.4 kcal/mol at the same level of theory.¹⁸ INT222 + CH₂N is 100.7 kcal/mol more endothermic than HMX. Further decomposition of INT222 to three MN molecules would require even higher energy. On the other hand, it could recombine back to RDX, which can undergo further dissociations.

Formation of RDR-o and INT222 in the thermal decomposition of HMX makes the connection between HMX and RDX decomposition mechanisms and supports the observed similarity in their experimental spectra. This will be discussed in more detail in the discussion section.

5.3.4. Subsequent NO₂ Elimination from HMR. **5.3.4.1. Elimination of second NO₂.** The elimination of a second NO₂ group from HMR becomes difficult due to formation of a biradical (unpaired spin on each of the two N radical centers). This high-energy conformation can be avoided by H-migration with simultaneous NO₂ elimination. This leads to TS3, as shown in Figure 4. As the N–NO₂ distance increases in TS3, the H atom from the neighboring CH₂ group migrates to the N-atom and the adjacent C–N bond (between the N radical in HMR and H migrating C) gains partial double bond character (1.330 Å). The breaking N–N bond in TS3 is 2.010 Å and the migrating H atom is 1.450 and 1.245 Å away from the N and C atoms, respectively. TS3 has a barrier of 51.5 kcal/mol over HMR and goes to INT204. Since TS3 involves a hydrogen migration, it has a large negative eigenvalue of 2008 cm⁻¹. INT204 is a relatively stable intermediate with only 10.2 kcal/mol endothermicity over HMX.

5.3.4.2. Elimination of Third NO₂. The third NO₂ elimination from INT204 involving N–NO₂ homolytic cleavage requires an additional 43.4 kcal/mol. Thus the formation of radical intermediate INT158 does not have any appreciable reaction barrier similar to the formation of HMR from HMX.

5.3.4.3. Elimination of Fourth NO₂. INT158 can further undergo NO₂ elimination in a way similar to the second NO₂ elimination from HMR. The transition structure TS4 involves simultaneous NO₂ elimination and H migration to avoid the formation of the high-energy biradical species. TS4 has a barrier of 49.9 kcal/mol over radical intermediate INT158 and properly connects INT158 with INT112. Elimination of NO₂ and subsequent H migration to the N-atom allows π bonding between N-radical and H migrating C. This in turn brings planarity to the ring. Intermediate INT112 has both the C–N π bonds at ~1.28 Å.

5.3.4.4. Concerted Breaking of INT112. INT112 can further decompose in a concerted way to two CH₂NCHNH (INT56, *M* = 56) via TS5. The breaking CN bonds in TS5 are 2.076 and 2.097 Å, respectively. The degradation product INT56 has a planar structure and was also found in the subsequent NO₂ elimination pathway of RDX.¹⁸

5.3.4.5. HONO Elimination from INT204. Instead of eliminating the third NO₂, an alternate pathway for the decomposition of INT204 might be HONO elimination and subsequent decomposition. We looked for an alternative low-energy pathway of formation of INT56. The HONO elimination preferentially takes place via the elimination of CH₂ hydrogen next to NH in INT204 and neighboring NO₂ group. The breaking N–N bond in TS6 is 2.165 Å apart and the migrating H atom is 1.351 and 1.272 Å away from C and O atom. Formation of CN π bond brings more planarity to INT157. TS6 has a barrier of 47.0 kcal/mol over INT204. Thus the barrier for HONO elimination is higher than the third NO₂ elimination from INT204. But the associated lower endothermicity in the subsequent decomposition makes the latter pathway more favorable.

5.3.4.6. Decomposition of INT157 to MN + INT56 + HCN. INT157, which is 11.1 kcal/mol less stable than HMX, can further dissociate to MN + INT56 + HCN. We looked for a possible concerted decomposition pathway for this. Instead, we find a stepwise mechanism via the formation and decomposition of INT130. The barrier for the formation of INT130 at TS7 is 45.0 kcal/mol. The formation of INT130 occurs by the elimination of an HCN molecule from INT157 through a ring-breaking mechanism. INT130 was also observed as an intermediate in our earlier RDX decomposition mechanism, which upon further decomposition leads to MN and INT56. INT130 formed here is a ring-opened structure of INT130 formed in the RDX decomposition mechanism. The ring-opened INT130 is a very unstable intermediate and requires only 2.5 kcal/mol to decompose to MN and INT56. The decomposition transition state TS8 has the breaking CN bond at 1.839 Å. The final products are 48.9 kcal/mol more endothermic than HMX.

