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Excited Electronic and Vibrational State Decomposition of Energetic Materials and Model Systems on Both Nanosecond and Femtosecond Time Scales

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14. ABSTRACT

Energetic materials are studied as isolated species to learn the kinetics and dynamics of their unimolecular behavior. The behavior of these species is then compared with that of very similar model systems in order to enable the synthesis of new materials that will be energetic by design. This must be the first step in the determination of the unique characteristics that comprise energetic molecules. We now understand the properties of nitramine, furazan, tetrazine, tetazole and other high nitrogen content energetic molecules based on experimental and theoretical studies. We are presently studying the new imidazole systems that show important new behavior and

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# Report Title


## ABSTRACT

Energetic materials are studied as isolated species to learn the kinetics and dynamics of their unimolecular behavior. The behavior of these species is then compared with that of very similar model systems in order to enable the synthesis of new materials that will be energetic by design. This must be the first step in the determination of the unique characteristics that comprise energetic molecules. We now understand the properties of nitramine, furazan, tetrazine, tetazole and other high nitrogen content energetic molecules based on experimental and theoretical studies. We are presently studying the new imidazole systems that show important new behavior and systematics that promise to generate new concepts for energetic species. The experimental data for these systems consist of initial products and their energy content and partition, and parent molecule potential energy surfaces and conical intersections.

**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

| Received | | Paper |
|---|---|---|
| 02/21/2013 | 12.00 | Elliot R. Bernstein, Zijun Yu. On the Decomposition Mechanisms of New Imidazole-Based Energetic Materials, The Journal of Physical Chemistry A, (02 2013): 0. doi: 10.1021/jp312527u |
| 02/21/2013 | 15.00 | Yuanqing Guo, Atanu Bhattacharya, Elliot R. Bernstein. Ultrafast SUltra Fast S1 S0 internal conversion dynamics for DMNA through conical intersections, The Journal of Physical Chemistry A, (09 2011): 0. doi: 10.1021/jp109150u |
| 02/21/2013 | 14.00 | Zijun Yu, Elliot R. Bernstein. Experimental and theoretical studies of the decomposition of new imidazole based energetic materials: Model systems, The Journal of Chemical Physics, ( 2012): 0. doi: 10.1063/1.4752654 |
| 02/21/2013 | 13.00 | Atanu Bhattacharya, Yuanqing Guo, Elliot R. Bernstein. A comparison of the decomposition of electronically excited nitro-containing molecules with energetic moieties C–NO2, N–NO2, and O–NO2, The Journal of Chemical Physics, ( 2012): 0. doi: 10.1063/1.3668139 |
| 11/14/2011 | 2.00 | Yuanqing Guo, Atanu Bhattacharya, Elliot R. Bernstein. Ultrafast S1 to S0 Internal Conversion Dynamics for Dimethylnitramine through a Conical Intersection, The Journal of Physical Chemistry A, (09 2011): 9349. doi: 10.1021/jp109150u |
| 11/14/2011 | 3.00 | Atanu Bhattacharya, Elliot R. Bernstein. Influence of Turn (or Fold) and Local Charge in Fragmentation of the Peptide Analogue Molecule CH, The Journal of Physical Chemistry A, (10 2011): 10679. doi: 10.1021/jp203909y |
| 11/14/2011 | 4.00 | Zijun Yu, Elliot R. Bernstein. Decomposition of pentaerythritol tetranitrate [C(CH2ONO2)4] following electronic excitation, The Journal of Chemical Physics, (10 2011): 154305. doi: 10.1063/1.3652893 |
| 11/14/2011 | 5.00 | Atanu Bhattacharya, Joong-Won Shin, Keven J. Clawson, Elliot R. Bernstein. Conformation specific and charge directed reactivity of radical cation intermediates of ?-substituted (amino, hydroxy, and keto) bioactive carboxylic acids, Physical Chemistry Chemical Physics, (12 2010): 9700. doi: 10.1039/c003416a |
| 11/14/2011 | 6.00 | Atanu Bhattacharya, Yuanqing Guo, Elliot R. Bernstein. Nonadiabatic Reaction of Energetic Molecules, Accounts of Chemical Research, (12 2010): 1476. doi: 10.1021/ar100067f |
| 11/14/2011 | 7.00 | Joong-Won Shin, Feng Dong, Michael E. Grisham, Jorge J. Rocca, Elliot R. Bernstein. Extreme ultraviolet photoionization of aldoses and ketoses, Chemical Physics Letters, (04 2011): 161. doi: 10.1016/j.cplett.2011.03.027 |
| 11/14/2011 | 8.00 | A. Bhattacharya, E. R. Bernstein. Nonadiabatic Decomposition of Gas-Phase RDX through Conical Intersections: An ONIOM-CASSCF Study, The Journal of Physical Chemistry A, (05 2011): 4135. doi: 10.1021/jp109152p |

