Chemical Decomposition of Solid Cyclotrimethylene Trinitramine

Maija M. Kuklja

Michigan Technological University, Houghton, MI, 49931, USA, mmkukla@mtu.edu

ABSTRACT

Quantum-chemical simulations of the thermal decomposition of solid RDX at the Hartree-Fock level are performed. It is shown that a rupture of the N-NO_2 chemical bond requires less energy for an isolated molecule than for a molecule placed in the bulk of the solid. The situation changes if the molecule is close to the free surface of the crystal. In this case, less energy is required to break the bond, than for a bulk molecule. Mechanisms of solid RDX decomposition, the relevant experimental data, and possible applications of the obtained results are discussed in great detail.

Keywords: RDX, electronic structure, defects, surface induced effects, decomposition, energetic barriers.

1 INTRODUCTION

A critical issue for modern science, especially for interdisciplinary nanoscience, is the ability to understand, model, and simulate the behavior of the small structures and to make the connection between structure, properties, and functions. More realistic than currently existent simulations are needed to address multiscale and multiphenomena processes. There is a need for a multidisciplinary and system-oriented approach for the development of more generic models and simulation methods, achieved through the cross-fertilization of ideas across research fields. Nanotechnology arises from the exploitation of physical, chemical and biological properties of systems that are intermediate in size between isolated atoms/molecules and bulk materials, where phenomena length scales become comparable to the size of the structure. In this paper, we will show how traditional solid state chemistry approach applied to the essentially molecular problem of the energetic barrier for decomposition gives qualitatively new results and, in fact, brings very new perspectives in the initiation/detonation theory development at large.

Selected for this study cyclotrimethylene trinitramine ($C_3H_6N_6O_6$), also known as RDX, belongs to the wide class of molecular crystals. It is often used as high explosive and propellant. Mechanisms of initiation in liquid and gas phase explosives are pretty fair understood. Much less is known about processes on atomic/electronic level in solid explosives. It is generally believed that initiation can start in small (nano- to micro-size) regions, so-called hot spots, which are able of accumulating of mechanical energy of impact/shock wave and transfer it into chemical energy starting a reaction. However, even simple questions such as the nature of the initial step in the thermal decomposition of energetic materials, in particular RDX, are still a subject of debate. Among many suggested initial steps in the thermal decomposition, the most supported mechanism for condensed phase decomposition is N-NO_2 bond rupture [1,2]. The experiments on samples with isotopically labeled nitrogen also showed that decomposition of RDX is mostly unimolecular and involves the removal of only one NO_2 [3]. Activation energies vary from 24.7 to 52.1 kcal/mol and reported preexponential factors vary from 10^{17} to 10^{20} s^{-1} for overall decomposition [4]. The most recent and the most accurate at present ab initio study based on gradient-corrected density functional theory found the activation barrier of 34.2 kcal/mol for the N-NO_2 dissociation mechanism of the gas phase RDX [4].

As a nanosystem a molecule in complex organic crystals is too small for direct measurements and simultaneously too large to be described by current rigorous first principles in theoretical and in computational methods. Moreover, it is difficult to interpret the condensed phase experiments due to the many possible product species.

We have shown earlier how lattice nano-size defects, which are always in large amount in RDX samples, modify the electronic structure of equilibrium and shocked crystals [5]. Quantum-chemical simulations of the thermal decomposition of solid RDX at the Hartree-Fock level are presented in this investigation. Our main interest was to find out how the crystalline environment affects energetics of RDX molecule decomposition. Also, whether or not the energy of the bond rupture can be changed near a free surface of the material. It is shown that a cleavage of the N-NO_2 chemical bond requires less energy for the isolated molecule than for the molecule placed in the bulk of the solid. The situation essentially changes if the molecule is located near a free surface of the crystal. In this case, less energy is required to break the N-NO_2 bond than that for both the bulk crystal molecule and the isolated molecule. We also discuss how the obtained conclusion can serve for the better understanding of the well-known mechanism of pore collapse and other processes taking place in hot spots. Mechanisms of thermal decomposition of solid energetic materials are discussed on the illustrating example of RDX. Different sensitivities to detonation initiation of porous and solid, perfect and defective explosives are also analyzed and explained.

