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Article

RDX AND HMX FORMATIONS FROM HEXAMINE – A DFT BASED POSTULATE

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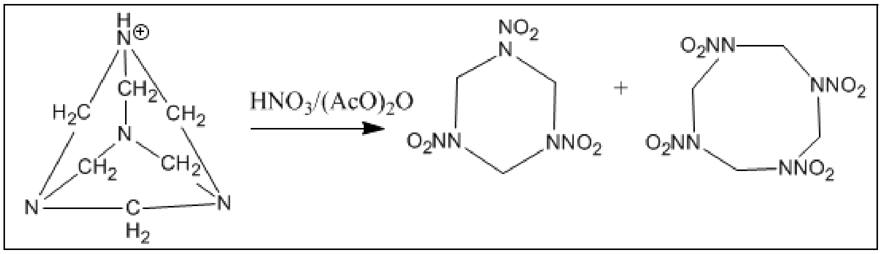
ABSTRACT

Hexamethylene tetramine (HMTA) is used as the starting material for the synthesis of well known explosives RDX and HMX. The present study postulates series of reactions to rationalize the formation of these explosives from HMTA, based on density functional theory calculations at the level of B3LYP/6-31G(d,p).



Keywords: Hexamine, hexaminedinitrate, RDX, HMX, DFT calculations.

1. INTRODUCTION

Cyclotrimethylene trinitramine or 1,3,5-trinitrohexahydro-*sym*-triazine (RDX) and cyclotetramethylene tetranitramine or 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX, Her Majesties' explosive) [1] are important explosives which have been in use for long. RDX is mainly obtained in the industry by direct nitrolysis process (Woolwich) in which hexamethylene tetramine is directly treated with a large excess of strong HNO_3 at a temperature of 20-25 °C [1-4]. On the other hand, in the Bachman (Combination Process) process, which is also an industrial process for RDX, the reaction mixture contains HNO_3, NH_4NO_3, acetic anhydride and acetic acid in addition to hexamine [1,2,4]. The product, RDX,

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[♣] Tel:+90 312 2103244, Fax:+90 312 2103200, E-mail: lturker@metu.edu.tr of the Bachman process is higher in yield compared to the previous one, produces RDX (B) which contains 10 % HMX.

HMX/octogen is a superior explosive than RDX/cyclonite because of its higher chemical stability, higher density, higher velocity of detonation and higher ignition temperature, however its cost and sensitivity are higher than RDX [1,2].

Hexamine (hexamethylene tetramine, HMTA) is a heterocyclic organic compound having highly symmetrical cage-like structure. It is prepared from ammonia and formaldehyde [5]. Although it is feebly basic, protonates in strongly acidic media, to form salts. The reaction of hexamine with nitric acid has prime importance because of energetic properties of nitramine type products such as RDX and HMX.

Hexamethylene dinitrate (HDN) can be used as a precursor for manufacturing of RDX and its industrial method of preparation is described in the literature [6]. HDN shows weak explosive character, heating or ignition causes violet deflagration. Its hygroscopic nature prevents its usage in explosive formulations.

Besides the experimental studies on RDX, there are some computational studies on its reaction mechanism [7], conformations and bond dissociation energies [8, 9] and gas-phase structure [10]. RDX formation mechanism has been studied either experimentally [11] or computationally [12].

The present study considers series of reactions to rationalize the formation of RDX and HMX from HMTA, based on density functional theory calculations.

