REPORT DOCUMENTATION PAGE	Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
27-01-2017	Final Report	15-Jul-2013 - 14-Jul-2016

4. TITLE AND SUBTITLE

Final Report: Effect of Dynamics in the van der Waals Region on the Chemical Kinetics of Nitrogen Containing Molecules

5a. CONTRACT NUMBER
W911NF-13-1-0251

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

6. AUTHORS

Stephen J. Klippenstein, Albert F. Wagner

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES

University of Chicago
5801 South Ellis Avenue

Chicago, IL 60637 -5418

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
62052-CH.2

12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

We explored the role of the roaming radical mechanism in the thermal decomposition of three small molecules that contain the nitrite and amine groups which are commonly found in propellants. In particular, we studied CH3NO2, which is the smallest nitrite containing molecule to show the effects of roaming, (CH3)2NNH2 (UDMH, for unsymmetrical dimethyl hydrazine), which is used as a bipropellant (with N2O4) in hypergolic rocket fuels, and (iii) CH3NHNO2, which is one of the smallest propellants with both amine and nitrite groups. These molecules exhibited a wide variety of roaming mechanisms, with many of these of considerable importance. The most

15. SUBJECT TERMS

Propellants, Roaming Radical, Theoretical Kinetics, UDMH, CH3NO2, CH3NHNO2

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Stephen Klippenstein
UU	UU	UU	UU		19b. TELEPHONE NUMBER 630-252-3596

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

Report Title

Final Report: Effect of Dynamics in the van der Waals Region on the Chemical Kinetics of Nitrogen Containing Molecules

ABSTRACT

We explored the role of the roaming radical mechanism in the thermal decomposition of three small molecules that contain the nitrite and amine groups which are commonly found in propellants. In particular, we studied CH_3NO_2, which is the smallest nitrite containing molecule to show the effects of roaming, $(CH_3)_2NNH_2$ (UDMH, for unsymmetrical dimethyl hydrazine), which is used as a bipropellant (with N_2O_4) in hypergolic rocket fuels, and (iii) CH_3NHNO_2, which is one of the smallest propellants with both amine and nitrite groups. These molecules exhibited a wide variety of roaming mechanisms, with many of these of considerable importance. The most complex of these, the roaming mediated mechanism for conversion of CH_3NHNO_2 to CH_2NH + HONO, exhibited four separate saddle points in the long-range region of the potential energy surface. Generally, the presence of stronger dipoles, nitrogen lone-pairs, and hydrogen bonding in these nitrogen materials leads to more complex roaming dynamics with lower energy roaming saddle points.

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
08/25/2015	1	Christopher J. Annesley, John B. Randazzo, Stephen J. Klippenstein, Lawrence B. Harding, Ahren W. Jasper, Yuri Georgievskii, Branko Ruscic, Robert S. Tranter. Thermal Dissociation and Roaming Isomerization of Nitromethane: Experiment and Theory, The Journal of Physical Chemistry A, (07 2015): 0. doi: 10.1021/acs.jpca.5b01563
TOTAL:	**1**	

Number of Papers published in peer-reviewed journals:

(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

1. Oral Presentation at ARL, Aberdeen Proving Grounds, Dec. 8, 2016
Roaming Mechanisms for Nitrogen Containing Compounds:
CH3NO2, (CH3)2NNH2, CH3NH(NO2), and HNNOH

Stephen J. Klippenstein, Alexander Landera, Lawrence B. Harding, Yuri Georgievskii, Ahren W. Jasper
Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, United States

We will describe our explorations of the decomposition kinetics of four sample nitrogen containing compounds: (i) CH3NO2, which is the smallest nitrite containing molecule to show the effects of roaming, (ii) unsymmetrical dimethyl hydrazine (UDMH), (CH3)2NNH2, which is a bipropellant with interesting flammability properties, (iii) CH3NHNO2, which is one of the smallest bipropellants with both an amine and nitro group, and (iv) HNNOH, which is a key intermediate in thermal DeNOx chemistry. The thermal decomposition of nitromethane provides a classic example of the competition between roaming mediated isomerization and simple bond fission. The UDMH molecule is of interest as it shows two separate sets of roaming reactions related to N-N and C-N bond fissions. For CH3NHNO2 the presence of both amine and nitro groups yields interesting affects on the long-range interactions that lead to a wide variety of roaming mechanisms. The HNNOH case provides an interesting example where the tight and roaming pathways for molecular formation are merged.

2. Oral Presentation at ARO Workshop on Roaming and Cold Molecules, Emory University, Oct. 8, 2016
Roaming Mechanisms for Nitrogen Containing Compounds:
CH3NO2, (CH3)2NNH2, CH3NH(NO2), and HNNOH

Stephen J. Klippenstein,1 Alexander Landera,1 Lawrence B. Harding,1 Yuri Georgievskii,1 Ahren W. Jasper2
1 Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, United States
2 Combustion Research Facility, Sandia National Laboratories, Livermore, California 94551-0969, United States

We will describe our explorations of the decomposition kinetics of four sample nitrogen containing compounds: (i) CH3NO2, which is the smallest nitrite containing molecule to show the effects of roaming, (ii) unsymmetrical dimethyl hydrazine (UDMH), (CH3)2NNH2, which is a bipropellant with interesting flammability properties, (iii) CH3NHNO2, which is one of the smallest bipropellants with both an amine and nitro group, and (iv) HNNOH, which is a key intermediate in thermal DeNOx chemistry. The thermal decomposition of nitromethane provides a classic example of the competition between roaming mediated isomerization and simple bond fission. The UDMH molecule is of interest as it shows two separate sets of roaming reactions related to N-N and C-N bond fissions. For CH3NHNO2 the presence of both amine and nitro groups has interesting affects on the long-range interactions. The HNNOH case provides an interesting example where the tight and roaming pathways for molecular formation are merged.