5.3.5. Summary of N–N Homolysis Pathway Calculations. Four different product channels have been identified for the N–N homolysis pathway (Figure 4). Two of these channels, degradation of HMX to RDR-o and INT222, relate the decomposition mechanism of HMX to RDX.

5.4. Reaction Pathway 2: Concerted HONO Elimination. The most exothermic reaction pathway found in our earlier RDX decomposition mechanism was the consecutive HONO elimination leading to 3HONO + 3HCN.¹⁸ We searched for similar pathway in the HMX decomposition.

Due to the weak equatorial N–N bond and close nonbonded CH::O contact, HONO elimination can occur by preferential elimination of equatorial NO₂ in HMX. TS9 is the transition structure for first HONO elimination and has a barrier of 44.6 kcal/mol over HMX. Thus, the initiation of HONO elimination requires an additional 5.6 kcal/mol over N–N homolytic cleavage. The structure of TS9 is very similar to the HONO elimination TS found in RDX and other related compounds: dimethylnitramine³⁵ and MN.^{33,36} The breaking N–N bond is 2.058 Å and the forming CN π and OH σ bonds are 1.342 and 1.248 Å. The HONO elimination barrier in HMX is 4.8 kcal/mol higher than in RDX. HONO elimination leads to INT249, which is 4.0 kcal/mol endothermic than HMX (Figure 5).

5.4.1. Second and Third HONO Elimination. INT249 can eliminate a molecule of HONO via TS10 to form INT202, leading to TS10 with energy 45.0 kcal/mol above HMX. INT202

can subsequently eliminate another molecule of HONO via TS11. TS11 has a barrier of 36.0 kcal/mol over HMX, leading to a stable intermediate INT155. The successive HONO elimination sites from INT249 and INT202 were chosen based on the closest nonbonded O...H contacts. INT202 and INT155 are respectively 2.5 and 12.9 kcal/mol more exothermic than HMX.

5.4.2. Fourth HONO Elimination. INT155 can subsequently eliminate another HONO molecule via TS12 to form a stable intermediate (INT108). TS12 is 28.3 kcal/mol above HMX. The decomposition of HMX to 4 HONO + INT108 is exothermic by 19.3 kcal/mol. Of the various unimolecular decompositions from HMX, this is the most exothermic (energy released) pathway found in the present study. This is also in agreement with our earlier RDX decomposition study.¹⁸

In TS12 the breaking N–N bond is 2.131 Å and the C–H bond is 1.317 Å whereas the forming OH bond is 1.332 Å and the CN π bond is 1.346 Å, respectively. The CN π bonds in INT108 are localized due to its nonplanar conformation. Thus, there are two distinct sets of C–N bonds of double (1.283 Å) and single (1.383 Å) character.

5.4.3. INT108 Concerted Decomposition. INT108 is a stable intermediate and it decomposes through a concerted mechanism to four HCN through an energy barrier of 106.7 kcal/mol (TS13) located by simultaneously scanning all the four CN σ bonds. We did not put any symmetry restriction to locate TS13. Considering that INT108 + 4HONO is 19.3 kcal/mol more exothermic than HMX, the overall energy required for the decomposition is 87.4 kcal/mol with respect to HMX. The final products, 4HCN + 4HONO are 18.9 kcal/mol endothermic from HMX.

TS13 is a nonplanar TS with the breaking CN bonds at \sim 1.9 Å, while the fragment HCN molecules are each close to the final product linear structure (H–C–N angles \sim 144°).

5.5. Reaction Pathway 3: CH₂O + N₂O Formation. Formation of CH₂O and N₂O has been extensively considered as the major decomposition products in the thermal decomposition of HMX.^{2–17} However, there is no conclusive experimental identification of the source of these molecules. Two possible mechanisms has been proposed:

- (i) direct decomposition of HMX via oxygen migration and subsequent decomposition, and
- (ii) secondary decomposition from MN.

