Journal of Hazardous Materials 169 (2009) 454–459

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Contemplation on spark sensitivity of certain nitramine type explosives

Lemi Türker*

Middle East Technical University, Department of Chemistry, 06531, Ankara Turkey

ARTICLE INFO

Article history:
Received 24 November 2008
Received in revised form 25 March 2009
Accepted 25 March 2009
Available online 2 April 2009

Keywords:
Spark sensitivity
Explosives
Nitro compounds
Nitramines

ABSTRACT

Spark sensitivity of explosives is an important subject. Presently, some correlations are sought between the spark sensitivity and certain molecular orbital characteristics of some nitramine type explosives. For that purpose certain semi-empirical and DFT calculations have been carried out. Investigations have revealed that the nitramines considered undergo decomposition in the electric field mainly via their anionic states.

1. Introduction

Spark discharges occur between conductors with different electrical potentials. A spark is a discrete discharge that leaks through a gap between two conductors in the form of a ionization path in which the stored energy is transferred swiftly. The spark is triggered when the breakthrough field strength is reached at a certain point in the gap. Also, sufficiently high field strength is required in the whole space between the electrodes so that the discharge can travel through that space. A homogeneous electrical field between the electrodes is an important requirement.

In contrast to spark discharges, corona discharges are typical one-electrode discharges which occur in an inhomogeneous electrical field at conductive and earthed sharp end points.

A solid material in an electric field acts as a dielectric material and when the field strength is sufficient, electric and/or electrothermal breakdown occurs. An electric breakdown develops as a result of interaction of free charged particles (electrons and ions) accelerated by an electric field with the particles of a dielectric, or as a result of inelastic displacement of bound charges in a dielectric under the action of an external electric field [1].

Whatever the discharge type is, organic molecules exposed to an electric field should be affected due to polarization depending on the field strength. It is known that the polarizability increases with the size of the atom and with the number of electrons it possesses [2–4]; this can be understood in terms of it being easier for a field to distort the electronic distribution when the electrons are far from the nucleus or well shielded from its charge. Similar generalizations also hold for molecules.

A polar molecule has a permanent dipole moment and most of the explosives molecules fall into this class. Nitro groups and some other explorophores on an explosive molecule make that one to have a permanent dipole moment as long as the geometry and symmetry considerations allow.

The spark sensitivity of various explosive molecules has been the subject of very many articles in the literature [5–15]. In the present study, certain correlations have been sought between the computational data obtained from ionic forms of some nitramines and their spark sensitivity values excerpted from the literature [12].

2. Method

The initial geometry optimizations of all 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 [16,17] at the unrestricted level (UHF/PM3) [18]. Then, further geometry optimizations were achieved using STO and UHF levels of theory and then within the framework of density functional theory (DFT, UB3LYP) [19] at the levels of 6-31G(d,p) and 6-31+G(d) (unrestricted open shell, note that open shell structures are in doublet state) [18]. The exchange consists of hybrid Hartree–Fock and local spin density (LSD) exchange functions term of B3LYP with Becke's gradient correlation to LSD exchange [20]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [21] and Lee, Yang, Parr (LYP) correlation correction functional [22]. The normal mode analysis for each structure resulted in no imaginary frequencies for

* Fax: +90 312 2103200.
E-mail address: lturker@metu.edu.tr.

