



Electronically nonadiabatic decomposition mechanisms of clusters of zinc and dimethylnitramine



Anupam Bera, Sonal Maroo, Atanu Bhattacharya*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

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ABSTRACT

Electronically nonadiabatic decomposition mechanisms of dimethylnitramine (DMNA) in presence of zinc metal clusters are explored. Complete active space self-consistent field (CASSCF) calculation is employed for DMNA–Zn and ONIOM (Our own N-layered integrated molecular orbital and molecular mechanics) methodology is coupled with CASSCF methodology for DMNA–Zn₁₀ cluster. Present computational results show that DMNA–Zn clusters undergo electronically nonadiabatic reactions, rendering nitro-nitrite isomerization followed by NO elimination. The overall reactions are also found to be highly exothermic in nature. This is the first report on electronically nonadiabatic decomposition pathways of DMNA–Zn_n neutral clusters.

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1. Introduction

Energetic materials encompass substances (composed of organic molecules containing C, H, N, and O) that are potent sources of large chemical energy which is released upon their rapid decomposition or detonation. They constitute a major part of propellants, explosives, and pyrotechnics and their applications span over a wide region from mining, construction and demolition to safety equipments (signal flares and fire suppression systems), rocketry and space exploration. It is because of their great practical importance that researches are being carried out to understand and to optimize the performance, burning behavior, stability, and detonation properties [1–3]. The focus is often laid on quantifying the amount of energy released, identifying key reaction mechanisms, or investigating ways in which the energy release can be controlled. In order to accomplish these tasks, however, we must understand the fundamental steps in the overall decomposition of energetic materials. Even the initial steps in the overall decomposition of energetic molecules are complex, involving numerous chemical and physical events in a concerted and synergistic fashion, often influenced by a variety of factors. If the dissociation/detonation of energetic materials is initiated by sparks, shock waves or arcs then the decomposition can begin with promoting energetic molecules to the electronically excited states [4]. For an example, 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 [4e], which is comparable to the excitation energies of the low lying excited electronic states of most of the energetic molecules, such as RDX, HMX, CL-20 [5]. Recently, Bernstein and his co-workers have firmly established, both theoretically and experimentally, that conical intersections, which create a funnel-like topography of potential energy surfaces (PESs) due to the crossing of multidimensional electronic PESs, are a controlling factor in the excited electronic state decomposition of energetic molecules [6]. Thus, the initial decomposition steps of the energetic molecules are electronically non-adiabatic in nature, because of the involvement of more than one electronic PES.

For a long time, molecular energetic materials, which are composed of oxidizer and fuel in one molecule such as RDX, HMX, CL-20, were used as rocket propellants for their ability to release high energy during decomposition or detonation; however, recently, metalized energetic materials, which are the mixture of these molecular energetic materials and metal particles (e.g., Zn, Al, Fe, etc.), are found to be better propellants over molecular energetic systems. The efficiency of energy release of metalized energetic materials is twice as compare to the best molecular energetic materials [7], shortening the ignition delay time with complete combustion, faster energy release and more control over performance [8]. There is a wide consensus in the energetic materials community that this increase in efficiency of the energy release by metalized energetic materials is attributed to the exothermicity of stable oxide formation of the corresponding metal (e.g., heat of oxide formation for aluminium ($4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3$) is -1676 kJ/mol [9] and that for zinc ($2\text{Zn} + \text{O}_2 = 2\text{ZnO}$) is -347 kJ/mole [10]). But this explanation is not just sufficient

* Corresponding author.

E-mail address: atanub@ipc.iisc.ernet.in (A. Bhattacharya).

enough to explain all the other important noticeable behaviors of the metalized energetic materials over the molecular ones. Is there any other effect of metal surfaces and particles in the overall excited electronic state decomposition mechanisms of metalized energetic materials? Are the excited electronic state decomposition mechanisms of molecular energetic materials altered in presence of metal particles? These questions remain in literature mostly unanswered, so far. To address these questions, it is essential to obtain detailed knowledge about the electronically nonadiabatic decomposition mechanisms of the energetic molecules in presence of metal particles. Furthermore, as excited electronic states play an important role in the decomposition of energetic materials, it is also relevant to explore the excited electronic state potential energy surfaces of energetic molecules in presence of metal atoms and clusters.

Nitramine (N–NO₂) energetic molecules, such as RDX, HMX and CL-20, which are well-known molecular energetic systems, usually contain a number of N–NO₂ moieties. Each moiety, however, is not connected by π -conjugation and therefore, they can be viewed as chemically isolated energetic sites. As nitramine energetic molecules are large and chemically complex, a rather structurally simple analogue molecule, dimethyl nitramine (DMNA, containing one N–NO₂ moiety) has been subjected to laboratory-based detailed experimental and theoretical study [11], for a long time. These studies unravel intrinsic decomposition behavior of the nitramine moiety. To date, electronically nonadiabatic decomposition of isolated DMNA has been investigated experimentally and theoretically, in details [11]. Bhattacharya et al. provided the valuable insights on the decomposition mechanisms of DMNA following its electronic excitation both experimentally and theoretically [11a]. Isolated DMNA exhibits nitro-nitrite isomerization followed by NO elimination and these initial decomposition steps are found to be endothermic in nature. Recently, we have explored the excited electronic state surfaces of DMNA in presence of Al clusters [12], which clearly reveals that presence of Al metal atom brings about significant changes in the electronically nonadiabatic decomposition pathways of DMNA. While the isolated DMNA shows endothermic initial reaction steps, DMNA–Al clusters exhibit exothermic reaction steps. Following this DMNA–Al study, in the present work, we have explored the excited electronic state surfaces of clusters of DMNA and Zinc (Zn).

