



Investigation on NO₂ Catalysis Mechanism in Dimethylnitramine Decomposition Using DFT Method

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Abstract: Dimethylnitramine (DMN) is usually investigated as a model compound for nitramine explosives. In the present study, the reaction of DMN with NO₂ molecule and two possible initial channels of unimolecular decomposition of DMN in gas-phase (N-N bond scission and direct HONO elimination) were studied. Critical points on the potential energy surfaces (PES) of all reactions were optimized using the B3LYP density functional method (DFT). The barrier for the N-N bond homolysis is lower about 17 kJ mol⁻¹ than that for the direct HONO elimination. The PES of DMN reaction with NO₂ shows that the energy barrier for HONO elimination was descended about 79.3 kJ mol⁻¹ by the catalysis of NO₂. As a result, that N-N bond homolysis is the dominative initial channel in the unimolecular decomposition of DMN is supported in theory and NO₂ catalysis mechanism in DMN decomposition is presented.

Keywords: dimethylnitramine (DMN), DFT, decomposition, mechanism

Introduction

Nitramines such as 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, CL-20), and 1,3,3-trinitroazetidine (TNAZ) are important explosives with excellent performance. However, there are still different views on the initial decomposition mechanism (N-NO₂ bond scission and direct HONO elimination [1, 2]) and the role of NO₂ in decomposition process of nitramine explosives, although many studies [1, 7, 8] on their decomposition

have been carried out.

As a simple secondary nitramine, DMN is usually investigated as a model for nitramine explosives. In earlier experimental studies, autocatalysis in the decomposition of DMN was observed [9]. Fluornoy [1] considered that DMN could directly react with NO_2 , but could not give any evidence. Korsoonskii [1] experimentally demonstrated that NO_2 could accelerate the decomposition of DMN in gas state, but did not illustrate how NO_2 affected the decomposition of DMN.

By having summarized and analyzed the literatures on decomposition of DMN, Shu [1] concluded that the homolysis of N-N bond was the main decomposition channel, he also pointed out that the oxidation mechanism of NO_2 on DMN should be further studied.

In the present work, by DFT methods the possible initial steps of DMN decomposition in gas phase were investigated. The calculated results gave supports that the homolysis of N-N bond was the dominating channel in the initial decomposition of unimolecular DMN. The possible reaction mechanism of DMN with NO_2 was studied and NO_2 catalysis mechanism in DMN decomposition was proposed.

Computational Methods

With the Gaussian 98 program package [3], at DFT-B3LYP/6-31G* [4-6] level, the critical points on the potential profiles of initial reactions of DMN decomposition and the reactions of DMN with NO_2 were optimized. The natural bond orbital (NBO) theory [7] was used to analyze the bond orders and atom charges of optimized structure of DMN molecule. At the same level, frequencies and zero point vibration energy (ZPVE) were calculated and the products (number of imaginary frequencies: NIMAG = 0) and transition states (NIMAG = 1) were confirmed.

Results and Discussion

The Structure of DMN

The bond lengths, the bond orders and atom charges of the optimized DMN molecule obtained by NBO analysis are shown in Figure 1. Since the bond energies of C-H, C-N and N-N bonds are 415, 293 and 159 kJ mol^{-1} respectively and the N-N bond on DMN is a typical single bond (Figure 1), this bond is the weakest and easy to break when heated. There is a strong interaction between oxygen atoms of nitro group and hydrogen atoms on the methyl groups (their distance is 0.2396 nm), therefore the hydrogen atom may transfer from methyl

groups to nitro group resulting in loss of HONO. Because of the H atoms with positive charges on DMN and the O atoms with negative charges on NO₂ molecule, the O atoms on NO₂ can possibly attack the H atoms in DMN and then a series of reactions may occur.

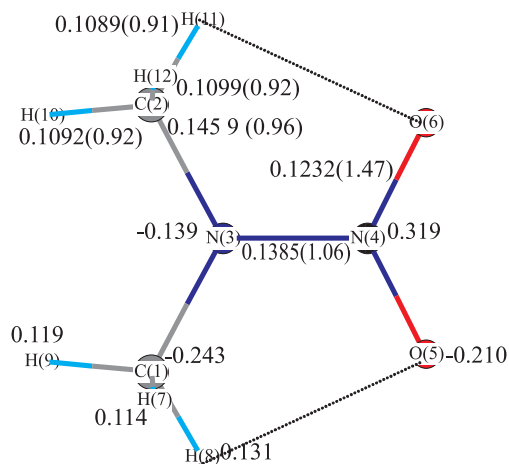


Figure 1. Optimized structure of dimethylnitramine (the data beside the bond are bond length and bond order, atom charges are marked beside each atom).

