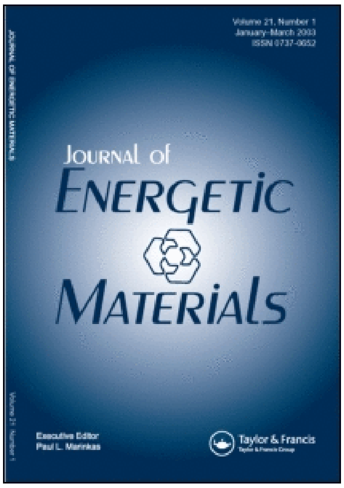

Journal of Energetic Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Microscopic initiation mechanisms in energetic material crystals

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To cite this Article Ramaswamy, Alba L.(2001) 'Microscopic initiation mechanisms in energetic material crystals', Journal of Energetic Materials, 19: 2, 195 — 217

To link to this Article: DOI: 10.1080/07370650108216126

URL: http://dx.doi.org/10.1080/07370650108216126

MICROSCOPIC INITIATION MECHANISMS IN ENERGETIC MATERIAL CRYSTALS

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The sensitivity to initiation of different crystalline polymorphic forms of the same energetic material is known to differ. Similarly single crystals of energetic materials such as PETN and nitromethane show a shock initiation sensitivity anisotropy. The crystal structure of the energetic materials is thus known to control the initiation sensitivity of the same. As will be described in this paper there is evidence to indicate that the orientation of the molecules surrounding a given molecule in the crystal lattice, influences the initial decomposition reaction of the molecule. Several microscopic mechanisms of initiation have been postulated. It is shown here that added to and above these mechanisms the crystal structure can be taken into account in a metastable intermolecular trigger reaction which explains the observed differences in initiation as a function of crystal structure.

Journal of Energetic Materials Vol. 19, 195-217 (2001)
Published in 2001 by Dowden, Brodman & Devine, Inc.

INTRODUCTION - INITIATION MECHANISMS

Most solid explosives or energetic materials used for practical purposes are in granular form. The individual grains consist of single crystals of the explosive. The single crystal thus forms the main sub-element or component of a solid explosive. In general explosives are sensitive to initiation by heat, electrostatic discharge, impact, friction, shock and laser irradiation. However the sensitivity of explosives to impact, shock and other mechanical deformation mechanisms has intrigued scientists since the early 1930s[1,2]. This is due to the fact that the estimated temperature rise[1] in an explosive caused by impact, when computed using energy conservation equations where the impact energy is directly transformed to thermal energy, is at a maximum of the order of ten °C which is insufficient to initiate an explosive thermally since temperature rises of the order of several hundred °C are needed.A wide interest thus opened up to try and understand what mechanisms were primarily responsible for the initiation of explosives during impact, shock and mechanical deformation. The earliest mechanisms were proposed in the 1940s and were "tribochemical" in origin. The combined application of high pressures and the rapid shearing of adjacent molecular layers was believed to cause a direct rupture of the molecule[1,2]. However the calculations demonstrated that the localized stresses were of insufficient magnitude to bring about these changes since the bond energies involved are of the order of 125-210 kJ/mol.

Experimental studies on energetic materials performed in the 1940s-50s, in particular at the Cavendish Laboratory of the University of Cambridge, revealed the formation of microscopic temperature flashes at the points of rubbing contact, during frictional initiation of short duration and with a temperature rise limited by the melting point of the rubbing solid[1]. This led to the idea that the external input energy was being concentrated into localized areas where energy was being concentrated to form "hot spots" with recorded temperatures of several hundred °C. Follow-on experimental analysis proved this hypothesis correct. Various physical mechanisms for the concentration of energy from different energy input sources to form "hot spots" were identified. These were found to consist in the formation of frictional "hot spots" on the confining surfaces, on extraneous grit particles, by intercrystalline friction of the explosive particles themselves, adiabatic compression of small entrapped bubbles of gas, viscous heating of the rapidly flowing explosive as it escapes from between the impact surfaces, shear banding etc. The "hot spots" were first recorded on rotating photographic plates (the precursor to high-speed photography) and by means of infra-red detection cells. From the time constant of the cells, the time duration of the flashes was found to be of the order of

10-1000 μs and the detected intensity revealed temperature rises of up to several hundred °C[1,2,3,4]. The size of the "hot spots" was found to be of the order of 10^{-5} to 10^{-3} cm in diameter, which is large, compared to the molecular dimensions.