Recent thermal decomposition study of RDX (containing three N–NO₂ moiety) molecules in presence of Zn nanoparticles [8] features that addition of zinc nanoparticles to RDX reduces the ignition delay time by 20%, triples the temperature and decreases the emergence time of the products by 10–40%. The excited electronic state decomposition mechanisms of nitramine energetic molecules in presence of various Zn metal clusters, however, have not been explored yet, both experimentally and theoretically. To address the role of Zn metal in the overall electronically nonadiabatic decomposition mechanisms of one nitramine (N–NO₂) moiety, we have selected two different systems, namely, DMNA–Zn and DMNA–Zn₁₀ and have explored the excited electronic state surfaces of these two clusters. For the present study, we have chosen Zn₁₀ cluster because a recent DFT study on the structures and electronic states of zinc clusters (Zn_n, $n = 2–32$) identifies Zn₁₀ as one of the most stable clusters formed by zinc. Its stability is attributed to its high binding energy and shorter bond length [13]. For DMNA–Zn cluster we have employed complete active space self-consistent field (CASSCF) calculations to explore its excited electronic state surfaces. For DMNA–Zn₁₀ cluster, on the other hand, a hybrid methodology, called Our Own N-layered Integrated Molecular Orbital and Molecular Mechanics (ONIOM), which was originally developed by Morokuma and co-workers [14], is employed. In ONIOM methodology, DMNA along with one Zn atom is placed at high layer, which is treated with CASSCF methodology,

while remainder of the Zn₁₀ cluster is treated with universal force field (UFF) molecular mechanics and Møller–Plesset second order perturbation (MP2) theory. In order to incorporate dynamic correlation in CASSCF calculations we have employed single point CASMP2 [15] calculations. Present computational results reveal that DMNA–Zn exhibits N–N bond dissociation, followed by Zn–O bond dissociation, which finally leads to nitro-nitrite isomerization followed by NO elimination. DMNA–Zn₁₀ also shows N–N bond dissociation followed by isomerization; however, one intermediate, which is present in the overall decomposition of DMNA–Zn following electronic excitation, does not take part in that of DMNA–Zn₁₀. In the present work, exothermicities associated with the overall decomposition reaction for DMNA–Zn and DMNA–Zn₁₀ clusters are also examined.

2. Theoretical procedure

All geometry optimizations at the ground and excited electronic states of DMNA–Zn are performed at the complete active space self-consistent field (CASSCF) level of theory with 6-31G(d) basis set (denoted as CASSCF/6-31G(d)) using Gaussian 09 [16]. In the CASSCF method, multiconfiguration wave function is variationally optimized with respect to simultaneous variations of the orbitals and configuration coefficients; however, all possible configuration state functions (CSFs) are prepared based on the active orbitals, which comprise active space in the CASSCF calculation. The active orbitals, used in the CASSCF calculation for DMNA–Zn, are depicted in Fig. 1. The active space comprises 14 electrons distributed in 11 orbitals, denoted as CASSCF(14,11). The orbitals are selectively chosen to include all the important bonding, nonbonding and antibonding orbitals in N–NO₂–Metal active moiety. Thus, the orbitals used for DMNA–Zn include σ_{ONO} , $n\sigma_{\text{O}}$, π_{ONO} , $n\sigma_{\text{O}}$, σ_{ONO} , $5s_{\text{Zn}}$, nd_{Zn} , σ_{ZnO} , π_{ONO}^* , σ_{ONO}^* , and σ_{ONO}^* .

For DMNA–Zn₁₀, we have employed ONIOM methodology using two layer QM:MM (Quantum Mechanics: Molecular Mechanics) and QM:QM combinations, in which one part of the cluster (mainly, DMNA and immediate binding site at the metal cluster) is treated at the CASSCF(14,11)/6-31G level of theory (QM), while the remainder of the cluster is treated either at the UFF level (MM) or at the MP2 (QM) level. The basic idea of ONIOM calculation results from the realization that for a large cluster photochemical processes are often localized only in a segment (called *active site*) of the cluster; the effect of the rest of the cluster on the active site can often be only steric or electrostatic. Therefore, the photochemical process, localized at the *active site* and being investigated, can be treated at an appropriate high-accuracy multiconfiguration QM method (e.g., CASSCF), while the remainder of the cluster can be treated only with a lower level of theory (e.g., MP2 QM or UFF MM). The 11 active orbitals, which are treated with CASSCF level for DMNA–Zn₁₀ cluster, have been depicted in Fig. 2.

Vertical excitation energies are calculated by state-averaging over the ground and excited states with equal weights for each state. Critical points (minima and conical intersections) are optimized by using the algorithm implemented in Gaussian 09. The lowest energy point on the conical intersection seam, called lowest energy conical intersection, is optimized and localized using a projected gradient algorithm, as implemented in Gaussian 09. In this search, the energy of the excited state is minimized. At the same time, the energy difference between the excited state and the closest lower energy state is minimized. Minimum and transition states are optimized using Berny algorithm implemented in Gaussian 09. Stability of the structure is checked against frequency calculations. Transition state geometry exhibits one unstable normal mode of vibration, which is characteristic of the reaction pathway.

Some of the reaction pathways of DMNA–Zn_n clusters are explored through potential energy scanning. A relaxed potential

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