The possible initial steps in the decomposition of DMN

Homolysis of N-N bond

As mentioned above, N-N is the weakest bond in DMN. It is easily broken to generate NO₂ and radical CH₃NCH₃ (INT44, the structure is shown in Figure 2) when heated:



This reaction is a typical direct bond scission and the barrier approximately equals to the bond dissociation energy (BDE) for this type reactions. For DMN, the BDE of N-N obtained by calculation is 172.83 kJ mol⁻¹ (including ZPVE correction, same as the following energy calculation), which is very close to the literature value [9] 171.4 kJ mol⁻¹.

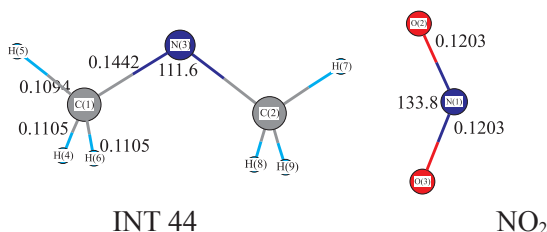
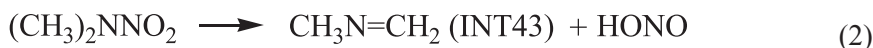


Figure 2. Optimized structures of products in direct N-N rupture reaction channel.

Elimination of HONO



For RDX, the required energy of HONO elimination is only about 0.8 kJ mol⁻¹ higher than that of N-N bond homolysis, and HONO elimination is an exothermic reaction while the following reactions (open-ring or another N-N bond homolysis) of N-N homolysis all require much more energies, so Debashis Chakraborty *et al.* [8] suggested that HONO elimination was the most energy favorable channel for RDX decomposition. But for DMN, direct elimination of HONO from DMN to generate CH₂=NCH₃ (INT43) through transition state TS1 needs about 189.83 kJ mol⁻¹ (the structures of transition state and products are shown in Figure 3), which is about 17 kJ mol⁻¹ higher than that of N-N bond scission. So for DMN, the channel of HONO elimination is unfavorable.

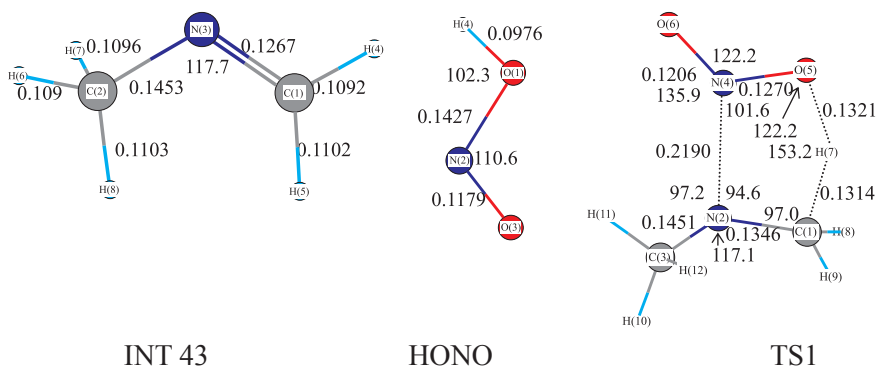
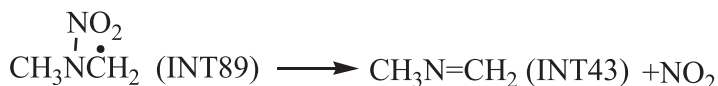


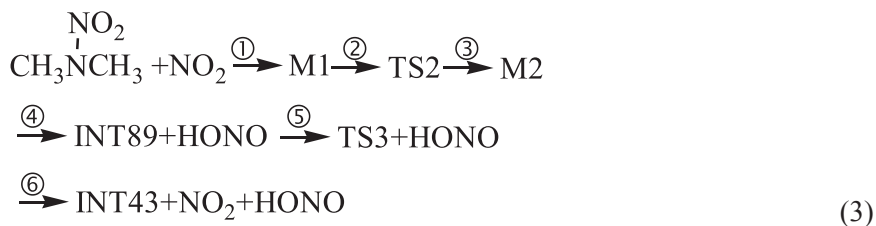
Figure 3. Optimized structures of products and TS in HONO direct elimination.

The Reactions of NO₂ with DMN

On the basis of the charge distribution of DMN which was detailed earlier, the reactions between NO₂ and DMN are below:



Under this reaction framework, the calculated results give more detail reaction mechanism (intermediate products and transition states are shown in Figure 4): firstly, NO₂ can react with DMN to form a complex M1, then M1 will convert into an intermediate complex M2 by transition state TS2 (energy barrier is 117.46 kJ mol⁻¹), unstable M2 will finally decompose to product HONO, CH₃N=CH₂ and NO₂ (see reactions (3)). So, the total reaction can be seen as HONO elimination from DMN with the catalysis of NO₂, and the total barrier is 110.53 kJ mol⁻¹. The potential profiles of N-N bond scission, direct HONO elimination and reactions of DMN with NO₂ are shown in Figure 5. It can be seen that the required energy of elimination HONO from DMN with NO₂ catalyzing is lower 62.3 and 79.3 kJ mol⁻¹ respectively than that of the N-N bond scission and directly HONO elimination. So when there is NO₂ in reaction system, HONO elimination from DMN will be the most energy favorable decomposition channel.