To understand the mechanism of CH₂O and N₂O formation, we examined the former mechanism.

To locate the transition state of oxygen migration, we scanned one of the nonbonded C...O distance in HMX. As the oxygen atom of NO₂ group approaches the C atom, the HMX ring opens up via the breaking of the neighboring CN bond, leading to a ring-opened INT296 intermediate (Figures 2 and 6). The oxygen migration generally leads to a oxy-ring type structure, which can undergo further decomposition to smaller products. The 10-member cyclic oxy-ring molecule might not be stable in the case of HMX and instead the neighboring CN bond breaks in TS14 to form an acyclic biradical intermediate INT296. TS14 has a barrier of 55.3 kcal/mol over HMX. The forming C–O bond is 1.624 Å and the breaking CN bond is 2.293 Å in TS14. INT296 is a ring-opened structure with one end having a four-member oxy-ring and the other end the N–NO₂ radical. The radical center in N–NO₂ is delocalized toward the O atom. The larger N–O bond (1.22–1.27 Å) and shorter N–N bond (1.40–1.33 Å) is evidence for this. The structure and energy of INT296 are very close to the TS14 and only 0.3 kcal/mol more stable than TS14 without ZPE correction. With ZPE correction the

energies of TS14 and INT296 are very close, but optimization along the reaction coordinate of the imaginary frequency in TS14 leads to INT296. INT296 can further decompose to INT222 and the four-membered oxy-ring (–OCH₂NN(O)–, MN-oring) structure. Scanning the CN bond reveals that the formation of INT222 + MN-oring is a barrier less process from INT296 with an overall endothermicity of 80.3 kcal/mol with respect to HMX. INT222 has the same ring-opened RDX structure found in the N–N homolysis pathway.

MN-oring is the stable intermediate formed in the oxygen migration pathway of MN to form CH₂O and N₂O. This has also been identified as a stable intermediate in MN decomposition mechanism.³³ Decomposition of MN-oring to CH₂O + N₂O requires 25.3 kcal/mol. This is in good agreement with the G2M calculated energy barrier of 25.8 kcal/mol.³³

5.5.1. Formation of CH₂O + N₂O from RDX. As mentioned above, CH₂O and N₂O can be formed directly from RDX or HMX by an oxygen transfer mechanism in addition to the much considered MN decomposition pathway. We examined this an additional decomposition pathway of RDX after our earlier work.¹⁸

To locate the transition structure of oxygen migration, we scan one of the nonbonded C...O distances similar to HMX. As the oxygen atom of the NO₂ group approaches the C atom of the CH₂, the CN bond between the N atom (containing the NO₂ group) and the C atom breaks to form an eight-member oxy-ring intermediate (RDX-oring). As mentioned earlier, this results in a ring-opened intermediate in HMX, instead of forming a similar 10 member oxy-ring structure. The RDX-oring formed via the O-atom migration is quite stable intermediate and has 14.0 kcal/mol more energy than RDX (Figure 6b). The transition structure for O migration TS15 has a barrier of 52.7 kcal/mol over RDX. This is quite high compared to the other two initial decomposition processes in RDX: N–N homolysis 39.0 kcal/mol and HONO elimination 39.2 kcal/mol. TS15 has a very loose structure. The breaking C–N and N–O π bonds are 2.333 and 1.272 Å, and the forming C–O and N–N π bonds are 2.346 and 1.335 Å. Transits in the forward and backward directions along the imaginary frequency reaction coordinate confirm that TS15 properly connects RDX with RDX-oring.

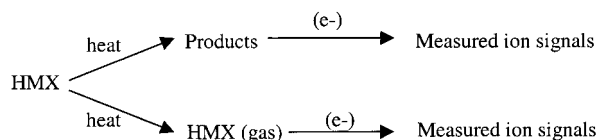
The N–O, C–O, and N–N bonds are 1.545, 1.401, and 1.248 Å, respectively, in RDX-oring. The structure of RDX-oring is shown in Figure 2. RDX-oring can further dissociate to CH₂O + N₂O + 2MN in a concerted manner via TS16. The barrier for this concerted breaking is 24.2 kcal/mol. The structure of TS16 is shown in Figure 3. The final products are 10.5 kcal/mol endothermic than RDX. The N₂O fragment in TS16 is quite close to its isolated structure and the breaking C–N and N–O bonds are 2.026 and 2.233 Å. The dissociating CH₂O fragment has an intermediate character with the breaking C–N bond at 1.592 Å, only 0.13 Å longer than the C–N bond in RDX. The C–O bond in the CH₂O fragment is 1.321 Å, between a double and single bond character. The other two MN fragments are still connected with the dissociating C–N bond at 1.513 Å, but will undergo dissociation along the reaction coordinate to form two MN fragments.