**TOTAL:** **11**

**Number of Papers published in peer-reviewed journals:**

## (b) Papers published in non-peer-reviewed journals (N/A for none)

| Received | Paper |
|---|---|
| 08/01/2013 16.00 | Z.Yu, Elliot R Bernstein. On the Decomposition Mechanisms of new Imidazole-Based Energetic Materials, J. Phys. Chem. A, 117, 1756 (2013)., (02 2013): 0. doi: |
| 08/02/2013 17.00 | Y.Q Guo, A. Bhattacharya, Elliot R Bernstein. Decomposition of Excited Electronic State s-Tetrazine and its Energetic Derivatives, J. Chem. Phys. 134, 024318, (01 2011): 0. doi: |
| **TOTAL:** | **2** |

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## (c) Presentations

**Number of Presentations:** 0.00

## Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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## (d) Manuscripts

| Received | | Paper |
|---|---|---|
| 07/24/2012 | 9.00 | Elliot R. Bernstein, Zijun Yu. Decomposition of pentaerythritol tetranitrate [C(CH2ONO2)4] following electronic excitation, J Chem Phys (01 2011) |
| 07/24/2012 | 10.00 | Yuanqing Guo, Elliot R. Bernstein, Atanu Bhattacharya. A comparison of the decomposition of electronically excited nitro-containing molecules with energetic moieties C–NO2, N–NO2, and O–NO2, J. Chem. Phys. 136, 024321 (2012) (01 2012) |
| 07/24/2012 | 11.00 | Zijun Yu, Elliot R Bernstein. Experimental and Theoretical Studies of the Decomposition of New Imidazole Based Energetic Materials: Model Systems, J Chem Phys (submitted) (01 2012) |
| 11/14/2011 | 1.00 | Atanu Bhattacharya, Yuanqing Q. Guo, Elliot R. Bernstein. A Comparison of the Decomposition of Electronically Excited Nitro-Containing Molecules with Energetic Moieties C-NO2, N-NO2, and O-NO2,, (11 2011) |

**TOTAL:** **4**

**Number of Manuscripts:**

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## Books

| Received | Book |
|---|---|

**TOTAL:**

| Received | Book Chapter |
|---|---|

**TOTAL:**

## Patents Submitted

## Patents Awarded

## Awards

## Graduate Students

| NAME | PERCENT_SUPPORTED |
|---|---|
| **FTE Equivalent:** | |
| **Total Number:** | |

## Names of Post Doctorates

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|---|---|
| Zijun Yu | 1.00 |
| Shi Yin | 1.00 |
| Bing Yuan | 1.00 |
| **FTE Equivalent:** | **3.00** |
| **Total Number:** | **3** |

## Names of Faculty Supported

| NAME | PERCENT_SUPPORTED |
|---|---|
| **FTE Equivalent:** | |
| **Total Number:** | |

## Names of Under Graduate students supported

| NAME | PERCENT_SUPPORTED |
|---|---|
| **FTE Equivalent:** | |
| **Total Number:** | |

## Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

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## Names of Personnel receiving masters degrees

NAME

**Total Number:**

## Names of personnel receiving PHDs

NAME

**Total Number:**

## Names of other research staff

| NAME | PERCENT_SUPPORTED |
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**FTE Equivalent:**
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## Inventions (DD882)