The formation of "hot spots" was found to be a general phenomenon in the initiation of energetic materials, where the input energy, irrespective of its original form i.e. impact, friction, shock, is degraded into heat and concentrated in small regions or "hot spots". Thermal ignition of the explosive then occurs at the "hot spots". The "hot spot" was determined to be the critical nucleus of decomposition from which a self-supporting reaction could occur in the remaining mass of explosive. By using advanced techniques of "high-speed photography" it was found that the "hot spots" also play an important role in the growth and propagation of an explosion.

The different "hot spot" energy concentration and shear banding mechanisms determined were used in subsequent years for the theoretical prediction of the shock-to-detonation transition of explosives[6]. The predictions provided good results but were not applicable to all experimental situations. Furthermore many initiation phenomena still remained unexplained. These included the spontaneous detonation of crystals of lead azide as they grow in solution, the explosion of ozone during its cooling or liquefaction to form oxygen, the application of gas pressure to

300 atm. on nitrogen iodide, which causes its spontaneous detonation. In addition the differences in the initiation sensitivity of different crystalline polymorphs of the same energetic material could not be understood as well as the shock initiation anisotropy of single crystals of energetic materials.

A classic experiment performed by J.J. Dick[7,8] in 1990, demonstrated the crystal shock initiation sensitivity anisotropy of crystals of PETN. The PETN crystals were initiated by plane shock waves incident along different crystalline orientations. The [110] direction was found to be the most shock initiation sensitive direction. The [001] direction is the next most favorable shock sensitive direction whereas the [100] direction is unfavorable. The results were explained by a steric hindrance mechanism to shear along specific crystalline planes where the molecules' probing O-NO_2 arms presented obstacles to each other's passage in the shear flow and would thus break. Some orientations were considered to be more favourable to this mechanism than others.

In 1990 M.D. Fayer and D.D. Dlott[9] proposed a mechanism where the shock wave passing through an energetic material results in considerable intramolecular vibration which leads to bond rupture in the explosive molecule. This was referred to as the "multiphonon-vibron up-pumping mechanism". In summary the shock front is considered to excite a narrow region of material, which becomes phonon rich. The energy from the phonon states is transferred to intramolecular vibrations in the explosive molecules, by the process of multiphonon up-pumping. The intramolecular vibrations cause the breaking of the first bond in the explosive molecule. The up-pumping model is handled using a mathematical simplification, termed as the quasi-temperature model[9] where a temporary phonon overheating followed by an up-pumping of the phonons to vibrations via anaharmonic coupling, leads to an intramolecular overheating.

However when the velocity of detonations is considered, one is puzzled by the fact that heat, momentum transfer etc. are all processes which cannot fully account for the velocity of detonations. On the other hand electron transfer/ excitation processes appear rapid enough. This generated the question of whether a different mechanism of initiation is responsible for the shock initiation sensitivity compared to low impact or thermal initiation. In 1995 J.J. Gilman[10] proposed a mechanism of solid metalization during shock. He noted that the shock velocity associated with detonation is about 7 km/s (0.7 x 1014 Angstroms/s), the shock fronts are sharp (5 Angstroms) and the rise time very short (70 femtoseconds) with lattices compressed by about 50%. Thus he noted that the shock velocity is not compatible with ground state thermal, chemical models or mechanical deformation mechanisms. Gilman's proposition was that the 50% solid compression produced in a shock front allows some electron delocalization to ensue and produce a metallization effect. Based on this question B. Kunz made some detailed studies in subsequent years where he applied standard solid state calculations to determine the electron population in the valence and conduction bands of explosive materials. He noted that during compression the band gap is notably reduced.