5.5.2. Summary of *o*-Migration Calculations. Additional pathways for the formation of CH₂O and N₂O directly from RDX and HMX have been identified. Associated large endothermicity suggests that CH₂O and N₂O formation preferably occur through the secondary decomposition of MN for HMX. In contrast, the direct oxygen migration pathway is an important reaction channel for the formation of CH₂O and N₂O in RDX.

6. Discussion

The commonality between the HMX and RDX decomposition pathways led us to propose a unified mechanism. This is pictorially presented in Figure 7. Majority of the decomposition products observed experimentally can be accounted for by the present scheme. It should be noted that the present work and our earlier paper¹⁸ study gas phase kinetics. There is some correlation of gas phase mechanisms with condensed phase experimental results. Furthermore, the present scheme cannot explain some of the mass fragments resulting from bimolecular reactions such as ONTNTA or ONDNNTA observed by Behrens and Bulusu^{10,37} in the thermal decomposition of RDX and HMX.

6.1. Identification of Mass Fragments with $M \geq 100$. HMX pyrolysis is a complex phenomena involving nonlinear processes as demonstrated by the temporal dependence of the thermally decomposed products.^{10–12} Most recent experiments on HMX^{10–12,14,15} detected mass fragments of $m/z \leq 100$ as the major thermal decomposition products. Behrens has argued that the higher molecular weight fragments detected in some earlier experiments, such as flow reactor mass spectrometry (FRMS) and solid probe mass spectrometry (SPMS) and those using appearance energy measurements,^{3,4} could not be unambiguously considered as thermal decomposition products. These higher molecular weight fragments could have originated from ion fragmentation of HMX vapor (second channel below):



In these experiments, HMX is heated in a vacuum environment and then electron bombardment is used to ionize and subsequently measure the mass fragments. These higher molecular weight species are similar to those detected in the mass spectrum of HMX.^{2b} Therefore, in our discussions, the calculated high molecular weight mass fragments are compared primarily with the mass spectroscopic data^{2b} and with earlier thermal decomposition data^{3,4} where appropriate. Within the scope of the present ab initio study we cannot characterize the ion fragmentation process of HMX, which requires cross sections for electron bombardment reactions.

Our present scheme can explain the following mass fragments with $m/e \geq 100$: 296, 250, 249, 222, 204, 202, 176, 175, 158, 157, 155, 149, 130, 128, 108, and 102. Many of these fragments are from the short-lived intermediates, which undergo further decomposition instantaneously and hence might not be observed experimentally. Ions of m/z values of 75, 120, 128, 148, and 222 are the major ions observed in the mass spectrum of HMX.^{2b} On the other hand, larger mass fragments detected experimentally in the thermal pyrolysis are 280, 250, 249, 222, 206, 176, 175, 148, 132, 128, 120, and 102. However, Zhao et al. detected only two of these larger mass fragments at 120 and 102 in their laser photolysis of the RDX molecular beam.¹ Masses at $m/e = 280$ (ONTNTA) and 206 (ONDNTA) were detected by Behrens and Bulusu in the thermal pyrolysis of HMX and RDX.^{10,37} These nitroso compounds were considered as resulting from removal of a NO_2 group followed by association of NO radical at the N-radical center of RDX or HMX. Such bimolecular formations of nitroso compounds have not been addressed in our unimolecular decomposition scheme.