## Scientific Progress

see attached

## Technology Transfer

Final Report ARO 2010 to 2014

A. Tetrazine and Tetrazine N-0xide Energetics (DAATO, DATA, ACTO)

As we proceed through these different energetic species, the general discussion will require fewer details and more reference to the original studies. We can understand now the general theme of these theoretically derived reactions mechanisms: interacting adiabatic PESs through non-adiabatic terms omitted from the simple, zero order, B.O. Hamiltonian. In large measure, pictures (slices) of the surfaces along the reaction coordinate and statements of the calculational levels employed should serve the general understanding for our purposes.

Two motivating factors have driven the synthetic community toward high nitrogen content energetic materials: 1. the importance of $N_2$ as a product with a very stable bond to generate a highly exothermic reaction for compounds with a positive $\Delta H^{\circ}_{f}$; and 2. $N_2$ would be an environment friendly final product for the decomposition chemistry. As we will soon see, neither of these hopes are supported by either the theory or experiments, in this instance.

These studies initially include the tetrazine N-oxide derivatives, DAATO, ACTO, DATO, all of which are energetic molecules. The only model non-energetic species we have studied in the general group is tetrazine itself and it will be discussed and following description of the behavior of the three energetic systems. NO is observed to be the initial product of the decomposition reactions of DAATO, DATO, and ACTO following their electronic state excitation. The NO from ACTO and DAATO is rotationally cold and vibtationally hot, while the NO from DATO is rotationally hot and vibrationally cold. ACTO and DAATO are structurally different from DATO, with regard to the N-oxide ring positions, and this is suggested to be an explanation of the decomposition difference. Final transition state calculations are consistent with this dynamical difference for NO products. CASSCF/CASMP2 theory level calculations predict a ring contraction mechanism for generation of the initial NO product from these molecules, through an $(S_1/S_0)_{CI}$.

ACTO and DATO are calculated at the CASSCF (14,10)/6-31G(d) level and the chosen orbitals for the active space are found. Recall that the active space orbitals must be chosen with the desired chemistry in mind; that is, the experiments guide the calculations and the calculations determine a reaction mechanism, (i.e., a set of CIs, barriers, transition states along the reaction coordinate, steepest descent path). One need not do this if a full configuration interaction calculation can be done and all possible reaction coordinates can be explored. In such an instance, the lowest energy, most coupled, steepest descent reaction coordinate pathway would be found and identified as such. For a CASSCF calculation we must know the outcome required to choose the active space (i.e., the orbitals to be considered for the calculation). The calculated surface paths for $S_1$ ($n\pi^*$), $S_2(\pi\pi^*)$ $S_3(\pi\pi^*)$ excitation for ACTO and DATO are found. NO is generated on the $S_0$ surface, well away from the FC equilibrium point: in both cases, a ring opening/contraction mechanism is suggested that does not involve an $N_2O$ intermediate. An $N_2$ product is not observed from either ACTO or DATO. CIs dominate

the reaction kinetics and dynamics and the rotational and vibrational excitation of the product NO are governed by the final transition states and the reaction coordinates. The low vibrational excitation of NO from DATO may suggest more energy is in its translational degrees of freedom that more of energy is used to open the ring. Detailed calculations for DAATO have not been attempted to date because of the size, complexity, low symmetry of the molecule, and potential couplings of it moieties. We also searched for $N_2$ from DATO, ACTO, and DAATO. In each case the experiment was negative: $N_2$ is not a decomposition product from those energetic molecules following excitation to their valence electronic states.

The model or base system for those energetic molecules is tetrazine itself and we have studied the excited electronic state kinetics, dynamics, and chemistry of this system, as well. Different pathways for tetrazine and its derivatives can be considered for decomposition.