The initiation mechanisms developed this far are extremely valuable. However many questions still remain open. A full theoretical prediction of the initiation of an energetic material cannot as yet be made. A detailed study of the mechanisms described above shows them to be mainly physical with the chemistry, in many cases, added at the end of the mechanism, as the breaking of one bond in the molecule. Such physical mechanisms can also be applied to inert materials. The question is what makes an explosive different from an inert? It is shown here that the chemistry of the initiation of energetic materials does not simply involve or start with the breaking of one bond in the explosive molecule but is more complex. Thus the decomposition or initiation reaction of an explosive molecule appears to be susceptible to the surrounding environment of the molecule and hence to the crystal lattice structure of the energetic material. An introductory description of the results is given in this paper. They have been incorporated in a physio-chemical mechanism for initiation referred to herewith as "metastable trigger intermolecular initiation mechanism". The mathematical model is being developed as well as further supportive experimental evidence and will be published in another paper. The mechanism is in agreement with other initiation mechanisms described earlier. However it is an atomistic physio-chemical view of the initiation which can explain many observed phenomena in energetic materials and further enhances or complements other initiation models by filling a void or providing that "missing link" between the physics and chemistry of an explosive.

EVIDENCE FOR METASTABLE TRIGGER INTERMOLECULAR INITIATION MECHANISM

The four polymorphs of HMX are known to have different sensitivities to initiation as well as thermal stability properties. Table 1 summarizes the impact sensitivity data for the polymorphs. The crystal structure somehow affects the process of initiation be it mechanical or thermal. Calculations[2] have shown that a steric hindrance effect, as postulated for the shock initiation of PETN, does not create sufficient energy in impact to break the strong covalent HMX intramolecular bonds.

The crystal structure of the different polymorphs of HMX have thus been analyzed in detail. This was performed by reproducing the crystal structure of the polymorphs from x-ray crystal diffraction data for the alpha, beta, gamma and delta forms of HMX, obtained from the literature[11,12,13], using a Crystalmaker computer code[14]. The atomic environment for each terminal atom of an HMX molecule, formed by the surrounding HMX molecules in the crystal lattice, was determined in detail with the code. By environment is meant all the nearest neighbor atoms, the distance apart, whether the atoms are located within the same molecule or the neighboring molecule and the angular relations of the same. To facilitate the analysis, a sphere of given radius was drawn around say each terminal oxygen (the oxygen atoms in the NO_2 groups), with the radius of the sphere larger but of the

HMX-polymorph	Density (g/cm3)	Drop-height for initiation (cm)
Delta	1.80	19.2
Gamma	1.76	13.8-33.9
Alpha	1.82	15.6-26.4
Beta	1.90	21.2-24.9

TABLE 1
Impact initiation sensitivity of the HMX polymorphs[15]

order of the intramolecular bond distance (i.e. x~2 of the intramolecular bond length), and the atoms located within the sphere identified.

It was found that the molecular "environment" surrounding a given molecule in each polymorph differed considerably. For the most sensitive polymorph it was often found that two hydrogen atoms were placed/ located around a central oxygen atom with the H-O-H angle being very close to that of the water molecule. The formation of water is known to be a reaction product of the HMX decomposition and is one of the most common reaction products for the decomposition of energetic materials.

Six out of eight oxygen atoms in the delta-HMX molecule, the most sensitive polymorph of HMX, were found to be in atomic positions surrounded by hydrogen atoms such that the H-O-H angle is close to that of a water molecule and the H-O and O-H distances are close to ~x2 intramolecular bond lengths. In alpha-HMX, which is less sensitive, only two such oxygen atoms out of eight can be found. The results are summarized in Figure 1.Beta-HMX is the least sensitive polymorph of all four and there are four oxygen atoms out of eight in critical locations. However its density of 1.90 g/cm^3 is higher than that of alpha and delta-HMX which are respectively 1.82 and 1.80 g/cm^3. The effect of the density is described later in the paper.