Mass fragments of 250 and 176 are HMR and RDR radical generated after removal of NO_2 radical from HMX and RDX, respectively. These radicals have been identified in the con-

densed phase decomposition of RDX and HMX.^{4,8,9} Zhao et al. did not observe $m/e = 176$ in their IRMPD study.¹ Presence of excess energy in the laser pulse might cause further decomposition of this to smaller mass fragments. Mass fragments 249 and 175 result from elimination of the first HONO molecule from HMX and RDX. The computed HONO elimination pathway for RDX and HMX suggest that these mass fragments would not be very stable and should undergo further dissociation to smaller more stable species. Furthermore, the mass peak at 128 is assigned to the structure resulting from the second HONO elimination in RDX. Goshgarian³ and Fifer⁹ observed the mass peak at 128 resulting from HONO elimination from RDX and from the HMX fragments at $M = 222$. Similar structure for mass fragment $M = 128$ was postulated in the mass spectra of RDX and HMX.^{2b} Stability of these radicals in the condensed phase might be responsible for their detection. However, Zhao et al. did not detect larger mass fragments of 175 and 128 in their laser photolysis of RDX molecular beam.¹

Formation of mass fragments at $m/e = 222$ was found in N–N homolysis and O-migration pathways of HMX decomposition. This INT222, formed by the removal of CH_2N radical from HMR-o (Figure 4), or by the removal of MN-oring from INT296 (Figure 6a), has a ring-opened RDX structure. This could be cyclized to RDX as shown by the double arrow in Figure 7. Bulusu et al. observed an ion peak at m/z 222 in the mass spectrum of HMX.^{2b} Goshgarian³ and Fifer⁹ also observed this mass peak in the thermal decomposition of HMX. However, no definitive conclusion was reached as to whether the structure corresponds to RDX or its ring opened form.

Although $m/e = 120$ was detected by Zhao et al.¹ in the gas phase laser photolysis, in our RDX ab initio calculations we did not find a primary decomposition pathway for its formation. To account for $m/e = 148, 120$ in the mass spectra of HMX, Bulusu et al. considered migration of a CH_2 hydrogen to the neighboring NO_2 followed by ring contraction as the initiation mechanism.^{2b} They also proposed a HONO group migration in the formation of the ion at m/z 120. Our calculations clearly indicate that such migration will preferably lead to the exothermic HONO elimination. Alternatively, in an earlier thermal decomposition study,⁴ Farber and Srivastava suggested that the peak at m/z 120 might come from the reactions of gaseous products with the condensed phase. Bimolecular association of the MN molecule with the NO_2 radical could fit this postulate. Farber and Srivastava proposed a homolytic cleavage of the HMX ring to two $\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{NNO}_2$ biradicals, which can further undergo cyclization to a four-membered ring. We tried to scan this homolytic cleavage of HMX to generate radical 148. We did not find any converged structure for this because optimization of this radical always resulted in decomposition to two MN molecules. Our present scheme cannot account for these experimentally observed mass fragments. The mass peak at 102 results from the elimination of one MN molecule from RDR-o and can come from the decomposition of both RDX and HMX as shown in Figure 7. This peak was observed in condensed phase decomposition,^{4,8,9} in mass spectra,^{2b} as well as in the gas phase study.¹

The mass fragment at 108 is the result of successive 4HONO elimination from HMX, as shown in Figure 7. This mass peak was not detected experimentally. On the other hand, decomposition of HMX to 4HCN + 4HONO is considered to be one of the most important condensed phase processes.¹⁷ Figure 5 shows that decomposition of HMX to 4HCN and 4HONO must occur via the formation of INT108. In our calculations, INT108 was found to be the most exothermic decomposition product from

HMX, like the formation of TAZ (81) from RDX. The available energy in most of these experiments might be sufficient to overcome the decomposition barrier of INT108 (87.4 kcal/mol with respect to HMX). Further gas phase experiments with precisely tuned laser energy might provide more insight.

6.2. Identification of Mass Fragments with $46 \leq M \leq 100$.

The mass fragments in this range that can be explained by our present scheme are 81, 75, 74, 56, 47, and 46. Experimentally observed mass fragments in this range are 97, 81, 75, 74, 70, 59, 56, 54, 47, and 46.

Mass fragments at 46 and 47 were found in the N–N homolysis and HONO elimination pathways of RDX and HMX decomposition. These mass peaks are unambiguously identified as NO₂ and HONO in most of the experiments. However, the stability of HONO is questionable and its further decomposition to OH and NO may be responsible for its absence in some experiments.^{1,17} We computed a barrier of 49.6 kcal/mol for the latter process. Both 46 and 47 mass fragments could as well result from the decomposition of MN (74).

