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Prediction of electronically nonadiabatic decomposition mechanisms of isolated gas phase nitrogen-rich energetic salt: Guanidium-triazolate

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ABSTRACT

Electronically nonadiabatic decomposition pathways of guanidium triazolate are explored theoretically. Nonadiabatically coupled potential energy surfaces are explored at the complete active space self-consistent field (CASSCF) level of theory. For better estimation of energies complete active space second order perturbation theories (CASPT2 and CASMP2) are also employed. Density functional theory (DFT) with B3LYP functional and MP2 level of theory are used to explore subsequent ground state decomposition pathways. In comparison with all possible stable decomposition products (such as, N_2, NH_3, HNC, HCN, NH_2CN and CH_3NC), only NH_3 (with NH_2CN) and N_2 are predicted to be energetically most accessible initial decomposition products. Furthermore, different conical intersections between the S_1 and S_0 surfaces, which are computed at the CASSCF(14,10)/6-31G(d) level of theory, are found to play an essential role in the excited state deactivation process of guanidium triazolate. This is the first report on the electronically nonadiabatic decomposition mechanisms of isolated guanidium triazolate salt.

1. Introduction

One of the most recent developments in the field of high energy density materials is high nitrogen content energetic salts [1–11]. Salt-based energetic materials often possess advantages over nonionic molecules, as these salts tend to exhibit lower vapor pressure and higher thermal stability than their atomically similar nonionic analogues. They often exhibit strong hydrogen bonds, which result in remarkable stability and considerable insensitivity to physical stimuli, without much altering explosive performance. Furthermore, high energy propellant and explosive properties of energetic salts can be improved and optimized through judicious combination of different anions and cations. However, to improve and control propellant and explosive properties of energetic salts, it is essential to elucidate atomistic mechanisms of their decomposition reactions, which ultimately determine efficient release of stored chemical energy.

Ultimate release of the stored energy during detonation of any energetic material, which finally manifests explosion, definitely depends on phase. True energetic (explosive) behavior is typically displayed only in the condensed phase; an isolated gas phase cluster or molecule does definitely not explode. Nonetheless, the rapid decomposition process (which, in turn, releases stored energy) of energetic materials must be of molecular in nature prior to any intermolecular chain reaction that can occur in the condensed phase. Therefore, studying the unimolecular decomposition behavior of isolated energetic molecules or clusters (including energetic salt) in the gas phase is an important pursuit both experimentally and theoretically, if we want to understand and design them at a fundamental level.

Guanidium cation and triazolate anion are frequently found as nitrogen rich building block pair in many novel energetic salts [12]. Some of the known guanidium-triazolate-based energetic salts include bis-(triaminoguanidinium) 3,3′-dinitro-5,5′-azo-1,2,4-triazolate (TAGDNAT), triaminoguanidium-(3,3′-dinitroazoxy-1,2,4-triazolate) (TAGDNATO). Chemical structures of these energetic salts are illustrated in Fig. 1. These salts are found to be intrinsically non-volatile and thermally stable under normal conditions and are denser than atomically similar nonionic analogues. Understanding unimolecular decomposition reaction mechanisms of these ionic salts is an important task. However, these molecules are large and may exhibit complex decomposition reaction channels. This is why, taking reductionist approach in the present study, we have selected a structurally simple analogue salt, guanidium triazolate (see Fig. 1 for chemical structure), which can arguably serve as a model system for the entire class of guanidium triazolate-based energetic salts.

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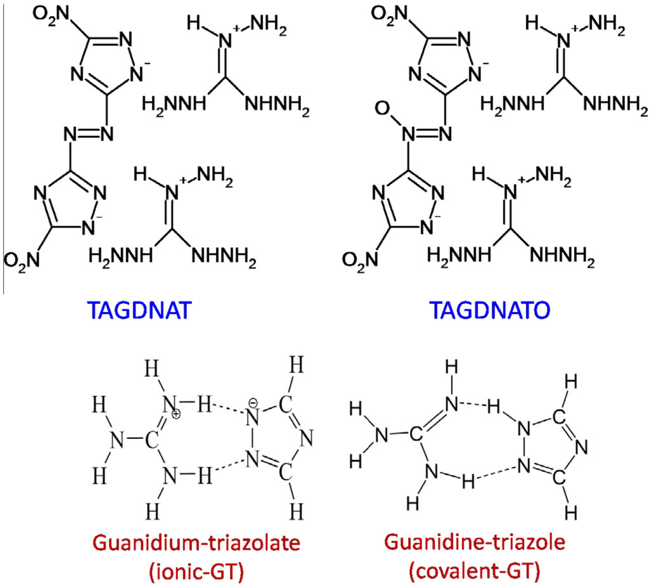

Fig. 1. Chemical structure of bis-triaminoguanidinium-(3,3′-dinitroazotriazolate) (TAGDNAT) and triaminoguanidium-(3,3′-dinitroazoxy-1,2,4-triazolate) (TAGDNATO), and a model system: guanidium triazolate.

Upon careful inspection of all the chemical structures given in Fig. 1, it is obvious to everybody that all guanidium triazolate-based energetic salts are nothing but organic molecules. They are decomposed under typical initiation events, such as shocks and pressure waves. Upon employing pressure using a mortar and a pestle, many organic compounds emit light flashes. This phenomenon is called triboluminescence [13] in which generation of electronically excited state species is anticipated. Many mechanisms for triboluminescence are suggested [14]; however, in general, it is well accepted that as crystal planes fracture, generation of large electric fields can electronically excite organic species. Thus, even shock waves from gentle hand grinding can excite organic molecules to the electronically excited states. These excitations are a fact and cannot be ignored in consideration of the decomposition of any energetic material. In fact, recent *ab initio* calculations show that shock compression at a pressure of 30 GPa or above can cause an electronic excitation equivalent to 2–5 eV [14e], which is comparable to the excitation energies of the low-lying excited electronic states of most of the energetic molecules. "How does such electronic excitation affect the decomposition of guanidium-triazolate-based salt?" is still an open question and no literature on the unimolecular decomposition of isolated guanidium triazolate salt following electronic excitation is found, thus far. This is why we have undertaken the task of understanding

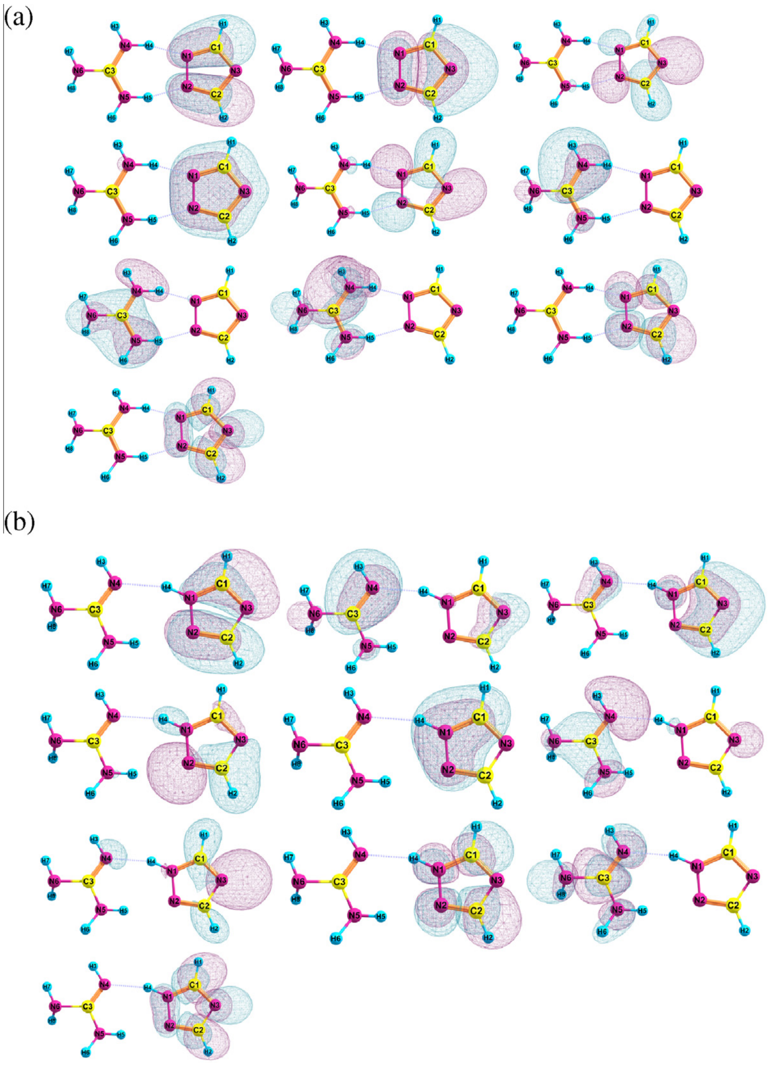

Fig. 2. Active orbitals used in the CASSCF, CASPT2 and CASMP2 calculations for ionic-GT (a) and covalent-GT (b).