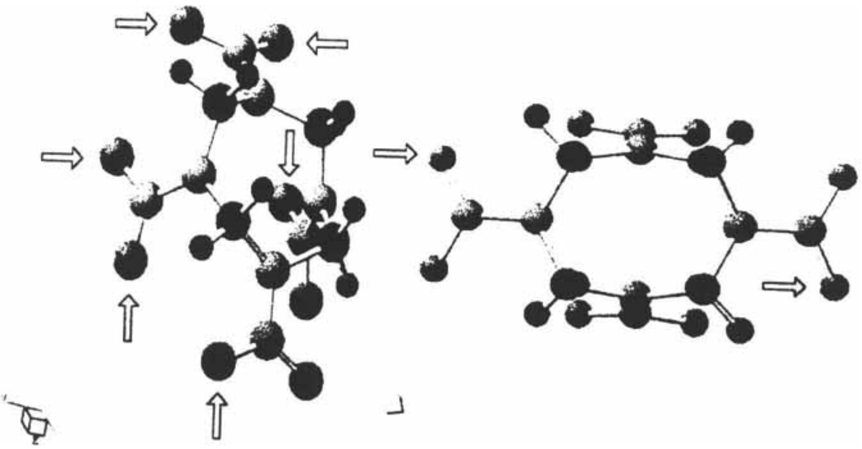

FIGURE 1
Six out of eight oxygen atoms in delta-HMX, the most sensitive polymorph, are critically positioned for trigger reactions in comparison to two out of eight for alpha-HMX.

Now what the observations are indicating is that the molecules of the explosive are surrounded by a molecular environment which differs drastically between the different crystal lattices of the polymorphs. The main difference which can be observed is the possibility for intermolecular oxidation-reduction reactions, since the atomic positions and separations in the most sensitive polymorphs appear to favor the formation of reaction products. Initiation models developed this far have assumed that the breaking of the first bond in an explosive molecule starts the exothermic explosive reaction. Thus physical mechanisms have been deduced which explain how input energy can be concentrated to create sufficient energy to break an intramolecular bond. Such mechanisms however can equally well be applied to inert materials. Also they are purely physical and do not include the chemistry of the energetic material. The behavior of an inert material is very different from that of an explosive. Thus one of the main questions is, what makes an explosive explosive? Explosives contain the oxidizer and oxidizable element in the same molecule. The fast reaction of explosives is indicative of the atomic closeness of the oxidizer and oxidizable elements. The observations described herewith indicate that in neighboring molecules the oxidizable and oxidizer atoms are facing each other and are already positioned to favor the formation of a reaction product. Furthermore neighboring molecules can be pushed close to each other in a compression wave, triggering such a reaction. An oxidation-reduction reaction within the same molecule can occur with greatest ease by participation of atoms from a neighboring molecule.

During impact or shock initiation a compression wave is known to cross the material. This can cause the neighboring molecules to come close enough to start a concerted reaction where an intermolecular oxidation-reduction reaction may be triggering the breaking of the first bond in the explosive molecule. This has been termed as a "metastable intermolecular trigger mechanism for initiation".

In the case of beta-HMX, the highest density polymorph, it requires a higher impinging/ incident force during initiation to force the atoms to a close enough distance or "reaction coordinate" separation to trigger a metastable intermolecular oxidation-reduction reaction. In fact it is known that the highest density polymorphs are always the most thermally stable and most energetic materials.

