Defence Technology 13 (2017) 367–375

Contents lists available at ScienceDirect

Defence Technology

journal homepage: www.elsevier.com/locate/dt

Destructive effect of magnesium and calcium atoms on TEX

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ARTICLE INFO

Article history:
Received 3 October 2016
Received in revised form
9 February 2017
Accepted 20 February 2017
Available online 21 February 2017

Keywords:
TEX
Magnesium
Calcium
Explosive
Structure
DFT calculations

ABSTRACT

The interaction of TEX (an explosive recently attracts attention) with Mg and Ca atom(s) has been investigated within the limitations of density functional theory at the level of B3LYP/6-311++G(d,p). The effect of Mg in 1:1 mol ratio is very drastic on TEX and one of the NO_2 moieties is expelled as preform of nitrite ion. The second Mg atom in the composite (1:2 mol ratio of TEX:Mg) shows balancing effect of the first Mg atom, thus no bond cleavage occurs but some distortions happen. As for the effect of calcium, in 1:1 and 1:2 (TEX:Ca) ratios nitramine bond cleavage(s) occur(s) drastically. Some structural and quantum chemical data are presented.

1. Introduction

4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazawurtzitane, known as TEX (see Fig. 1) is an energetic material which has attracted attention in recent years [1]. The synthesis of TEX was achieved couple of decades ago by Boyer and coworkers starting with formamide and glyoxal [2]. Structurally TEX is a nitramine type explosive. Beside, two nitramine groups, it additionally contains two embedded five-membered cyclic diethetic (also can be considered as acetal) structures resembling 1,3-dioxalane structure.

TEX is much less sensitive to impact and friction stimuli as compared to the well known explosives, RDX and HMX. In addition to those properties, it possesses high density (1.99 g/cm^3), excellent thermal stability (m.p > 240 °C) as well as high detonation velocity (8665 m/s) and pressure (370 kbar) [1–7].

The presence of two embedded 1,3-dioxalane structures in TEX molecule calls some well known reactions of ethers and acetals (acyclic or cyclic), such as the acid catalyzed ring opening reactions of cyclic ethers [8–10]. The embedded 1,3-dioxalane structure(s) in TEX can also be considered as full acetal of glyoxal (a dialdehyde ($C_2H_2O_2$)). Note that acetal formation and destruction reactions are acid catalyzed [8–10]. Computations based on density functional theory (DFT) have been highly employed on TEX molecule in order to predict the crystal densities [11], detonation velocity [12], bond dissociation energies and impact sensitivity [13], sensitivity and performance relation [14] etc. [15–17]. Zuo and coworkers considered the thermal stability of TEX in the presence of widely used RDX and HMX [18]. Various modeling work which involve TEX and other explosives within the realm of density functional theory (DFT) have been reported [19–21]. By employing the density functional theory at the B3LYP/6-31 + G(d,p) level of theory Schutt et al., calculated the heat of reactions of free dinitramidic acid ($HN(NO_2)_2$) with derivatives of 2,4-(R)-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}0^{3,11}]dodecane (R = H, CH_3, F, NO_2(TEX)) [22]. Zeng et al., calculated the heat of formation (HOF) for a caged wurtzitane analog compound (4,10-dinitro-2,6,8,12-tetraoxa-4,10-diaza-tetracyclododecane (TEX)) by using density functional theory (B3LYP method with 6-31 + G(d,p) basis set) [23].

On the other hand, certain metals usually are added into explosive compositions to improve their performances. Aluminum and magnesium are the most widely used materials for this purpose. Titanium, zirconium and tungsten are also used [24].

In the present study, interaction of magnesium and calcium atom(s) with TEX molecule (in 1:1 and 1:2 mol ratios) has been investigated within the limitations of density functional approach.

2. Methods of calculation

In the present study, all the theoretical methods have been

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Peer review under responsibility of China Ordnance Society.

http://dx.doi.org/10.1016/j.dt.2017.02.001

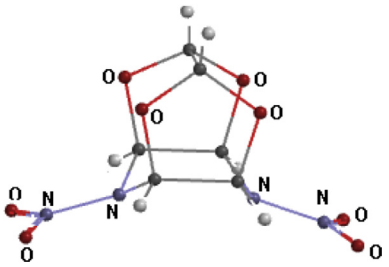

Fig. 1. Structure of TEX.

applied using the restricted level of theory, because all the structures considered are closed shell systems (no radicals) [25]. The initial optimizations of the structures leading to energy minima were achieved by using MM2 method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF-MO) method [25,26]. Then, further structure optimizations were achieved using successively STO and RHF levels of theory (6-31G(d,p)) and then within the framework of Density Functional Theory (DFT, B3LYP/6-311++G(d,p)) [26–28]. All the structures are dealt in their singlet states (restricted type calculations have been done). 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 [29]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [30] and Lee, Yang, Parr (LYP) correlation correction functional [31].