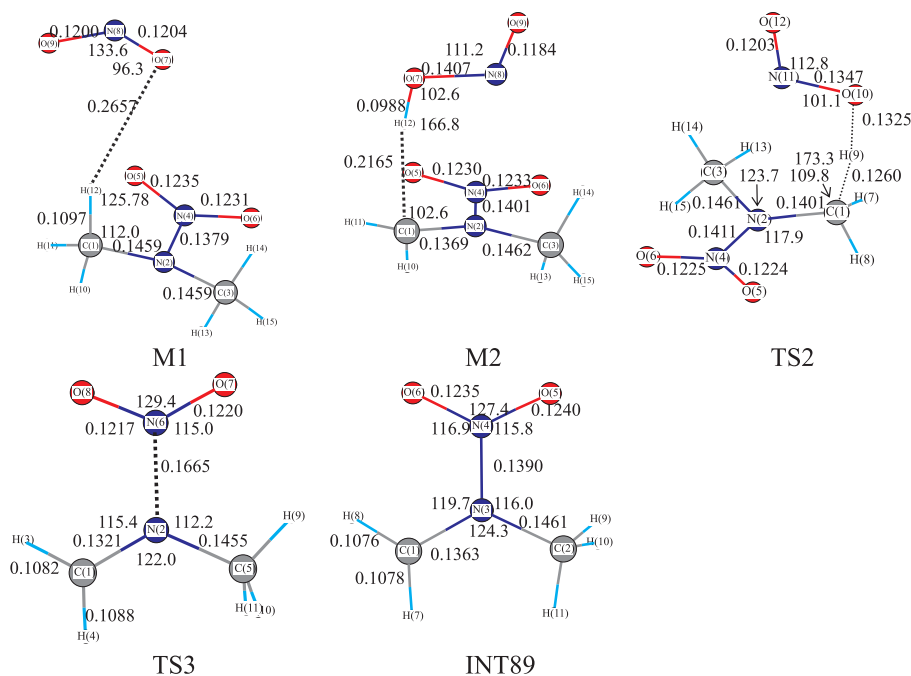


Figure 4. Optimized structures of products and TS in HONO elimination with NO_2 catalysis.

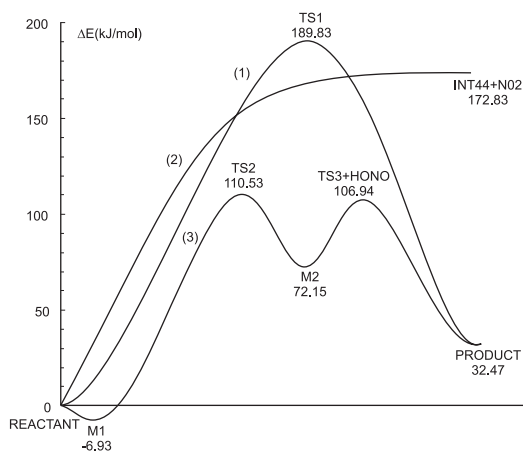


Figure 5. Potential profile of three react channel (base state energy of reactants are relative energy zero point).

Table. Absolute energies, imaginary frequencies(ν_i), and zero-point vibrational energies of all species

Structures	ν_i , cm ⁻¹	Energy, a.u.	ZPVE, kJ mol ⁻¹
DMN		-339.656556	251.54
INT44		-134.509486	203.69
INT43		-133.942337	180.10
NO ₂		-205.072206	23.17
HONO		-205.695212	53.30
M1		-544.732395	277.42
M2		-544.700190	271.73
TS1	-1415	-339.656556	251.54
TS2	-1304	-544.681566	260.79
TS3	-498	-338.988247	208.93
INT89		-338.999184	213.33

Conclusions

1) For unimolecular decomposition of DMN in gas-phase, homolysis of N-N bond is the most energy favorable channel. The barrier for N-N bond scission is 17 kJ mol⁻¹ lower than that for direct HONO elimination.

2) NO₂ can catalyze the decomposition of DMN. Under the existing of NO₂, the barrier for HONO elimination from DMN will lower about 62.3 kJ mol⁻¹ than that for N-N bond homolysis.

3) The autocatalysis in DMN thermal decomposition may be interpreted as the following: first DMN decomposition generates NO₂ by N-N bond homolysis, then NO₂ can catalyze and accelerate the decomposition of DMN.

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