2. METHOD

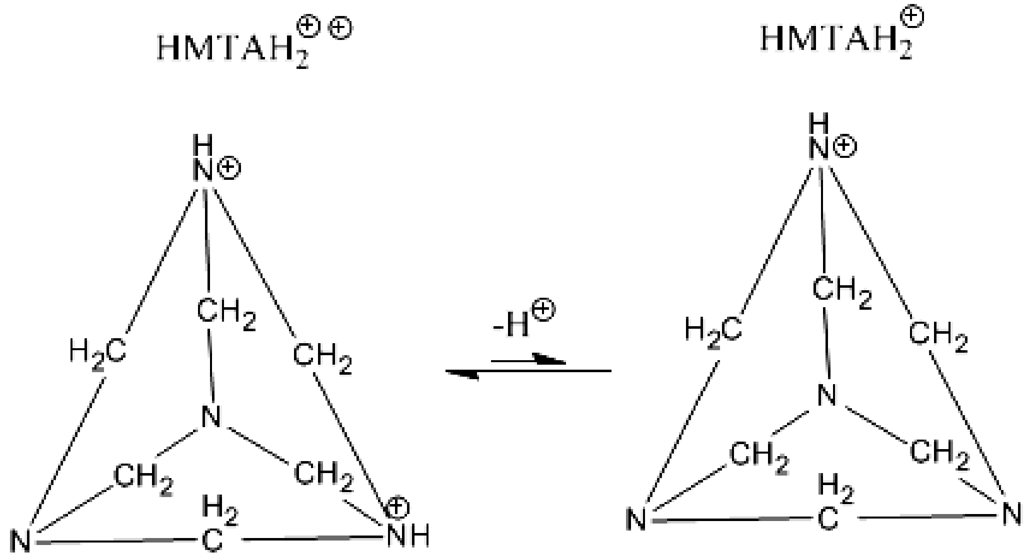
The initial geometry optimizations of all the structures leading to energy minima were achieved by using MM2 (molecular mechanics) method which are followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [13, 14] at the restricted level [15]. Then, geometry optimizations were achieved by using various restricted Hartree-Fock (RHF) methods successively and finally optimizing within the framework of density functional theory (DFT, B3LYP) [16,17] at the level of 6-31G(d,p). Note that the exchange term of B3LYP consists of hybrid Hartree–Fock and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [17,18]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [19] and Lee, Yang, Parr (LYP) correlation correction functional [20].

For each set of calculations, vibrational analyses were done (using the same basis set employed in the corresponding geometry optimization). The normal mode analysis for each structure yielded no imaginary