Total electronic energy calculations of all the considered structures finally have been done at B3LYP/6-311++G(d,p) level. The normal mode analysis (at the same level of calculations) for each structure yielded no imaginary frequencies, which indicates that each compound has at least a local minimum on the potential energy surface. The total electronic energies were corrected for zero point vibrational energies (ZPVE or ZPE). All these computations were performed by using Spartan 06 package program at standard conditions of 298.15 K and 1.00 atm [32].

3. Results and discussion

Metal additives are not uncommon in explosive composites. For condensed explosives, having metal particle additives, interaction of the detonation shock and reaction zone with solid inclusions yields high rates of momentum and heat transfer that consequently introduce non-ideal detonation phenomena [33,34].

Mg and Ca are just two of various elements used in fireworks (Mg is used as fuel and Ca salts for color agent) [35,36]. Mg can also be employed in thermobaric and enhanced blast explosives explosives as fuel [37]. Their wide application is due to their thermochemical properties that at the standard states Mg and Ca liberate considerable amount of heat energy (602 kJ/mol and 635 kJ/mol, respectively) as they form their oxides, MgO and CaO. Whereas Al, when oxides to Al_2O_3, produces 1669 kJ/mol of heat and 822 kJ/mol heat energy accompanies formation of Fe_2O_3 at the standard states [38]. Mg and Ca are in the second group of the Periodic Table and are highly electro positive, namely easily

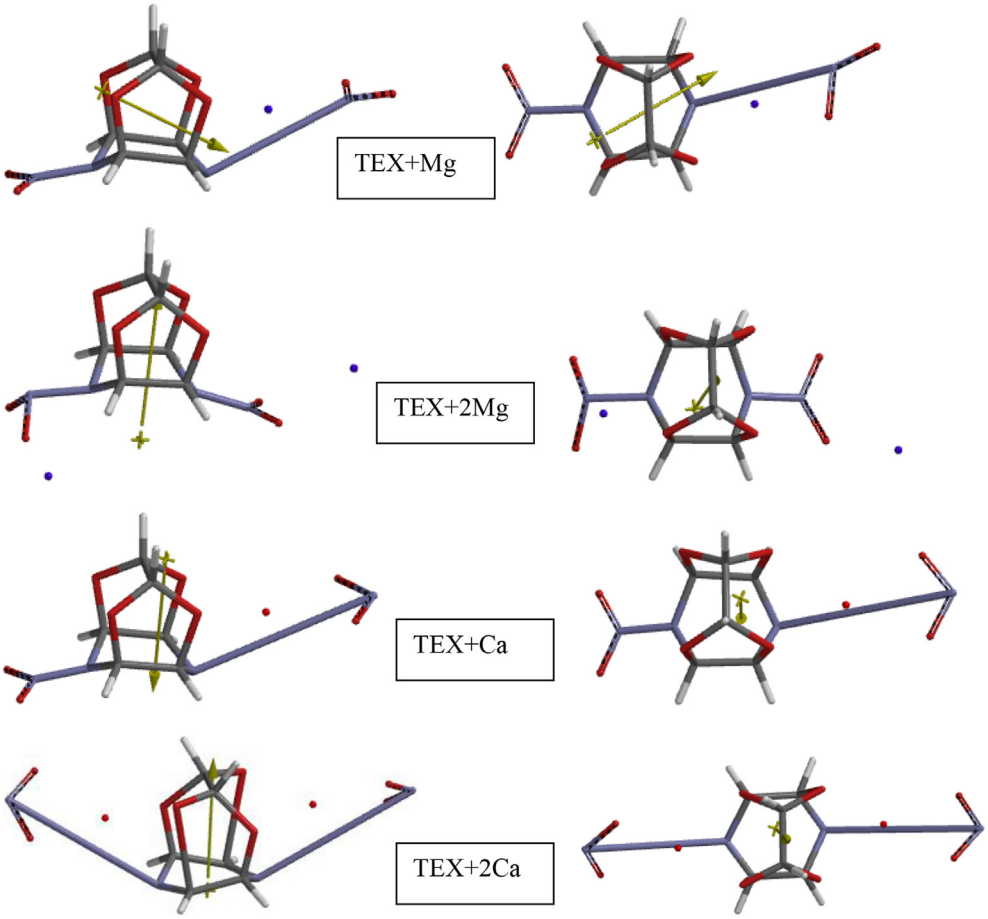

Fig. 2. Optimized structures of TEX composites considered (B3LYP/6-311++G(d,p)).