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14. ABSTRACT

The focus of this research was to apply efficient methods for using ab initio potential energy surfaces (PESs) computed with high levels of quantum chemistry theory to predict chemical reaction properties of energetic molecules. The project has provided results of direct relevance to understanding the chemistry of energetic materials, particularly, 1,3,3-trinitroazetidine (TNAZ)decomposition.

15. SUBJECT TERMS

energetic materials, electronic structure, potential energy sufaces

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Donald Thompson
UU	UU	UU	UU		19b. TELEPHONE NUMBER 573-882-0051

Report Title

Methods for Using Ab Initio Potential Energy Surfaces in Studies of Gas-Phase Reactions of Energetic Molecules

ABSTRACT

The focus of this research was to apply efficient methods for using ab initio potential energy surfaces (PESs) computed with high levels of quantum chemistry theory to predict chemical reaction properties of energetic molecules. The project has provided results of direct relevance to understanding the chemistry of energetic materials, particularly, 1,3,3-trinitroazetidine (TNAZ)decomposition.

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)

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

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

"A DFT and Ab Initio Study of the Thermal Decomposition of 1, 3, 3-Trinitroazetidine (TNAZ)," Jeffrey D. Veals and Donald L. Thompson, American Physical Society Prairie Section Fall 2013 Meeting,University of Missouri, Columbia, MO November 2013. (poster)

"A DFT and Ab Initio Study of the Thermal Decomposition of 1, 3, 3-Trinitroazetidine (TNAZ)," Jeffrey D. Veals and Donald L. Thompson, 40th National Organization for the Professional Advancement of Black Chemists and Chemical Engineers National Meeting, Indianapolis, IN October 2013. (poster)

Number of Presentations: 2.00

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

Received Paper

TOTAL:

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

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

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

None

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Rezvan Chitsazi	0.69	
Jamin Perry	0.31	
Yi Shi	1.00	
Mehdi Shakourian Fardjahromi	0.31	
FTE Equivalent:	**2.31**	
Total Number:	**4**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Jeffrey Veals	0.50
FTE Equivalent:	**0.50**
Total Number:	**1**

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

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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
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachment.

Technology Transfer

Several years ago we reported DFT calculations at the B3LYP/6-31g(d,p) level for the three main pathways commonly proposed for the decomposition mechanism of TNAZ (1,3,3-trinitroazetidine). [S. Alavi, L. M. Reily, and D. L. Thompson, J. Chem. Phys. **119**, 8297 (2003).] We considered the decomposition pathways in the mechanisms proposed by Zhang-Bauer [Y. X. Zhang and S. H. Bauer, J. Phys. Chem. A **102**, 5846 (1998).] and Lee. [D. S. Ames, J. C. Allman, Y. T. Lee, in *Chemistry of Energetic Materials*, G. A. Olah, D. R. Squire, Eds; (Academic Press: Sandiego, 1991) p. 27.] The common assumption is that the chemistry begins with either a C-N or the N-N bond fission. We reported values for the energies for N-NO_2 and C-NO_2 of 38.27 kcal/mol and 39.49 kcal/mol, respectively. We predicted the energy barriers for HONO elimination as 44.0 kcal/mol for formation from one of the C-NO_2 groups and 45.0 kcal/mol for formation from the N-NO_2 group.

Laura Butler (University of Chicago) brought to our attention a paper by Oftadeh and coworkers [M. Oftadeh, M. H. Khozani, M. Radhoosh, and M. H. Keshavarz, Comp. Theo. Chem., **964**, 262 (2011).] in which the energy for C-N bond fission was reported to be 76.6 kcal/mol and 69.3 kcal/mol for the N-N bond rupture, and a 149.3 kcal/mol energy barrier for HONO elimination. This prompted a completely comprehensive investigation of the decomposition pathways using better density functionals than were available when we did our study in 2003. We performed geometry optimizations at the B3LYP level of theory with the 6-31G(d,p) Pople basis set, and the optimized structures were used as starting structures for M06 [Y. Zhao and D. G. Truhlar, Theor. Chem. Acc. **120**, 215 (2008).] and M06-2X**Error! Bookmark not defined.** geometry optimizations using the 6-31G(d,p) basis set. After these preliminary results involving the C-N and N-N initialization pathways we concluded that the M06 density functional should be used with the cc-pVTZ basis set to perform more accurate geometry optimizations for the three decomposition pathways and their products. This decision was based on the slightly better agreement between the M06 energies and the experimental values; we believe it is unlikely that our conclusions would have changed much if the M06-2X functional had been used for the optimizations instead.