Tetrazine has been known for close to 40 years to photo-decompose into 2HCN and $N_2$, but the reaction mechanism and the dynamics for $N_2$ have not been specified, either experimentally or theoretically. Our experiments give the rotational distribution of $N_2$ from tetrazine to be cold (~20k) but the vibrational temperature has not yet been determined due to wavelength constraints. The calculations given above for DATO and ACTO are applied to tetrazine (CASMP2/CASSCF (14,11)/6-31G (d)).

The mechanism that these calculations generate has been published. For this system $S_1$ through $S_4$ are necessary to calculate at the CASSCF (14,11) /6-31G(d) and CASMP2 levels. Many CIs are generated for these PESs: $(S_4/S_3)_{CI}$, $(S_3/S_2)_{CI}$, $(S_2/S_1)_{CI}$, $(S_1/S_0)_{CI}$, and probably many others not uncovered are present. All of these are at points of near degeneracy for the PESs and are most likely strongly non-adiabatically coupled. Thus, tetrazine follows a minimum energy path through CIs from $S_4 \rightarrow_{...} \rightarrow S_0$ for the fragmentation reaction yielding 2HCN and $N_2$. This generates ~ 6 eV of vibrational energy in $S_0$ and a triple concerted dissociation is suggested. Little torque is generated on $N_2$ at the final dissociation $S_0$ transition state along the minimum energy reaction coordinate. Thus, $N_2$ is a product for the unsubstituted tetrazine, but the substituted energetic tetrazines (DATO, ACRO, DAATO) do not follow this pathway. This process is, as found in other cases, ultrafast (~$10^{-14}$ -$10^{-13}$ s) due to the PES non-adiabatic couplings.

B. PETN [$C(CH_2ONO_2)_4$]

PETN is a very interesting molecule both because of its high symmetry and its $ONO_2$ bonding. PETN is an obvious candidate for the ONIOM method and we employ an ONIOM [CASSCF (6,6)/6-31G(d);UFF] calculational level in an exact parallel to our treatment of RDX, etc., employing the Gaussian 09 program suite. No symmetry restrictions are employed throughout the calculational chain. Both IRC and scan algorithms are applied to map the surfaces following location of the CIs, transition states, and intermediates. The goal is to find the NO molecule product, generated by $S_n$ electronic excitation at ca. 226, 236, 248 nm with a cold rotational distribution and a hot vibrational distribution, which will then constitute a unique excitation energy independent, quantum mechanical, molecular mechanism for the PETN release of its stored chemical energy. The electronically excited PETN on the $S_1$ PES moves to the $(S_1/S_0)_{CI}$ to the ground electronic state, undergoes a nitro-nitrite isomerization on $S_0$, and

generates the product NO with the observed dynamics. The calculated reaction path is found. Structure for the various $S_1/S_0$ stationary points and CIs are published. The pathway, reaction coordinate in this instance from the initial FC position on $S_1$ involves motion to the minimum of the $S_1$ state ($S_{1,min}$), surmounting the $S_1$ PES energy barrier, and finally reaching the $(S_1/S_0)_{CI}$, and non-adiabatically transitioning to the $S_0$ PES: this is the steepest descent reaction coordinate. After the molecule returns to $S_0$ a number of reactions channels are energetically available. The PETN molecule can then return to the equilibrium FC point or follow the steepest descent path to a nitro-nitrite isomerization and generation of NO. If the molecule returns to the FC point (over a 2.6 eV barrier), it can generate an $NO_2$ molecule with a ca. 1 eV barrier. On the other hand, following the $(S_1/S_0)_{CI}$ the reaction coordinate is barrierless to a nitro-nitrite isomerization and then NO is generated with a ~1.eV barrier at the transition state $S_{0,ST,NO\text{-}elim}$. The unstable mode at this point puts little torque on the departing NO. All of this occurs in less than ca.100 fs through the CIs. The similarity of behavior here with nitramines can be attributed to the fact that both N-$NO_2$ and O-$NO_2$ $S_1$ states are $n\rightarrow\pi^*$ excitations. The difference between energetic and non-energetic species depends on $S_0$ or $S_1$ reaction coordinate decomposition, respectively.