0304-3894/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2009.03.117

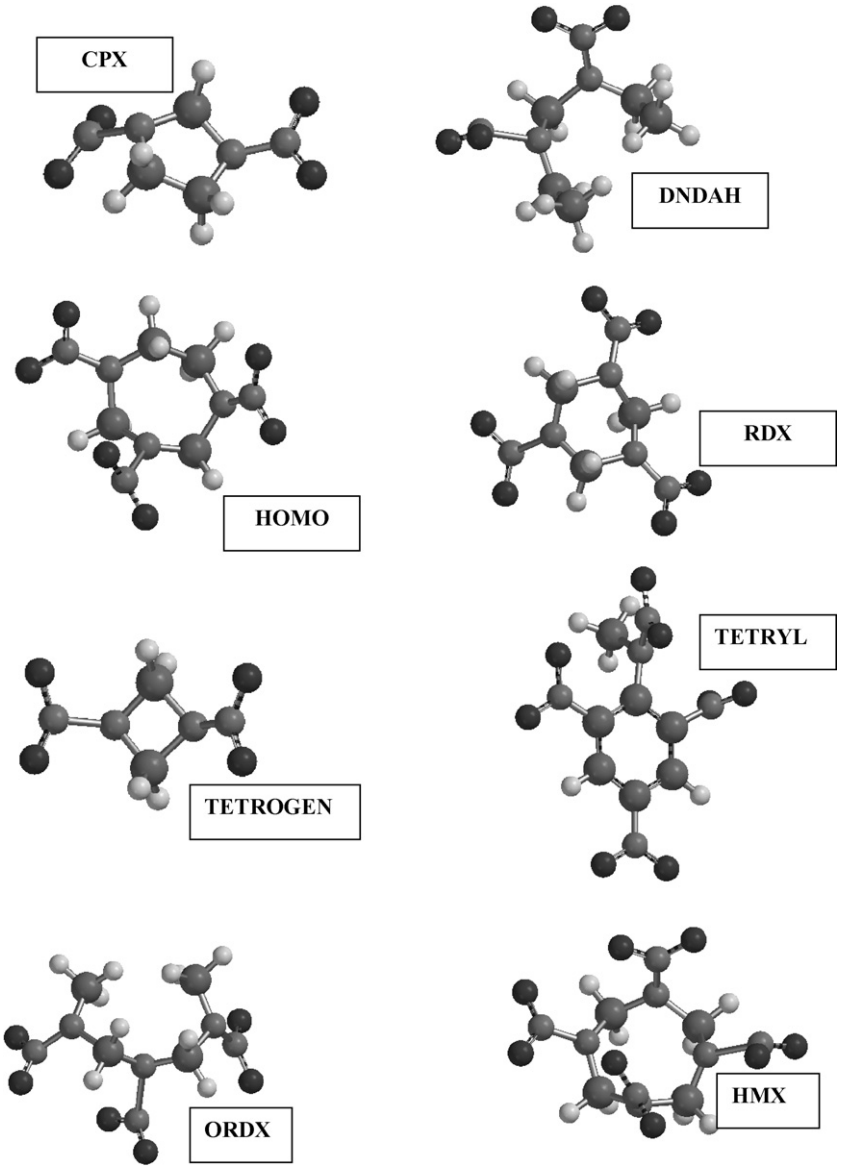

Fig. 1. Geometry optimized (UHF/PM3) anionic structures.

all the three methods of calculations and the spin contamination for open shell systems is acceptable (0.75 ± 0.02). All these computations were performed by using Spartan 06 package program [23].

3. Results and discussion

Initiation of explosives by electric spark has not attracted much attention in the past. Nevertheless, the electric spark sensitivity is an important characteristic of explosives, especially primers and propellants.

When an electric field is applied to an individual molecule, the electron distribution and the molecular geometry are distorted. The polarizability is a measure of the ease with which this occurs. In the electric field, as a result of distortion of the electron distribution, the bond dipoles and consequently the resultant dipole moment of molecules change. As the field strength increases, ionizations of the molecules occur. Depending on the structure and some other factors, especially the field strength, various forms of anionic and cationic species are generated which undergo decomposition starting from the weakest bond(s). To shed some light on to decomposition mechanism of nitramine type explosives in an electrical field, a group of test compounds having various acyclic and cyclic skeletons have been constituted. Of these 20 compounds a subgroup of 8 compounds have been found to exhibit consonance in character in many respects as explained below (see Fig. 1). This subgroup has been used as a test probe for the large group.

3.1. Frontier molecular orbital energy considerations

When a substance is placed in an electric field, it might be polarized and then ionized before undergoing any decomposition possible to occur under the applied conditions. Presently, at the beginning it is assumed that when sparkling occurs over an organic molecule, the structure gains or loses electron(s) prior to disintegration of the molecule to fragments. In other words, decomposition of the molecule in an electric field should occur via its anionic or cationic form(s). So, the following simplified possibilities could be the fates of the structures which are either neutral but polarized or singly or doubly charged structures, undergoing single electron transfer process involving the HOMO and/or LUMO levels.