frequencies for the $3N-6$ vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least one local minimum on the potential energy surface. All these computations were performed by using the Spartan 06 [21] package program.

3. RESULTS AND DISCUSSIONS

Experimental studies on RDX and related compounds go back to 1950s [22-24]. Those studies mainly consider the effect of certain component of the synthetic procedures on the product rates etc.

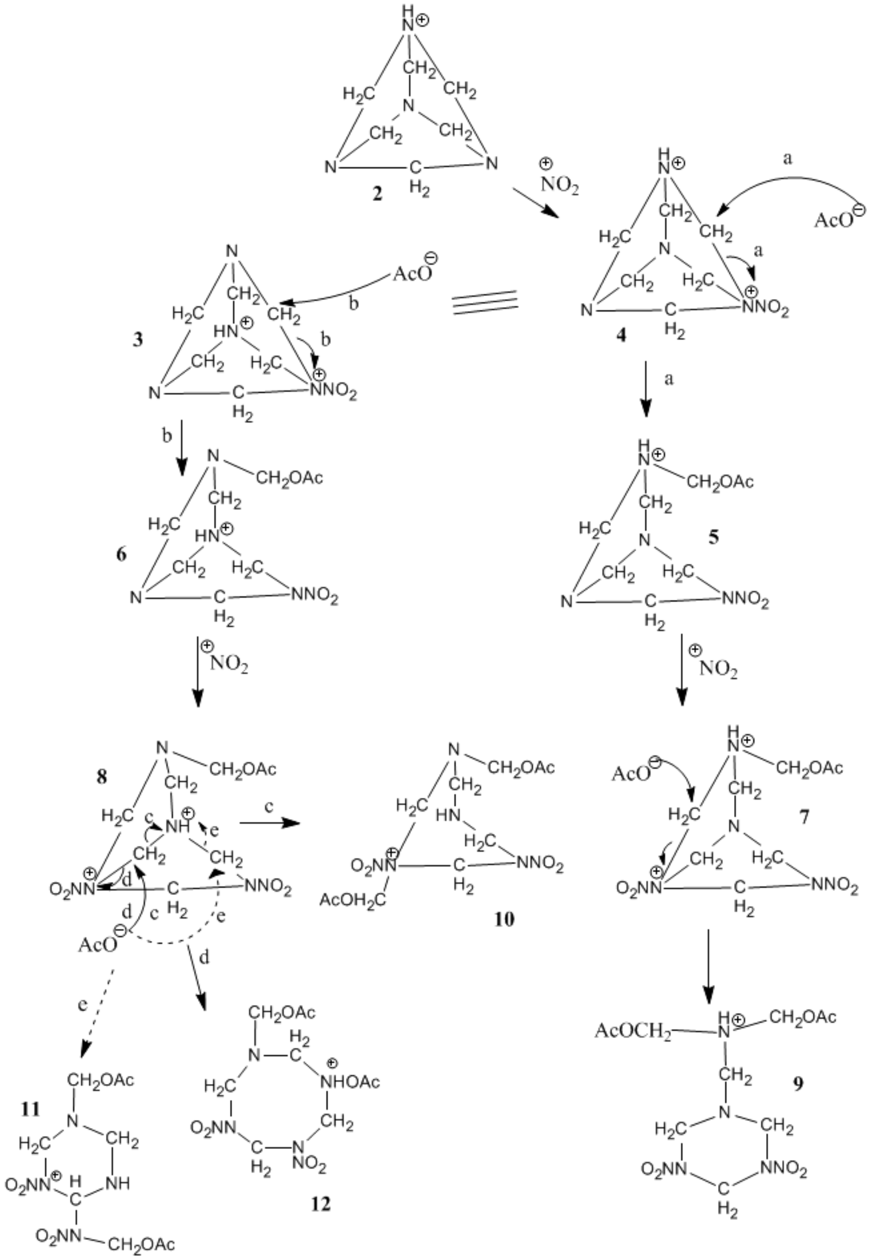
In strong acid HMTA is protonated. The first protonation should be easy but the second and third protonation cannot be so favorable because of the repulsive interactions developed between the protonated centers, thus more forcing conditions are needed. In strongly acidic medium, doubly charged cation of HMTA may have some existence (in the form of hexamine dinitrate (HDN) salt, hexamethylene tetramine dinitrate **1**) which may be in equilibrium with the mono-cation (**2**) (Scheme **1**) especially in solution.