C. Imidozoles: mono- and di-nitro.

Mono-nitroimidozoles are all non-energetic model systems for the energetic di-nitroimidozoles. The difference between those two sets of molecules is the same as we have noted above for the other energetic nitro containing species: the energetic molecules, following electronic excitation to $S_n$ PES (FC), all decompose on $S_0$ after a nitro-nitrite isomerization and generate NO with cold $T_{rot}$ and hot $T_{vib}$; the non-energetic molecules, under similar excitation conditions, render NO from their excited states (e.g., $S_1$) with $T_{rot}$ warm and $T_{vib}$ cold. In both instances the kinetics and dynamics are governed by CIs and transition states on each PES. The specific mono-nitroimidozoles that are calculated for non-energetic model systems are discussed below. The di-nitroimidozoles are challenging to treat theoretically because the 'active sites' are not separated or independent due to the aromatic π-ring system and because the excitation levels are to different types of excited states, e.g., $\pi\pi^*$, $n\pi^*$, etc. Consider first the non-energetic mono-nitroimidozoles. The calculations for the systems are accomplished in the now "usual way": a CASSCF (10,7)/6-31G(d) algorithm with active space orbitals two π-bonding ring orbitals, one NO non bonding $n\sigma_{NO}$ orbital, one π non-bonding $n\pi_0$ orbital, one $\varsigma$ non- bonding $n\varsigma_0$ orbital, one delocalized ONO π anti-bonding $\pi_{ONO*}$ orbital, and one π anti-bonding ring $\pi^*$ orbital. The first 5 orbitals are occupied and the last two are virtual. $S_1$ and $S_2$ states are $n\pi^*$ and $S_3$ is $\pi\pi^*$ in nature. For the ground state system, the CASSCF calculation shows that $NO_2$ and NO release require similar energies (~ 80 k cal/mol) and are thus competitive on $S_0$. These two pathways are located on very different parts of the $S_0$ PES, for different reaction coordinates, however.

The CASSCF scan and IRC calculations for the reaction coordinate on the $S_0$, $S_1$, $S_2$ surfaces are similar for the three mono-nitroimidazole molecules. Two possible decomposition paths can be found for all three of these molecules: $S_1$ or $S_2$ generation of NO. $S_1$ dissociation is chosen as the most likely path for the following reasons: the $(S_1/S_0)_{CI}$s are weak due to the substantial (> 100 $cm^{-1}$) adiabatic gaps between the two surfaces, and the NO product is not vibrationally very hot (<800 K) but is relatively cold

(ca. 50 K) rotationally, as is consistent with the $S_1$ transition state. ($S_{1,\ TS,\ NO\text{-}elim}$). The imidozole aromatic ring orbitals seem to play a major role in the excited electronic state ($S_1$, $S_2$) PESs and generated CIs that are important for the overall mono-nitroimidozole dynamics. The general kinetics and dynamics for this series of model species seems to be independent of the C-$NO_2$ ring position.

The di-nitroimidazoles are all energetic, and, in analogy to the DMNA/RDX situation, one can realize that the adjacent nitro moieties can have a significant affect on the $S_0$, $S_1$, $S_2$, $S_3$, PESs, especially with regard to CIs, barriers, and non-adiabatic couplings for the adiabatic states. Unfortunately, a large CASSCF would be required to express the true nature of the excited and even ground PESs: for example, a CASSCF (20,14) should be a good first guess. Another possibility would be an ONIOM calculation but the two "active $NO_2$ sites" are coupled by the ring π- system and thus are not isolated as required: the site and its remaining molecule strongly interact. A restricted active space (RAS) calculation can also be considered, but the excited states are not all of the same character. ($n\pi^*$, $\pi\pi^*$, etc), and different (restricted) active spaces would need to be considered for the various PESs.

