

First-principle studies of the initiation
mechanism of energetic materials

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To my family

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ABSTRACT

It is important to understand the initiation mechanism of energetic materials to improve and engineer them. In this thesis, first-principle calculation is used to study the initiation of several explosives and propellants.

The second chapter is focused on a new energetic material, silicon pentaerythritol tetranitrate (Si-PETN), DFT calculations have identified the novel rearrangement that explains the very dramatic increase in sensitivity observed experimentally. The critical difference is that Si-PETN allows a favorable five-coordinate transition state in which the new Si-O and C-O bonds form simultaneously, leading to a transition state barrier of 33 kcal/mol (it is 80 kcal/mol for PETN) and much lower than the normal O-NO₂ bond fission observed in other energetic materials (40 kcal/mol). In addition this new mechanism is very exothermic (45 kcal/mol) leading to a large net energy release at the very early stages of Si-PETN decomposition.

The third chapter is about nitrogen-rich compounds, which has high heat of formation and releases the energy by decomposing into stable N₂ molecules. Two families of compounds, azobistetrazoles and azobistriazoles, were studied. Based on the calculated mechanisms, for azobistetrazoles with four N atoms in the five-member ring, a clearly-defined N=N fragment can always be found in the ring, and its decomposition starts with ring-opening to free one end of N=N followed by N₂ dissociation and heat generation. This barrier is around 28-35 kcal/mol, which is low enough to dominate the sensitivity of material. For azobistriazoles, only 1,1'-azobis-1,2,3-triazole has a N=N fragment in the original 5-member ring and similar ring-opening - N₂ dissociation pathway is favored.

For the remaining compounds, an additional isomerization is necessary to release N_2 , which gives the barrier around 55~60 kcal/mol, making these compound less sensitive.

The fourth chapter shifts focus to hypergolic propellants. DFT calculations with B3LYP functional was applied to study the hypergolic reaction between N,N,N',N'-tetramethylethylenediamine (TMEDA), N,N,N',N'-Tetramethylmethylenediamine (TMMDA) and HNO_3 . Bond energies in TMEDA and TMMDA were calculated and compared with their alkane analogues to demonstrate that the lone-pair electrons on N atoms plays the role of activating adjacent chemical bonds. Two key factors relating to the ignition delay were calculated at atomistic level. The first factor is the exothermicity of the formation of the dinitrate salt of TMEDA and TMMDA. Because of the shorter distance between basic amines in TMMDA, it is more difficult to protonate both amines for the stronger electrostatic repulsion, resulting in the smaller heat of dinitrate salt formation by 6.3kcal/mol. The second factor is the reaction rate of TMEDA and TMMDA reacting with NO_2 to the step that releases enough heat and more reactive species to propagate reaction. In TMEDA, the formation of the intermediate with C-C double bond and the low bond energy of C-C single bond provide a route with low barrier to oxidize C. Both factors can contribute to the shorter ignition delay of TMEDA.

The fifth chapter is about the other pair of hypergolic propellant, monomethylhydrazine (MMH) with oxidizers NO_2/N_2O_4 . Experimentally several IR-active species were identified in the early reactions, including HONO, monomethylhydrazinium nitrite (MMH•HONO), methyl diazene ($CH_3N=NH$), methyl nitrate (CH_3ONO_2), methyl nitrite (CH_3ONO), nitromethane (CH_3NO_2), methyl azide (CH_3N_3), H_2O , N_2O and NO . In order to elucidate the mechanisms by which these

observed products are formed, we carried out quantum mechanics calculations (CCSD(T)/6-31G**//M06-2X/6-311G**++) for the possible reaction pathways. Based on these studies, we proposed that the oxidation of MMH in an atmosphere of NO_2 occurs via two mechanisms: (1) sequential H-abstraction and HONO formation, and (2) reaction of MMH with asymmetric ONONO_2 , leading to formation of methyl nitrate. These mechanisms successfully explain all intermediates observed experimentally. We concluded that the formation of asymmetric ONONO_2 is assisted by an aerosol formed by HONO and MMH that provides a large surface area for ONONO_2 to condense, leading to the generation of methyl nitrate. Thus, we proposed that the overall pre-ignition process involves both gas-phase and aerosol-phase reactions.

The sixth chapter is about another pair of hypergolic propellant, unsymmetrical dimethylhydrazine (UDMH) with oxidizers $\text{NO}_2/\text{N}_2\text{O}_4$. We carried out the same level of quantum mechanics calculations as MMH to study this pair. We proposed that the oxidation of UDMH in an atmosphere of NO_2 occurs via two mechanisms, similar with MMH: (1) sequential H-abstraction and HONO formation in gas phase, which has no more than 20 kcal/mol barrier and leads to the production of $(\text{CH}_3)_2\text{NNO}$ and HONO. (2)UDMH reacts with asymmetric ONONO_2 in aerosol phase, leading to formation of CH_3N_3 and then CH_3ONO_2 , with a 26.8 kcal/mol enthalpic barrier, which is 10 kcal/mol higher than the corresponding reaction barrier for MMH. Thus we predicted the low production rate of CH_3ONO_2 for UDMH/ NO_2 pair. Experimental evidences support our mechanisms for both MMH and UDMH reacting with NO_2 .

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