To further improve the energies we performed M06/cc-pVQZ single point calculations on all the M06/cc-pVTZ optimized structures. Finally, CCSD(T)/cc-pVTZ energies were obtained using the M06/cc-pVTZ geometries. The *ab initio* calculations were done as a precaution as well as another a means of gaining insight about the initial decomposition process. This extra effort was made in large part to shore up any final conclusions to be drawn our study.

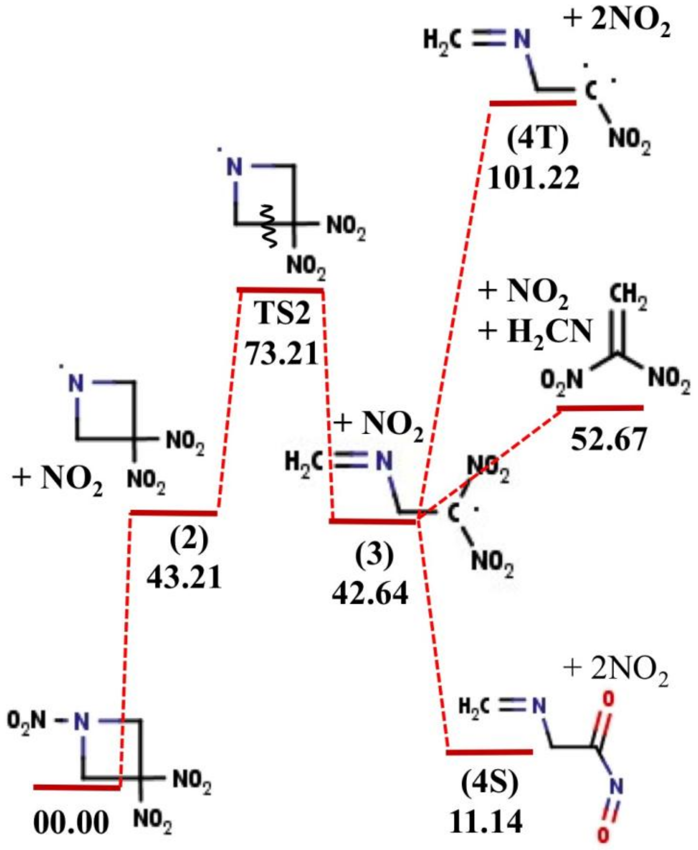
We performed the M06/cc-pVTZ optimizations and CCSD(T)/cc-pVTZ energies for the decomposition steps subsequent to these initial reactions because for several cases, particularly ring opening, a multi-configuration-based method would be needed to gain any further clarity. Since M06 was optimized for organometallics as well as typical organic molecules, we believe it is probably more accurate than other DFT (or MP2) methods for somewhat multi-configurational (bi-radicals, highly resonant, etc) species, and that only a dedicated multi-reference method would significantly improve upon the M06 predicted geometries, we settled for the latter. We are fairly confident that the M06 results give good qualitative descriptions of likely decomposition routes.

This work has been published: Jeffrey D. Veals and Donald L. Thompson, "Thermal Decomposition of 1,3,3-Trinitroazetidine (TNAZ): A Density Functional Theory and *Ab Initio* Study," J. Chem. Phys. **140**, 154306 (2014). The abstract of this paper is:

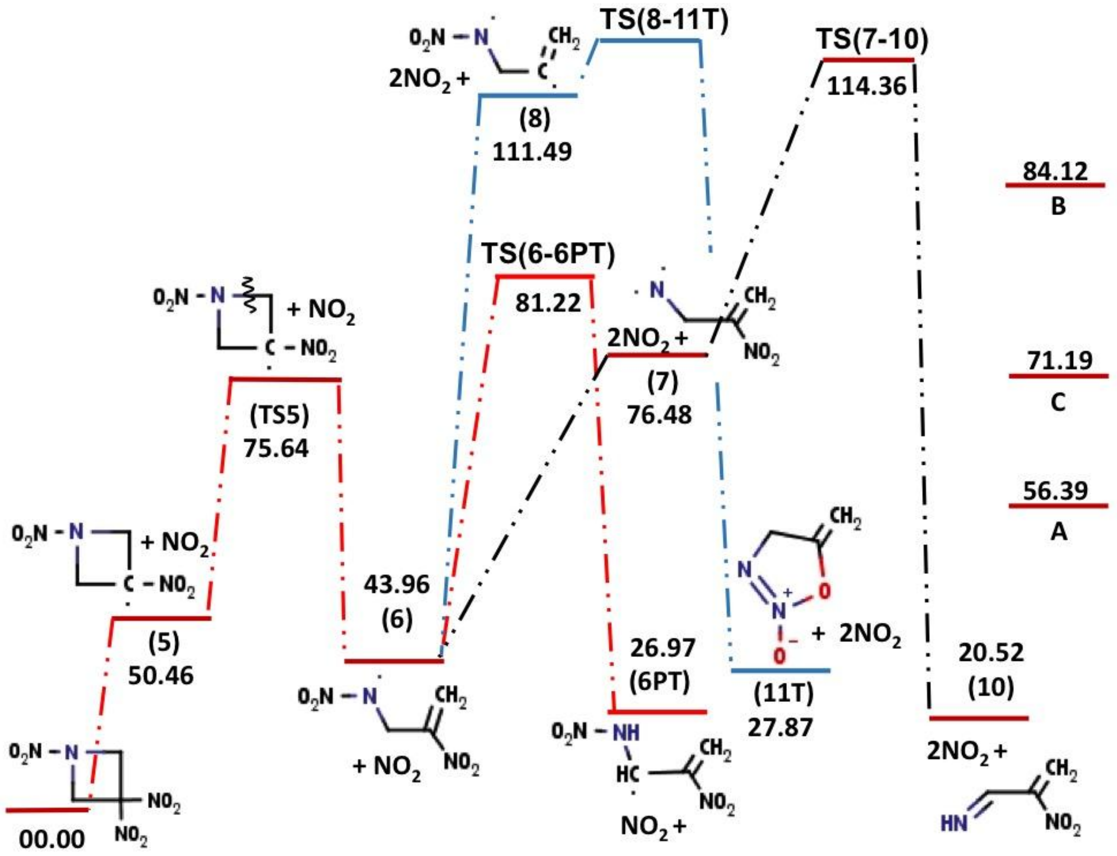
Density functional theory and ab initio methods are employed to investigate decomposition pathways of 1,3,3-trinitroazetidine initiated by unimolecular loss of NO_2 or HONO. Geometry optimizations are performed using M06/cc-pVTZ and coupled-cluster (CC) theory with single, double, and perturbative triple excitations, CCSD(T), is used to calculate accurate single-point energies for those geometries. The CCSD(T)/cc-pVTZ energies for NO_2 elimination by N-N and C-N bond fission are, including zero-point energy (ZPE) corrections, 43.21 kcal/mol and 50.46 kcal/mol, respectively. The decomposition initiated by trans-HONO elimination can occur by a concerted H-atom and nitramine NO_2 group elimination or by a concerted H-atom and nitroalkyl NO_2 group elimination via barriers (at the CCSD(T)/cc-pVTZ level with ZPE corrections) of 47.00 kcal/mol and 48.27 kcal/mol, respectively. Thus, at the CCSD(T)/cc-pVTZ level, the ordering of these four decomposition steps from energetically most favored to least favored is: NO_2 elimination by N-N bond fission, HONO elimination involving the nitramine NO_2 group, HONO elimination involving a nitroalkyl NO2 group, and finally NO_2 elimination by C-N bond fission.

Below are figures that summarize our results

Energy profile for decomposition beginning with N-N bond fission:



Potential energy profile for decomposition beginning with C-N bond fission:



Potential energy profile for HONO elimination: