Chapter 1

INTRODUCTION TO ENERGETIC MATERIALS

Energetic materials are a class of material that can release chemical energy stored in their molecular structure. Upon external stimulations, such as heat, shock, or electrical current, these materials will emit energy in a short time.[1] The earliest record of energetic material can be traced back to the text written in the 6th century by the Chinese alchemist Sun Simiao, in which the combustion of the powder mixture of sulfur and nitrate salts was described.[2] Later the invention was modified and applied in the war between the Song dynasty and Mongols. In 1867, Alfred Nobel invented and commercialized dynamite, a mixture of nitroglycerin and silica, which was more stable and safer to use, leading to its high demand in the First World War. Although firstly known for its military application, today energetic materials are used more in fields of civil engineering and space exploration, such as mining, construction, and rocket propelling.[3] Even with a long history of development, people are still seeking for saver, more powerful, and more cost-effective energetic materials. To make a knowledge-based improvement and engineering, it is the first priority to understand the chemistry of energetic materials. However, the fast reaction rate and extreme reaction conditions make direct experimental measurement difficult. Developing the knowledge through computer simulation provides a safer and convenient way to study the chemistry of energetic material. In this thesis first-principle calculation is used to study the initiation of several different energetic materials.

Based on their applications, energetic materials can be classified as explosives, propellants, and pyrotechnics. The first two are discussed in this thesis and shortly introduced here.

- Explosives:

Explosives are expected to release large energy and expand greatly in volume to generate force in the time scale of μs. To achieve high power output, it is necessary to propagate reaction rapidly through the whole material, as known as detonate. Detonation, deflagration, and regular fuel combustion are different phenomena distinguished by their rate-determining-step and propagation rate. For regular fuel combustion, the reaction rate is limited by diffusion of reactive species (mass transfer), which is relatively slow, leading to low propagation rate. In the case of deflagration, the oxidizer and fuel are premixed, therefore the diffusion of reactive species is no longer the rate-determining-step. Instead, the propagation of reaction zoom is controlled by heat transfer, resulting in its faster rate than regular fuel combustion. When energetic material detonates, the shockwave propagates through the material. At the wave front the material is highly compressed, leading to the temperature rise, which triggers exothermic chemical reactions and create a chemical reaction zoom after the wave front. The exothermic reactions increase the temperature and pressure to the point higher than the condition before the passage of shock wave, which provide energy to sustain the propagation of shock wave. Therefore detonation is in the speed of shock wave, which is supersonic, in contrast to the cases of deflagration and regular fuel combustion, which are subsonic.

Several parameters can be used to characterize explosives, as described below.

i) Sensitivity:

This represents how easily the explosives can be set off by external stimulus, such as impact, friction, shock, spark, and heat. Based on their sensitivity, explosives can be categorized into primary and secondary explosives. Primary explosives are highly sensitive and easy to undergo the deflagration-to-detonation transition (DDT). On the other hand, secondary explosives, or high explosives are less sensitive, but usually more powerful. A common way to take advantage of both explosives is to place a small amount of primary explosive adjacent to a large amount of secondary explosive, or so called explosive trains. The fast DDT of primary explosive helps to amplify the initial non-explosive impulse to shockwave, which then detonates secondary explosive.

ii) Heat of explosion (*Q*)

This represents the amount of heat released from the decomposition of explosive during explosion. This quantity can be well approximated as the difference of the heat of formation of combustion products and explosive itself. Large heat of formation is preferred for explosives because it leads to higher explosive power, which is defined as the product of heat of formation and the volume of gas product.

iii) Detonation velocity (*D*)

This quantity represents how fast the detonation wave propagates and therefore controls the rate of energy release of explosives. The value of detonation velocity increases with the density of packing of explosives in the column and is positively correlated with the detonation pressure. For most applications, such as rock cleaving and grenade, it is desirable for explosives to reach its peak pressure quickly to maximize the shattering power, and high velocity of detonation is necessary. The shattering power can be quantified by brisance, which is defined as the product of the loading density, the detonation velocity, and the specific energy (the maximum pressure through explosion multiplies volume of detonation gases).

There are many factors that determine the practicality of explosives. For the primary explosives, a fast deflagration-to-detonation transition is the requirement to be able to generate the shock wave to initiate the detonation of the secondary explosives. Despite their high sensitivities, the chemical and thermal stability of primary explosives are still necessary to have longer shelf life. Historically, heavy metal salts, such as mercury fulminate, lead azide and lead styphnate, have been used as the primary explosive. Their combustion products are hazardous if breathed in and cause the environment pollution, leading to a need to seek for metal-free primary explosives. For the secondary explosives, besides the performance requirements (high detonation velocity and large heat of explosion), it is very important to have low sensitivity and long term stability, which make it easier to store and handle these explosives in large amounts. The production cost is another important issue to determine if one kind of explosive is practical or not.