MN (74) was observed as one of the major products in almost all these reaction pathways. Concerted decomposition of RDX to three MN molecules, which requires 59.4 kcal/mol, was identified as the most important decomposition pathway for RDX by Zhao et al.¹ We could not find a similar transition state for HMX decomposition to four MN molecules. Thus, the MN fragments found in HMX decomposition must come from the other three decomposition channels, presented in Figures 4, 5, and 6. In addition, MN-oring found in the HMX O-migration pathway (Figures 6a and 7) has the same molecular mass of 74. MN-oring could well be generated via a similar O-migration mechanism from MN.³³ Behrens and Bulusu¹¹ observed a $m/e = 74$ for C₂H₆N₂O in their thermal pyrolysis of HMX. This was assigned to (CH₃)₂NNO. We believe that this species results from the bimolecular association of decomposition products and hence is not present in our scheme.

The mass peak at $m/e = 75$ is MNH formed from the decomposition of RDX-o as shown in Figure 7. Goshgarian observed this species in the thermal decomposition of RDX and HMX and considered MNH as one possible candidate.³

Mass fragment 56 was identified in laser pyrolysis³⁸ and photolysis¹ experiments and the chemical structure is CH₂N-CHNH. It can result from the N–N homolysis pathway in both RDX and HMX. As shown in Figure 4, a low-energy pathway for HMX involves elimination of two NO₂ radicals, followed by sequential elimination of HONO, HCN, and MN to form INT56.

The mass peak at 81 can be identified as TAZ, observed in most condensed phase experiments and also in the gas phase photolysis of RDX. This results from successive elimination of three HONO molecules from RDX and is the most exothermic pathway in our mechanism.¹⁸ TAZ cannot be formed directly from HMX except via the formation of RDX. Goshgarian³ and Fifer⁹ proposed the formation of TAZ from HMX via the formation and decomposition of species with $m/e = 222$. This could as well be RDX or its ring open form (INT222), as shown in Figure 7. Behrens and Bulusu³⁹ made no mention of this species in liquid phase HMX decomposition, but Behrens¹¹ observed this in electron ionization of HMX. Recently, Tang et al. concluded from their CO₂ laser assisted combustion of HMX that the peak at mass 81 could not be from the fragments of HMX in the ionizer.¹⁴

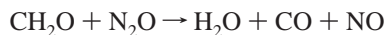
Masses 97 and 70 were postulated to have chemical formulas C₃N₃H₃O and C₂N₂H₂O, while their chemical structures remain uncertain. Oxy-*s*-triazine (OST) was considered as the most

plausible candidate for C₃N₃H₃O.^{14,37,38} Behrens and Bulusu³⁷ identified OST as the only unimolecular product in RDX decomposition. They also proposed a plausible mechanism for its formation and concluded that HONO elimination is the rate-controlling step. Tang et al. found a small amount of this species in their laser pyrolysis experiment.¹⁴ As mentioned in our earlier work on RDX,¹⁸ OST formation occurs preferably from INT128 (generated after 2 HONO elimination from RDX) but does not follow the Behrens and Bulusu mechanism. Nitro–nitrite rearrangement followed by HNO elimination (which has a 54.5 kcal/mol barrier with respect to RDX) or by O-migration from NO₂ to neighboring C-atom followed by rearrangement and HNO elimination (barrier of 64.8 kcal/mol with respect to RDX) from INT128 could be other possibilities. However, none of these mechanisms can justify HONO elimination as the rate-limiting step. 70 was assigned as a daughter ion formed from OST.³⁷ Lee et al. identified 70 as a true decomposition product from RDX.³⁸ We believe a possible formation route of 70 would follow the sequential elimination of HCN from OST.

Mass 54 was observed in the laser pyrolysis of RDX and HMX as a decomposition product of TAZ.^{14,38} This is only possible via a sequential elimination of HCN from TAZ. We believe that concerted decomposition of TAZ to 3HCN will be more favorable energetically. On the other hand, mass 59 was assigned to *N*-methylformamide (CH₃NHCOH) by Behrens and Bulusu.¹⁰ They suggested that such amide products are formed by bimolecular association of initial decomposition fragments or by the decomposition of the nonvolatile polyamide observed in their experiment.