Experimentally, a unique excitation wavelength independent NO with cold rotations and hot vibrations is generated as di-nitro imidazole energetics decompose following electronic excitation. The predicted reaction mechanism, now based on experience with the forgoing model and real energetic molecules, is that the molecule finds the steepest descent reaction coordinate through CIs and over barriers to $S_0$ and then undergoes a nitro-nitrite isomerization which leads to a transition state on $S_0$ that generates NO with the appropriate energy distribution. For C-$NO_2$ species, the $NO_2$ and NO reaction coordinates on $S_0$ at the FC point are energetically similar, but the N-$NO_2$ bond is much weaker and will generate the $NO_2$ molecule if only the $S_0$ PES(FC) is considered. The C-$NO_2$ species are more stable and the π-ring system enhances this stability and insensitivity to heat and impact/shock on $S_0$. The excited state reaction coordinates place the molecules far from the FC equilibrium point on $S_0$ and thus favor the nitro-nitrite NO reaction coordinate.

D. Decomposition of electronically excited nitro-containing molecules with different X–$NO_2$ (X = C, N, O) moieties has been intensively investigated over the past decades; however, their decomposition behavior has not previously been compared and contrasted. Comparison of their unimolecular decomposition behavior is important for the understanding of the reactivity differences among electronically excited nitro-containing molecules with different X–$NO_2$ (X = C, N, O) bond connections. Nitromethane (NM), dimethylnitramine (DMNA), and isopropylnitrate (IPN) are used as model molecules for C– $NO_2$, N– $NO_2$, and O– $NO_2$ active moieties, respectively. NO molecules are observed to be the major decomposition product from electronically excited NM, DMNA, IPN using R2PI techniques. The NO products from decomposition of electronically excited (226 and 236 nm) NM and IPN display similar rotational (600 K) and vibrational distributions [both (0–0) and (0–1) bands of the NO molecule are observed]. The NO product from DMNA shows rotational (120 K) and vibrational distributions (only (0–0) transition is observed) colder than those of NM and IPN. At the 193 nm excitation, electronically excited $NO_2$ products are observed from NM and IPN via fluorescence detection, while no electronically excited $NO_2$ products are observed from DMNA.

Additionally, the OH radical is observed as a minor dissociation product from all three compounds. The major decomposition pathway of electronically excited NM and IPN involves fission of the X– $NO_2$ bond to form electronically excited $NO_2$ product, which further dissociates to generate NO. The production of NO molecules from electronically excited DMNA is proposed to go through a nitro–nitrite isomerization pathway. Theoretical calculations show that a nitro–nitrite isomerization for DMNA occurs on the $S_1$ surface following a $(S_2/S_1)_{CI}$ conical intersection (CI), whereas $NO_2$ elimination occurs on the $S_1$ surface following the $(S_2/S_1)$CI conical intersection for NM and IPN. The present work provides insights for the understanding of the initiation of the decomposition of electronically excited X– $NO_2$ energetic systems. The presence of conical intersections along the reaction coordinate plays an important role in the detailed mechanism for the decomposition of these energetic systems

E. Study of nitropyrazoles and FOX-7

Decomposition of energetic materials 1,1-diamino-2,2-dinitroethylene, $C_2H_4N_4O_4$ (FOX-7), 3,4-dinitropyrazole (DNP) and two DNP related model molecules 4-nitropyrazole and 1-nitropyrazole are investigated both theoretically and experimentally.

The NO molecule is observed as an initial decomposition product from all four materials subsequent to UV excitation. The Observed NO products are rotationally cold (< 50 K) for all four systems. For FOX-7, the vibrational temperature of the NO product is about 2800 K. The vibrational temperature of the NO product from DNP is 3850 K, 1350 K hotter than that of the two model species.