2 DETAILS OF CALCULATIONS

Our calculations are done by means of the standard Hartree-Fock (HF) method for a periodic system (the band structure problem) by the code CRYSTAL95/98 [6]. For the present work, we used 6-21G split valence basis set with the scaling factor for outer (most diffuse) Gaussian basis vector of 1.10 for the all atoms (H, C, N, O). In the initial calculations, we use the experimentally determined crystalline structure of RDX and bond lengths, angles, and torsion angles of the RDX molecule [7]. The sketch of the structure of individual RDX molecule is shown in Fig. 1. Then, the optimal theoretical geometry of the crystal was found by varying the three lattice constants in proportion in a hydrostatic manner until a minimum of the total energy is achieved. The configuration of the individual molecules was left unaltered in accord with the rigid molecule approximation.

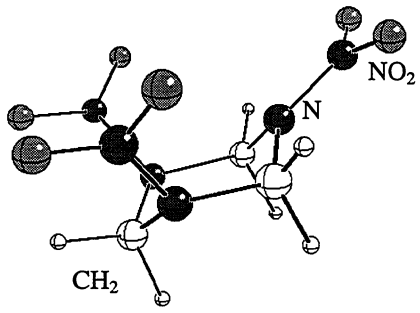

Figure 1. The structure of an RDX molecule. The monocyclic RDX molecule contains three N-NO_2 groups separated by CH_2 groups.

The simulation of a crystal containing a defect supposes that the defect perturbs only a limited region of the crystal lattice leaving the rest of the infinite crystal without any changes. In our case, the defect is an RDX molecule with the broken N-NO_2 bond whereas other molecules in the crystal have the perfect structure. The perturbations are expressed in displacements of atoms/molecules from their regular lattice positions and in a redistribution of electronic density in the crystal. The former is known as the lattice relaxation around the defect and hardly could be accurately included in the present study. The latter is an aim of our work since it can be taken into account and can provide some important information regarding the energetics of the initiation and/or detonation process.

The $\cdot NO_2$ radical formation is attributed to N-NO_2 bond breakage as a result of uv radiation [8]. In solution the molecule has C_{2v} symmetry, but in the solid state the NO_2 groups are not symmetrically equal [9]. This has been confirmed by a crystal structure determination of RDX, which shows that the molecule has C_1 symmetry [7]. The RDX molecule is locked into a chair configuration; consequently, there are two "axial" NO_2 groups and a single "equatorial" NO_2 group per molecule.

A cleavage of the N-NO_2 chemical bond was simulated for three basic situations, placing the molecule in different environments. That is, we studied an isolated molecule with the "crystal configuration," a molecule in the bulk of the crystal, and a molecule located near a surface of the crystal. For the bulk and surface calculations, two different solid state models such as the *molecular cluster* and the *periodic defect* were used. The molecular cluster consisted of several RDX molecules with their coordinates taken from periodic calculation. Thus, the molecule with the N-NO_2 group of interest was surrounded by <u>*all*</u> the nearest neighbor molecules as it is in the crystal. The long-range crystal field was neglected in this model due to van der Waals nature of RDX and also due to its relatively small value. The lattice and molecule relaxation was also neglected since both of these contributions are known to be small [4,5,10]. The RDX molecular geometry stabilization is between 2 and 6 kcal/mol for cleavage of N-NO_2 in gas-phase [4]. Electronic relaxation is thus the dominant mechanism: it accounts for 6-10 kcal/mol [4]. This contribution is included in our models. By using the periodic defect model, the relevant unit cell containing the molecule of interest was translated either in three crystalline directions (a molecule in the bulk) or in two directions in accord with the slab model [6] (a molecule near the surface). To simulate the bond rupture, all electrons and cores of the NO_2 group were removed from the crystal remaining the basis functions on the vacancies. Further, the corresponding decomposition energy was determined by the formula $E_{bond} = E_{perfect} - (E_{defect}+E_{NO2})$ as a difference between the energy of the perfect system and the combined energy of the defective system and an isolated NO_2 group. A comparison of the obtained results using the principle different descriptions of the solid with defect leads to more accurate conclusions and permits to perform a careful analysis of the process under investigation.

3 RESULTS AND DISCUSSION

Our main objective was to study energy barriers for the RDX molecule decomposition via rupture of one of the N-NO_2 chemical bonds. In particular, we were looking for an effect of a crystal environment such as the bulk and the surface on the energetics of the process. That is, we study an initiation of chemistry in a RDX molecule as a function of the molecule surrounding. The obtained results for the N-NO_2 bond dissociation energy are given in Table 1.