In their analytical pyrolysis-atmospheric pressure ionization (PY-API) tandem mass spectrometry study of HMX, Snyder et al.⁴⁰ identified mass peaks at m/z values 44, 46, 60, 74, 75, 85, 98, 30, 58, 69, 71, 83, and 141. The first seven ions were considered common to RDX and HMX decompositions. Moreover, isotope scrambling experiments revealed that except for the ion at $m/z = 75$, nitrogen atoms of all other observed ions are derived from the ring rather than the nitro group. Thus, the observed chemical species in this experiment is very different from the other experiments. They argued that the effects due to vaporization and ionization/fragmentation of undecomposed reactants were minimized or avoided by carrying out the pyrolysis at atmospheric pressure. Behrens also observed some of these mass fragments as true pyrolysis product.^{10–12} Such products might as well originate from intermolecular reactions among the decomposed products, especially at high pressures, and not be true unimolecular decomposition products. A majority of the thermal decomposition experiments on RDX and HMX observed some mass fragments, which could be only explained as originating from bimolecular reactions. Theoretical studies of these interactions require molecular dynamics of RDX and HMX crystals with a force field capable of treating molecular reaction. Such an effort has been initiated at our center.⁴¹

6.3. Gas Phase Chemistry. Smaller mass fragments from unimolecular decomposition lead to gaseous products via further reaction. Experimentally observed small mass fragments such as 46 (NO₂), 44 (N₂O), 30 (NO, CH₂O), 28 (CH₂N), 27 (HCN), 17 (OH) can be explained based on our scheme presented in Figure 7. Other small mass fragments detected experimentally such as 45 (formamide),^{14,37} 43 (HNCO),¹⁴ or 42 (C₂H₄N)¹⁴ might not be true decomposition products of RDX and HMX. Many of the smaller mass fragments such as CO, CO₂, H₂O, N₂, H₂ etc. results from bimolecular reactions such as



Reactions among these unique unimolecular decomposition species define the different zones in the flame structure of RDX and HMX combustion. The gas phase chemistry of nitramine combustion has been modeled recently.⁴²

7. Concluding Remarks

From our mechanistic studies in the gas phase we conclude the following:

(i) Consecutive HONO eliminations (leading to TAZ + 3HONO from RDX and INT108 + 4HONO from HMX) are energetically the most favorable pathways. Further decomposition of TAZ to 3HCN and INT108 to 4HCN requires relatively higher energy. However, decomposition of RDX and HMX to HCN and HONO (and OH + NO on further decomposition) is considered one of the most important global reactions for nitramines, both from experimental⁷ and theoretical²³ point of view.

(ii) Formation of CH₂O and N₂O can occur from RDX either by O-migration followed by concerted decomposition of the stable RDX-oring intermediate or by secondary decomposition of MN. The former is energetically more favorable and is one of the most important decomposition channels for RDX in addition to HONO elimination. In contrast CH₂O and N₂O formation in HMX occurs preferably from MN secondary decomposition.

(iii) Concerted decomposition of RDX to three MN molecules is another important pathway. Decomposition of RDX through this pathway requires higher energy than the other two, which is at variance with the inferred results from gas phase experiments. We did not find a similar pathway for HMX.

(iv) The N–N bond cleavage to form RDR from RDX or HMR from HMX is another favorable pathway but the associated endothermicity for further dissociation makes this channel less favorable. However, the N–N homolysis pathway unifies RDX and HMX mechanisms and can explain many of the common mass fragments observed experimentally.

(v) The unified scheme successfully accounts for majority of the mass fragments observed in the thermal decomposition of RDX and HMX. It does not include catalytic decomposition pathways or bimolecular reactions in condensed phase.

(vi) Predicted energetics of the RDX decomposition give good qualitative agreement with results of the gas phase molecular beam experiments. Similar gas phase experiments in HMX will allow more rigorous comparisons with experiments.

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Supporting Information Available: Optimized geometry of the intermediates and some important products and transition states. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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