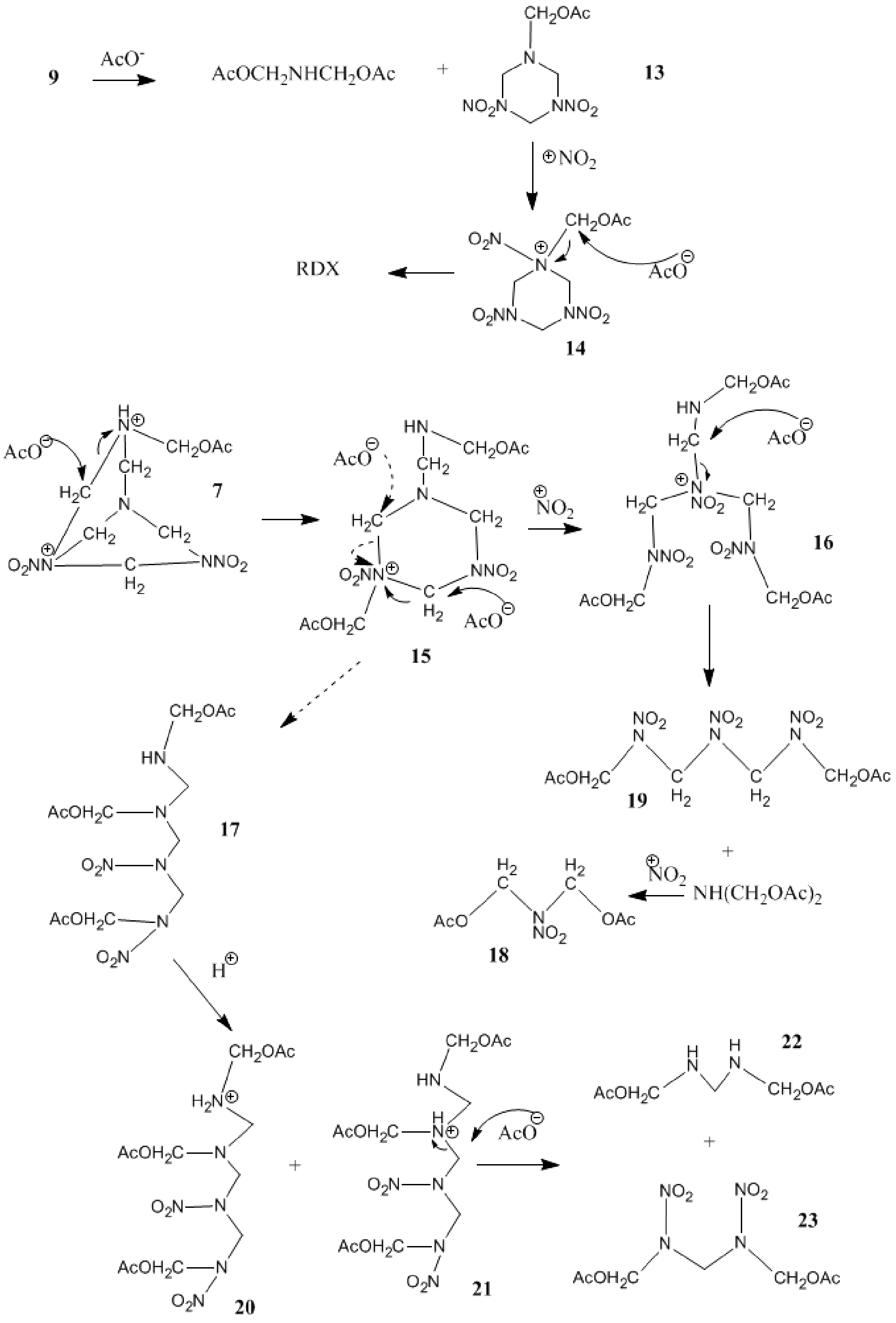
Scheme 1

Presently, this mono-cation is considered as having comparatively low concentration but playing a key role in RDX and HMX formation mechanisms. To shed some light on to these complex transformations, eventually yielding RDX and HMX, the reactions shown in **Schemes 2** and **3** are proposed and some quantum chemical calculations have been carried out. Although concentration of acetate ion in such a strong acidic medium has to be very low, it has been considered as the attacking nucleophile in the ring opening processes of HMTA skeleton. However, the acetate ion (AcO^-) could be replaced by acetic acid to play the same role. Structure **4** is a mononitrated double cation and structure **3** is the other view of it.

Depending on different protonation sites in the mono-nitrated (double cation) specie (**4** or **3**), isomeric acetoxy derivatives, **5** and **6** may form after the AcO^- (or AcOH) attack followed by ring opening reaction. Structure **5** seems to be more stable than **6** in the gas phase and aqueous phase (see Table 1). Thereafter, structures **5** and **6** produce **7** and **8**, respectively after dinitration so that the former one (**7**) is more favorable than its isomer **8** (see Table 1). The acetate attack on **7** forms **9** in which pro-RDX skeleton is discernable. The attack of acetate on different sites of **8** also forms a pro-RDX specie (**11**) and pro-HMX (**12**) and **10**.



Scheme 2


9
AcO⁻
AcOCH₂NHCH₂OAc
+
13
⊕NO₂
RDX
14
7
15
16
17
18
19
20
21
22
23
⊕NO₂
NH(CH₂OAc)₂
H⊕
AcO⊖
CH₂OAc
AcOH₂C
NO₂
NNO₂
O₂NN

Scheme 3

Table 1: Various energies of the structures considered

No	Formula	E	ZPE	E_{corr}	E_{aq}	$E_{aq\ corr}$	MW
5	$C_8H_{16}N_5O_4$	-888.79	0.2774	-888.51	-888.86	-888.59	246.247
6	$C_8H_{16}N_5O_4$	-883.61	0.3010	-883.31	-883.69	-883.39	246.247
7	$C_8H_{16}N_6O_6$	-1093.44	0.2874	-1093.15	-1093.72	-1093.44	292.252
8	$C_8H_{16}N_6O_6$	-1093.44	0.2892	-1093.15	-1093.69	-1093.40	292.252
9	$C_{10}H_{19}N_6O_8$	-1322.36	0.3421	-1322.01	-1322.42	-1322.08	351.296
11	$C_{10}H_{19}N_6O_8$	-1322.31	0.3398	-1321.97	-1322.38	-1322.04	351.296
12	$C_{10}H_{19}N_6O_8$	-1322.34	0.3420	-1321.99	-1322.41	-1322.07	351.296
20	$C_{12}H_{23}N_6O_{10}$	-1551.47	0.4068	-1551.06	-1551.53	-1551.12	411.348
21	$C_{12}H_{23}N_6O_{10}$	-1551.47	0.4066	-1551.06	-1551.53	-1551.13	411.348

Energies in au.