We considered three different positions of the molecule. First, an isolated molecule was examined (see the data for the model "isolated" in Table 1). In calculations, all parameters of the molecule such as bond lengths, angles, etc. were taken from X-ray diffraction experiments [7]. No neighbors were included in the calculations, i.e. no crystalline field around the molecule was taken into account. This model is different from the gas-phase molecule only by the changed geometry and reduced

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symmetry. As it follows from Table 1, the obtained energies are not equal in contrast to the gas-phase molecule [4], where all three $N\text{-}NO_2$ groups are equivalent. Besides, it is clearly seen how two axial $N\text{-}NO_2$ groups are distinguished from the equatorial $N\text{-}NO_2$ group. This is in accord with the symmetry reduction. This result is consistent with our previous investigation on the electronic structure of the RDX crystal. The band structure calculations found the RDX crystal orbitals of the upper valence band are formed by the 2p-functions of N and 2p-functions of O atoms similarly to upper bonding states of the molecule [10,11]. Also, the highest occupied orbitals (HOMO) of the bulk crystal and the RDX molecule as well are dominated by the 2p-states of the equatorial $N\text{-}NO_2$ group, while the next HOMOs are formed by the atomic functions of two axial $N\text{-}NO_2$ groups.

Furthermore, we are about to find out what happens if the molecule is surrounded by its neighbors, i.e. it is situated inside the crystal. We place the molecule in the center of two differently shaped quantum clusters: the molecular cluster represented by 9 molecules (see bulk: MC^1 in Table 1) and the molecular cluster in the form of RDX unit cell of 8 molecules (see bulk: MC^2 in Table 1). The equatorial $N\text{-}NO_2$ group is found to be the most sensitive to the presence of the crystal field in the model and the activation energy is visibly increased. This is observed for both clusters confirming accuracy of the conclusion. Even more interesting, the same trend is demonstrated in the periodic model (see bulk: UC) where the crystal was simulated by translating the unit cell with one broken bond in three crystallographic directions. Physically, it means one $N\text{-}NO_2$ bond in each unit cell in the infinite crystal is broken. In other words, one molecule suffers bond cleavage per 7 perfect RDX molecules. From this observation, an important conclusion follows. The molecule located in the bulk crystal has higher activation barrier for $N\text{-}NO_2$ rupture. Unlike axial groups, the equatorial group is more sensitive to the crystal field potential. This result is supported by the suggestions that the NO_2 groups are responsible for intermolecular cohesion [12] in the solid. The proposal was based on the temperature dependence of the Nitrogen-14 nuclear quadrupole resonance spectra experiments. It was established intermolecular electrostatic interactions are important because of the alternating relative positive and negative charges on the atoms comprising RDX. The oxygen atoms and amine nitrogen atoms are relatively negative while the carbon atoms and nitro nitrogen atoms carry relative positive charges [13]. One of the oxygens of the axial $N\text{-}NO_2$ groups situates in the molecular "pocket" of the neighboring molecule and attractively interacts with all three nitrogen atoms of the nitro groups. Other oxygen atoms attract neighboring pairs of molecules by interaction with nitro nitrogen of the equatorial $N\text{-}NO_2$ group. Thus, the cohesion results between all of the RDX molecule pairs because of the oxygen affinity.

Table 1: Calculated energies for the $N\text{-}NO_2$ bond dissociation in an RDX molecule. The values are given in eV (kcal/mol). I, II, III denote different $N\text{-}NO_2$ groups, R is the corresponding initial bond length in Ang [7].

Model	I	II	III
	R=1.3505	R=1.3985	R=1.3921
isolated	1.31 (30.18)	1.77 (40.91)	1.76 (40.79)
bulk: MC[1]	2.01 (46.39)	1.82 (41.97)	1.71 (39.34)
bulk: MC[2]	2.11 (48.72)	1.82 (41.97)	1.84 (42.36)
bulk: UC	2.27 (52.36)	1.93 (44.52)	1.64 (37.92)
surface: MC	1.44 (33.16)	1.49 (34.25)	1.52 (35.14)
surface: slab	-	1.49 (34.25)	-