Standard Arrhenius kinetic analysis seems to indicate that in the thermal decomposition of energetic materials the explosive reaction occurs as a result of the breaking of the first bond, say the C-N bond in the explosive molecule. However in the Arrhenius kinetic analysis a transitional excited state of the molecule, of which not much was known was assumed prior to bond breaking. It is this transitional excited state which appears to contain the intermolecular reaction. Since the transitional excited state is very short-lived, it can only be analyzed with the most advanced techniques of high-resolution temporal laser spectroscopy. Dr. A. Zewail, 1999 Nobel prize for chemistry for the development of femtosecond spectroscopy, studied the combustion reaction between hydrogen and carbon dioxide in the atmosphere. He found that the reaction,

$$H + CO_2 \rightarrow CO + OH$$

crosses a relatively long transitional state of HOCO (1000 fs). The transitional excited state incorporates a bonding oxidation-reduction reaction, which is followed by bond rupture only 1000 fs later. This is supportive of the mechanism described this far.

Figure 2 shows the differential scanning calorimetry plot of the thermal decomposition of HMX. The data shows that when melting commences in the material, exothermic decomposition also starts. This occurs also in RDX. The weak van der Waals

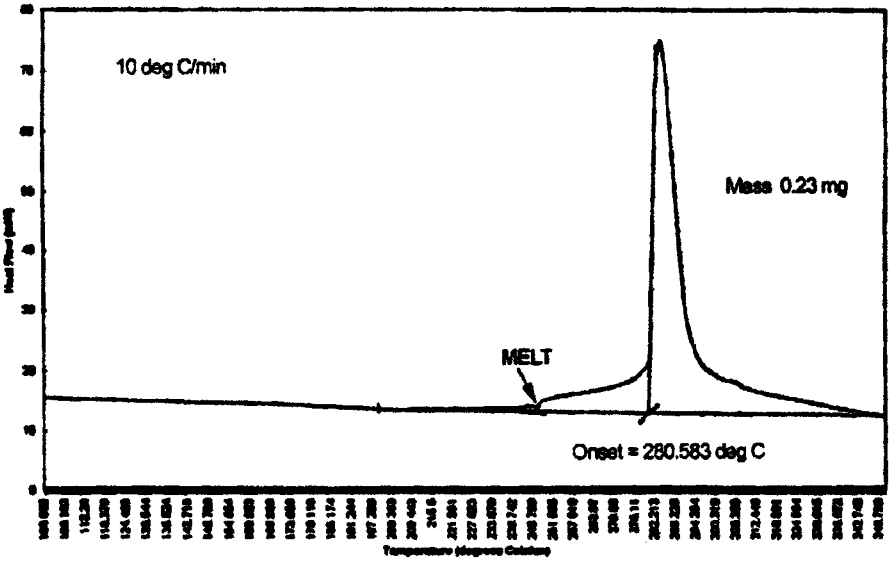

FIGURE 2
DSC scan for HMX at a heating rate of 10 degC/min showing that when melting commences, exothermic decomposition reactions also start

intermolecular bond energy in HMX is of the order of 30-60 kJ/mol. The intramolecular bond energy is about 150-210 kJ/mol. If the mechanism of thermal decomposition was merely one of intramolecular bond rupture, the melting would be separate from the decomposition by about a factor of two i.e. melting point at ~200°C and decomposition at ~400°C. However the superposition of the two peaks indicates that the same energy which affects the intermolecular bonds is also affecting initiation.

Further evidence for a "metastable intermolecular trigger reaction" comes from early work where the size of the smallest decomposition nucleus was being estimated[16]. Thus experimentally[17,18] it was found that when rapidly moving atomic and nuclear projectiles are "fired" onto a lead azide surface, detonation occurs except when alpha-particles or electrons are used as projectiles. Alpha-particles and electrons have the smallest cross-section and would only activate a single molecule of lead azide. When ions of argon and mercury were used, which are large enough to activate neighboring molecules, explosion takes place. This supports the fact that two neighboring molecules are necessary for the formation of the first "reaction site".