The initial decomposition mechanisms for these four materials are explored with complete active space self-consistent field (CASSCF) level. Potential energy surface calculations at the CASSCF(12,8)/6-31+G(d) level illustrate that conical intersections plays an essential role in the decomposition mechanism. Electronically excited $S_2$ FOX-7 or nitropyraozles can nonradiatively relax to lower electronic states through $(S_2/S_1)_{CI}$ and $(S_1/S_0)_{CI}$ conical intersection and undergo a nitro-nitrite isomerization to generate NO product either in the $S_1$ state or $S_0$ state. In model systems, NO is generated in the $S_1$ state, while in the energetic materials DNP and FOX-7, NO is produced on the ground state surface, as the $S_1$ decomposition pathway is energetically unavailable. The theoretically predicted mechanism is consistent with the experimental results, as DNP decomposes in a lower electronic state than do its model systems and thus the vibrational energy in the NO product from DNP should be hotter than from the model systems. The observed rotational energy distributions for NO products are consistent with the final structures of the respective transition states for each molecule. Meanwhile, ground state FOX-7 decomposition agrees with previous work: the nitro-nitrite isomerization has the lowest average energy barrier, the C-$NH_2$ bond cleavage is unlikely under the given excitation conditions, and HONO formation on the ground state surface is also a higher energy process.

F. Study of TKX-50 and MAD-X1

Decomposition of energetic salt materials TKX-50 and MAD-X1 (dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate and dihydroxylammonium 3,3'-dibitro-5,5'-bis-1,2,4-triazole-1,1'-diol, respectively), following electronic state excitation, is investigated both experimentally and theoretically. Different from previous

energetic materials we studied before which are mainly organic molecules, it is the first time we start working on the salt energetic sample.

The NO and $N_2$ molecules are observed as initial decomposition products from the two materials subsequent to UV excitation. Observed NO products are rotationally cold (< 25 K) and vibrationally hot (> 1500 K). The vibrational temperature of the NO product from TKX-50 is 2600 K, 1100 K hotter than MAD-X1. Observed $N_2$ products of these two species are both rotationally cold (< 30 K). The NO detection method is the same as before while for $N_2$ detection, a single pump/probe laser is used at 283 nm to both sample initiation and $N_2$ detection following a one color (2+2) resonance-enhanced four photon ionization (REMPI) scheme [$a^1\Pi_g(v'=1) \leftarrow X^1\Sigma_g(v''=0)$ and $I \leftarrow A$ transitions] through TOFMS.

Initial decomposition mechanisms for these two electronically excited salts are explored with complete active space self-consistent field (CASSCF) level. Potential energy surface calculations at the CASSCF(8,8)/6-31G(d) level illustrate that conical intersections play an essential role in the decomposition mechanism. Electronically excited $S_1$ molecules can non-adiabatically relax to the lower electronic state through $(S_1/S_0)_{CI}$ conical intersections. Both TKX-50 and MAD-X1 have two $(S_1/S_0)_{CI}$ conical intersections between $S_1$ and $S_0$ states related and leading to two reaction paths forming $N_2$ and NO products, respectively. $N_2$ products are released by the opening of the tetrazole or triazole ring of TKX-50 and MAD-X1. NO products are released from the amine N-oxide moiety of TKX-50 and for MAD-X1: they are produced through nitro-nitrite isomerizations. The observed rotational energy distributions for NO and $N_2$ products are consistent with the final structures of the respective transition states for each molecule on their $S_0$ surfaces.

G. Research on N-rich energetic materials without $-NO_2$ group or N-oxide moiety

The energetic materials we studied previously produce NO as one of the initial decomposition product. The energetic materials we are now studying are N-rich systems without $-NO_2$ group or N-oxide moiety and in this case, $N_2$ is the initial decomposition product while NO is not observed. We detected $N_2$ decomposition product in 5,5'-bistetrazole, 1,5'-bistetrazole, bis(ammonium) 5,5'-bistetrazolate, bis(triaminoguanidinium) 5,5'-azotetrazolate, azidotriazolyl-tetrazole, bistetrazolyhydrazine, 1,1-ditetrazolylethane, 5,5-ditetrazolylethane and 5,5'-bistetrazolylamine energetic materials. Their theoretical decomposition mechanisms are still in the process of being calculated.

We are presently doing 2 parallel studies involving equipment construction and reconfiguring. We are building a photoelectron spectrometer to study the ion state of energetic materials which we think also play a roll in their decomposition. This work is supported by our new DURIP grant. We are also looking at the kinetics of energetic material decomposition through fs spectroscopy with especial attention given to $N_2$ generating systems, which have never before been studied.

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