Finally, we study the activation energies for molecules (more precisely, $N\text{-}NO_2$ bonds) located near a surface of the crystal. We model this again using a molecular cluster (see surface: MC in Table 1) and a periodic approach (see surface: slab in Table 1). Several different clusters were used. The presence of all the nearest neighboring molecules of the $N\text{-}NO_2$ bond in the given surface and under it was used as a criterion for the cluster selection. It is obvious all molecules (and interactions) above the given surface were missing. It is perfectly seen from Table 1, the activation energies for all three NO_2 groups are decreased. The same conclusion follows from the periodic model calculations. The cleavage of the given bond on the (210) surface was simulated in the slab model. In doing so, the relevant unit cell was translated in two crystallographic directions reproducing a semi-infinite system with thickness of 6 molecular layers. The two dimensional periodicity resulted again in one broken bond per unit cell describing simultaneous rupture of many equivalent bonds in the slab. Good agreement of the obtained energy with the value obtained by the MC model provides additional evidence for accuracy of our results. The lower energy for a molecule near a surface with respect to the bulk crystal can be understood in terms of intermolecular interactions. The molecule surrounded by other molecules is stronger bound with the crystal than if some of the interactions are missing. Therefore, the molecule placed on the surface (or close to it) can be easier ruptured. From this, it is reasonable to suppose that the initiation of chemistry will start near the surface. The energetic barriers for all three bonds in this case are pretty close to each other. Hence, the comparison of activation energies hardly permits to select a particular $N\text{-}NO_2$ group responsible for the first chemical reaction. This suggestion is consistent with the EPR spectra of NO_2 radicals produced by uv photolysis of RDX single crystals [8,14]. It can be established where $N\text{-}NO_2$ bond breakage takes place to form these radicals. In particular, a comparison of the direction cosines of g_{max} for NO_2(I), NO_2(II), and NO_2(III) with the directions calculated from atomic coordinates of the crystal structure suggests that

[1] The molecular cluster consists of 9 RDX molecules.
[2] The molecular cluster is in the form of RDX unit cell.

NO_2(I) forms by cleavage of the equatorial N-NO_2 bond and does not significantly change its orientation in the lattice. The radicals NO_2(II) and NO_2(III) are consistent with cleavage of the axial N-NO_2 bonds, if a rotation of 60° about the O-O direction of each NO_2 radical is showed. NO_2 radicals are known to rotate about the O-O direction at liquid nitrogen temperatures [15-16]. Thus, it was concluded that there is no select N-NO_2 position where NO_2 radicals form in uv-irradiated RDX. The single crystal EPR spectra are consistent with NO_2 radical formation at both the axial and equatorial N-NO_2 positions of the parent molecule [8]. As it follows from energetic considerations obtained in our study, the essential difference of 8-15 kcal/mol appears if the molecule is displaced from the bulk crystal to its surface, and no preference can be made for the equatorial or the axial NO_2 group decomposition.

4 CONCLUSIONS AND APPLICATIONS

We have investigated the mechanism of the solid phase molecular decomposition of RDX. Among all possible reaction pathways, we considered only the most supported by experiments N-NO_2 bond rupture channel. The ab initio Hartree-Fock method combined with two essentially different solid state models such as a molecular cluster and a periodic defect was applied to this problem. A range of molecular clusters and unit cells were probed to ensure that the final conclusion does not depend on computational methods. We have found that the energy for RDX N-NO_2 dissociation is strongly dependent on the environment of the molecule. Thus, an isolated RDX molecule exhibits some difference in energies for the cleavage of the equatorial and the axial bonds against all equal energies for the gas-phase molecule. This is due to bond length changes and symmetry reduction. Furthermore, the equatorial bond of the molecule inside the crystal is sensitive to the crystal field and is characterized by the visibly increased energy comparing to the gas-phase dissociation energy. Finally, significantly lowered energy barriers by 8-15 kcal/mol are obtained for the molecule placed near the surface. Based on energetic considerations, no preference can be made for the equatorial or the axial NO_2 group decomposition. The obtained results are supported by experimental data and previous theoretical investigations.

The important conclusion follows from our study, the molecule located near surface can easier dissociate than the molecule located in the bulk crystal. This may have application in explaining the initiation and detonation behavior of explosive materials. So-called hot spots are known to be associated with the lattice defects such as vacancies, voids, pores, cracks, dislocations, and others. They are able of triggering a fast chemical reaction and explosion. It is well established that defective solids, in particular, RDX typically has high concentration of imperfections even at low temperatures, are much more sensitive to initiation than high quality (perfect) crystals. Our results lead us to the suggestion that one of the reasons for initiation on hot spots is the reduced energetic barrier for the decomposition of molecules placed on defects. Obviously, the surface induced effect must be taken into account studying the initiation mechanisms. A good illustrating example is the well examined pore collapse mechanism. The performed analysis of energetic barriers for decomposition of RDX molecules, placed in different environment, may help in consistent interpretation of existing experimental data, and to provide useful insights for the understanding of mechanisms for detonation initiation of explosive molecular solids. Besides fundamental interest, the obtained conclusions are of great practical importance for safety issues and for the control of sensitivity of explosive crystals to detonation initiation, for storage and handling of energetic materials, for prevention of accidental explosions and fires, and also for manufacturing efficient and safe explosive sensors.

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