Note that **9**, **11** and **12** are isomeric structures ($C_{10}H_{19}N_6O_8$) having the same charge (mono cation). The stability order of them has the sequence of **9**>**12**>**11** both in vacuum and aqueous phase. The dinitrated products **7** and **8** are isomeric dications ($C_8H_{16}N_6O_6$) and **7** is more stable than **8** (in vacuum and aqueous phase).

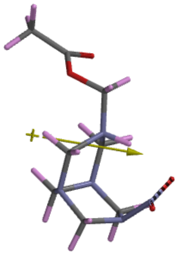
Similarly, in both media **5** is more stable than its isomeric structure **6** (both are monocations). Then, the **5-7-9** sequence of reactions produce more stable structures in each step than the **6-8-12** and **11** sequence. The calculations indicate that optimized structure of **10** is characterized with some elongated bonds. Therefore, it has been out of consideration.

On the other hand, **9** after AcO^- attack may form RDX via structures **13** and **14** (see **Scheme 3**). Similarly, the attack of AcO^- on **7** first yields **15** then eventually **20** and **21** are produced.

However, there seems another route to exist involving the AcO^- attack on **15**, accompanied by nitration to produce **16** which is an acyclic compound.

The acetate attack on **16** as shown in the **Scheme 3** produces **19** (1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane) and another product which is nitrated to yield **18** (1,3-diacetoxy-2-nitro-2-azapropane). Both of these products were experimentally detected [25]. Figure 1 shows the optimized structures of the presently considered molecules.

Figure 1: Optimized structures of some of the compounds considered



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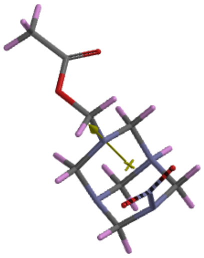

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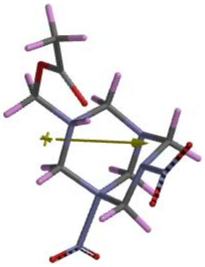

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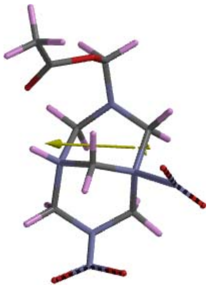

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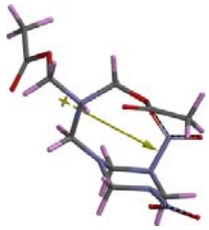

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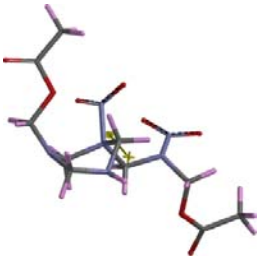

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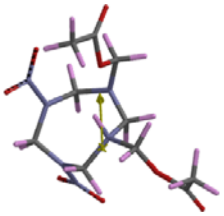

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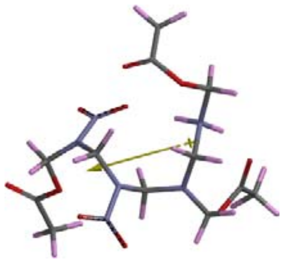

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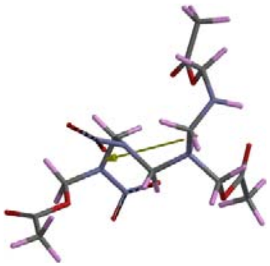

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4. CONCLUSION

The present DFT study (B3LYP/6-31G(d,p)) puts some light on the formation mechanisms of RDX, HMX and some side products from HMTA in acidic conditions. Although the present mechanisms based on computational studies (based on the stabilities of the proposed structures) have some postulative character, however they may enlighten which of the alternative series of routes (of various branches of reactions) are to be favored etc. It should be noted that the present calculations are mainly true for gas and aqueous phases however it should be noted that in reality ionic and acid strengths of the medium etc. also play a vital role in the course of reactions.

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