The compression of a crystal lattice under shock initiation thus appears to bring the molecules near enough to initiate the "trigger reactions". This would explain the phenomena not readily explicable by the classical "hot spot" theory. Thus when ozone is cooled, the position of the oxygen atoms comes closer. This facilitates bond formation and it becomes more energetically favorable to form oxygen molecules from ozone molecules, hence the explosion of ozone on cooling. Similarly the crystallization of lead azide from solution is bringing the atoms or molecules closer for bond formation and thus nitrogen molecules are more energetically favorable than azide ions, causing the explosion of the lead azide crystals during growth in solution. And finally the fact that explosives are particularly susceptible to initiation by impact, shock or mechanical deformation and the detonation of nitrogen iodide subjected to a 300 atm. pressure, are all indicative of the mechanism described above, since in all cases a compression wave is generated through the material which causes the atoms in neighboring molecules to come closer at certain instances in time.

Thus when the shock initiation of PETN and its crystal lattice structure are analyzed in detail, further support for the mechanism is obtained. As described in the Introduction, the [110] direction was found to be the most shock initiation sensitive direction in PETN. The [001] direction is the next most favorable shock sensitive direction where as the [100] direction is unfavorable to initiation. In fact, as can be seen in Figure 3 when a shock or compression wave is propagated along the [110] direction, the position of the molecules/ atoms in the crystal lattice is such that the greatest number of neighboring O and H atoms come close in the intermolecular space between the neighboring molecules. In the next favorable direction, the number of O and H atoms directed towards each other in the intermolecular space is less and finally in the [100] direction, the unfavorable direction to initiation, there are no O atoms facing the H atoms.

Finally a "metastable intermolecular trigger initiation mechanism" is in agreement with the "hot spot" mechanisms. Thus utilization of analytical equipment with higher spatial and temporal resolutions than were used in the past has shown that initiation does in fact start at microscopic sites smaller than the critical "hot spot" size and is highly inhomogeneous[19, 20]. As described in the literature "reaction sites" form on the crystal surfaces, which are smaller than the critical "hot spot" size but lead to and develop into "hot spots". The "reaction sites" have been found to have crystallographic shape or structure which vary according to the energetic material and the crystal habit on which they form[19,20,21,22] Chemical reaction or decomposition was confirmed in the "reaction sites" by x-ray photoelectron spectroscopy[19,23]. The crystallographic shape of the "reaction sites" is further evidence for the fact that the precise position of the atoms/ molecules in the crystal lattice controls the