- Propellants:

Propellants are not expected to detonate, but combust in a controlled manner, i.e., DDT is not desired for propellants, different than explosives. The most important performance parameter of propellants is specific impulse (I_{sp}), which is defined as the gain of impulse (impulse=force × time, or mass × velocity)[4] when one unit mass of propellants is consumed, and it can be roughly perceived as the exhaust velocity. Since I_{sp} is normalized to per unit mass, it is a material-specific parameter and not dependent on the burning rate of propellant if the thrust comes from only the exhaust gas.

Propellants can be in liquid or solid form. Common solid propellants are mixtures of oxidant (nitrate or perchlorate salts) and reductant powder (C, Al, etc.). Explosives, such as RDX or HMX, can also be used as propellants, as long as there is no shockwave generated during the combustion to start the detonation. Rocket motors powered by solid propellants have high propellant fraction in weight because there is no liquid pump or cryogenic tank, and they are more reliable to operate. The drawback is that once the motor starts, there is little control over the combustion of the solid propellants.

Liquid propellants can be further categorized into monopropellants and bipropellants. Common monopropellants, such as hydrogen peroxide and hydrazine, are able to decompose catalytically to release gas products and heat. However their I_{sp} are not as high as bipropellants, and this is usually due to their smaller ΔH. Thus, monopropellants they are only applied on missions with small loading.

Bipropellants include oxidizer and fuel that are injected and mixed in the combustion chamber. One important type of bipropellants is hypergolic propellants, which are pairs of fuel and oxidizer that ignite spontaneously upon mixing. They facilitate the design of rocket thrusters by simplifying the ignition system, and are widely used in propulsion systems in which variable and/or intermittent thrust capabilities are needed. Besides I_{sp}, the most important parameter of hypergolic propellant is ignition delay, which is defined as the time interval from the touch of two liquid surfaces to the flame appearance. Shorter ignition delay implies faster response and easier motion control. Hydrazine and its derivatives, such as monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) are commonly used hypergolic fuels combining with HNO_3 or nitrogen tetroxide (NTO) as oxidizer. However hydrazine derivatives are carcinogens and to replace them with safer fuels, such as alkylamines, is desirable.

At atomistic level, the initiation of energetic material involves two processes, molecule activation and energy propagation, which form a positive feedback loop. Starting with the cold, unreacted material, the external stimuli drive molecules in ground state going over barriers. At the condition that stimuli are not too strong, only low-lying reaction channels are activated. As these reactions proceed, some of them are exothermic and raise the local temperature. The heat and mechanical energy propagate to neighboring unreacted molecules as the external stimuli and repeat the process. In the above mechanism there are three factors affecting propagation rate of reaction zoom: 1.) the barrier height of reactions, which controls the accessibility of reaction channels, 2.) the exothermicity of reactions, which associates with the amount of heat that is released to raise the local temperature, and 3.) the efficiency of energy transfer to neighbor molecules. The energy can be transferred via the coupling of vibrations between adjacent molecules or via the momentum carried by ballistic gas molecules generated and accelerated in the exothermic, gas-releasing reactions. These three factors determine the sensitivity of energetic materials, as one or more highly exothermic channels with low barrier height will lead to the high sensitivity.

It is possible to theoretically characterize the overall combustion process of energetic material via multi-paradigm multi-scale simulations. Firstly the reaction mechanism, such as the barrier height and exothermicity of unimolecular or bimolecular reactions starting from the unreacted molecule can be constructed with first-principle based methods. Based on these reaction mechanisms and potential energy surfaces, one can develop force field for the simulation of molecular dynamics (MD), which can be applied to study multimolecular process such as energy transfer between molecules and reactions occurring in condense phase. Finally, one can construct a combustion model containing rate constant and exothermicity of reactions for all species based on MD simulation results. The model can describe the time-evolution of all species and when combined with continuum fluid dynamics (CFD), a detailed simulation of engine operation including macroscopic phenomena, such as diffusion and heat transfer, can be achieved.

The focus of this thesis is to use first-principle method to develop the early reaction mechanisms of different energetic materials, where the temperature is still low and channels involving direct bond-fission are not accessible. Such mechanisms at the early stage are important to determine the sensitivity and initiation of energetic materials. In the second chapter, a newly synthesized, Si-based explosive, Si-PETN, is studied. Its colossal sensitivity is found to be correlated to a particular reaction path that is with low barrier and high exothermicity. The third chapter studies the decomposition mechanism of a new class of energetic material, azobis(tetrazole) and azobis(triazole), which contain very high percentage of nitrogen. The fourth chapter discusses the reaction mechanism of two hypergolic fuel and oxidizer pairs, N,N,N',N'-tetramethylethylenediamine (TMEDA) and N,N,N',N'-tetramethylmethylenediamine (TMMDA) with nitric acid. The difference in their ignition delays is explained based on the reaction mechanism and the exothermicity for formation of the dinitrate salt from TMEDA or TMMDA. The fifth chapter studies the reaction mechanisms of hypergolic pair, MMH/NTO. The sixth chapter covers the other hypergolic pair, UDMH/NTO, in the preignition environment. The gas products were found to consistent with the experimental results.

References:

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