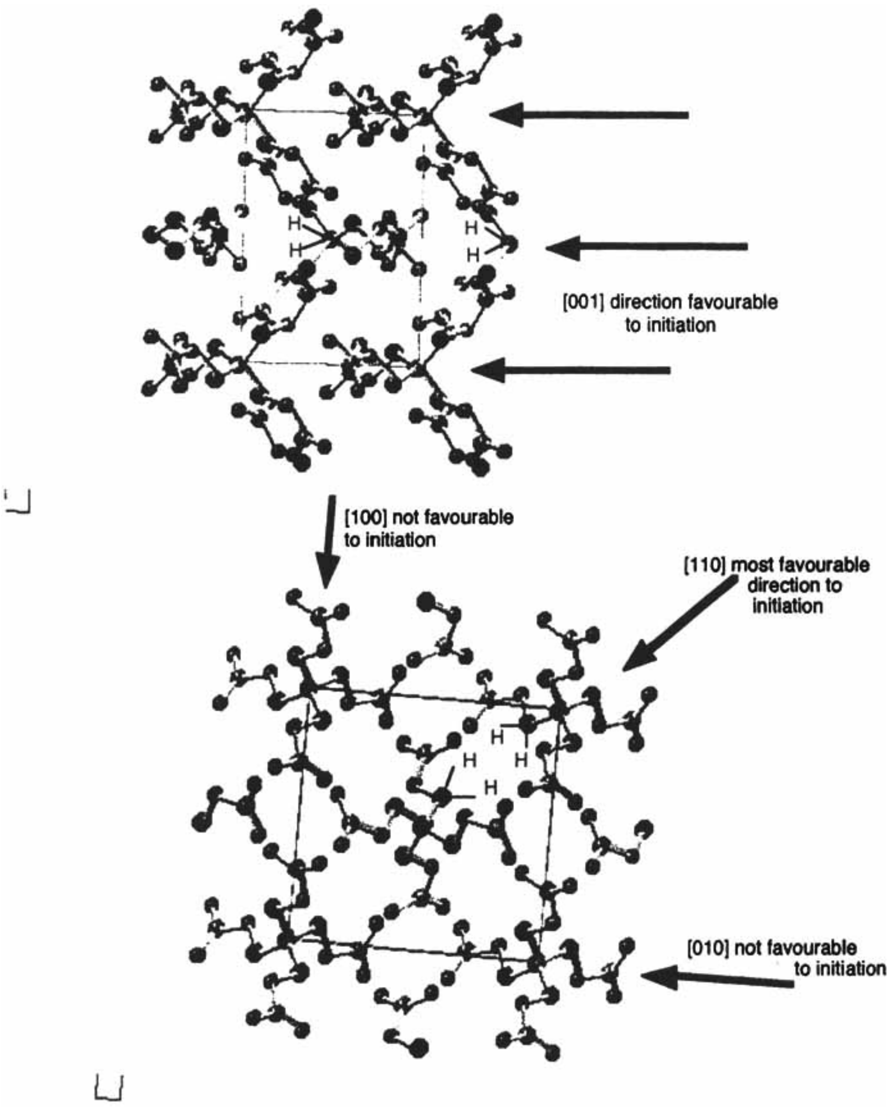

FIGURE 3
PETN shock initiation anisotropy

initiation and is in agreement with a "metastable intermolecular trigger reaction". Thus the localization of the reactions in a "reaction site" or "hot spot" shows that the site begins at an atomic/ molecular level at a single point, which may be obtained where two neighboring molecules come together or close enough to "trigger" the formation of a reaction product and subsequent bond-breaking and forming reactions. Further experimental evidence and a mathematical model for the "metastable intermolecular trigger mechanism" are being developed.

DISCUSSION

Evidence has been given here for the role of a "metastable intermolecular trigger reaction" during initiation. Different physical mechanisms may be occurring during the process of thermal, impact and shock initiation but one constant binds them all and that is the atomic closeness of the oxidizable and reducable elements of the chemical explosive material and thus the possibility of the co-participation of neighboring molecules in the reaction. An oxidation-reduction reaction requires the re-arrangement of the electrons in the orbitals and is thus fundamentally electronic. This agrees with the band gap observations by B. Kunz and the detonation velocities of energetic materials. The beauty in the crystals of solid explosives is that the 3-D arrangement and repetition of atoms is "frozen" in space and reactions start to occur in the solid phase. Thus different arrangements provide for more or less favorable oxidation-reduction reactions. It may thus be possible in the near-future to better predict the initiation of solid energetic materials and to develop inclusions which may hinder or block critical "trigger" reactions until a higher threshold is achieved thus giving the potential of generating a new class of insensitive energetic materials which maintain the required performance characteristics.

ACKNOWLEDGMENTS

This work was supported by ONR. Very special thanks go to Dr. Richard Miller. Thanks go to Dr. Judah Goldwasser for his valuable guidance and directives. Thanks also go to Dr. Jagadish Sharma for many enlighting years of close collaboration. Thanks also to Dr. Bob Wardle and Tom Highsmith for the very valuable scientific exchange, discussions and encouragement. Further thanks go to Dr. Joe Heimerl for his valuable encouragements. Many thanks to the CAD/PAD Dept. of NSWC Indian Head, for allowing me to learn from many real-world practical "energetic" scenarios. Further thanks go to the following manufacturers and laboratories for their valuable data/assistance; Thiokol, NSWC Indian Head, Army Research Laboratory, Cambridge University (Cavendish Laboratory) and University of Maryland at College Park. And finally many thanks to my parents.

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