3. Oral Presentation at TACC (Theory and Applications of Computational Chemistry), Aug. 28-Sept. 2, 2016

Ab initio kinetics for the decomposition of methylnitroamine (CH3)NHNO2

Alexander Landera, Stephen J. Klippenstein, Lawrence B. Harding
Chemical Sciences and Engineering Division,
Argonne National Laboratory, Argonne, IL
landera@anl.gov

Keywords: kinetics, roaming, trajectories

Abstract: Nitro containing compounds, RNO2, are an important class of chemical propellants. They have been found to be energetically powerful, yet stable enough to find utility in the propulsion of satellites and rockets. A quantitative understanding of their decomposition kinetics is central to the development of quantitative models for their use as a propellant. A model representative member of this class of compounds is methylnitroamine. It is small enough that it lends itself to scrutiny by some of the best theoretical methods available, and its decomposition is complicated enough to warrant study. A priori predictions for the decomposition kinetics of methylnitroamine have been made. Our analysis employs a combination of high level ab initio electronic structure theory, potential energy surface fitting, rigid body reduced dimensional dynamics, transition state theory, and master equation calculations.

Featuring a weak N-N bond, methylnitroamine can also readily rearrange, through a 1-3 hydrogen shift, reducing its nitro group to RN(OH)O. This rearrangement opens up two primary dissociation pathways leading to either NO2 or OH loss. Produced through simple N-N and N-O bond fissions, these two radical loss channels produce two radicals that interact generally through both strong dipole-dipole interactions and through hydrogen bonding interactions. As a result, the potential energy surface (PES) for the interactions between the two incipient radicals is remarkably complex showing multiple minima and multiple pathways to a variety of products. In this work, we present a detailed exploration of the PES for methylnitroamine on the basis of high level ab-initio calculations. Analytic representations of the interactions for the N-N and N-O fissions are obtained via fits to ~105 multi-reference ab initio data points. These analytic surfaces are utilized in rigid body dynamics (RBD) simulations of the branching between simple bond fission and other roaming related channels. Finally, utilizing the results of these RBD calculations, and the high level ab initio calculations for the tight transition state, the master

equation (ME) is solved to obtain high level predictions for the full set of thermal rate coefficients over a range of temperatures and pressures.
Our results reveal that there exists strong competition between a roaming mediated isomerization (RMI) path interconverting the nitro group (RNO2) to a nitrite group (RONO), prompt NO2 dissociation, OH dissociation, and OH roaming pathways. At low temperatures, our results suggest that the isomerization pathway involving a 1,3 hydrogen shift dominates, and at higher temperatures the RMI pathway, and NO2 dissociation dominate.

4. Poster Presentation at Dynamics of Molecular Collisions, XXV, 50 Years of Reaction Dynamics, July 12-17, 2015

Ab initio kinetics for the decomposition of unsymmetrical dimethyl hydrazine (CH3)2NNH2

Alexander Landera,1 Lawrence B. Harding,1 Yuri Georgievskii,1 Ahren W. Jasper,2 Stephen J. Klippenstein,1
1Chemical Sciences and Engineering Division,
Argonne National Laboratory, Argonne, IL
2Sandia National Laboratories,
Combustion Research Facility, Livermore, CA
landera@anl.gov

Abstract:
Unsymmetrical di-methylhydrazine (UDMH) is an important compound in propellant chemistry. When combined with other molecules, or gelled, it has been found to be safe, and has found great utility in the propulsion of satellites, as well as rockets. One reason generally given for its explosive behavior is the existence of an N-N bond, a common feature found in many explosives.

These N-N bonds are often weak, and any C-N bonds are only slightly stronger. The simple N-N and C-N bond fissions produce two radicals that interact generally through both strong dipole-dipole interactions and through hydrogen bonding interactions. As a result, the potential energy surface (PES) for the interactions between the two incipient radicals is remarkably complex showing multiple minima and multiple pathways to a variety of products.

In this work, we present a detailed exploration of the PES for UDMH on the basis of high level ab-initio calculations. For illustrative purposes we have generated a set of contour plots, which highlight the topography of the long-range interactions, for a range of N-N and C-N fragment separations. Analytic representations of the interactions for the N-N and C-N fissions are obtained via fits to ~105 CASPT2 (2,2)/avdz ab initio data points. These analytic surfaces are then utilized in rigid body dynamics (RBD) simulations of the branching between simple bond fission and other roaming related channels involving various H abstractions. Finally, utilizing the results of these RBD calculations, and the high level ab initio calculations for the tight transition states, the master equation (ME) is solved to obtained high level predictions for the full set of thermal rate
coefficients over a range of temperatures and pressures.

5. Introductory Discussion at Dynamics of Molecular Collisions, XXV, 50 Years of Reaction Dynamics, July 12-17, 2015

Navigating Complex Potential Energy Surfaces: Exploring; Representing and Visualizing; Rates

Stephen J. Klippenstein,
Chemical Sciences and Engineering Division,
Argonne National Laboratory, Argonne, IL

Number of Presentations: 5.00

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

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Alex Landera	1.00
FTE Equivalent:	**1.00**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Stephen Klippenstein	0.05	
Albert Wagner	0.03	No
FTE Equivalent:	**0.08**	
Total Number:	**2**	

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

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

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

Final Report

Effect of Dynamics in the van der Waals Region on the Chemical Kinetics of Nitrogen Containing Molecules

Overview

Propellants commonly contain a variety of nitrate and/or amine groups. To explore the possible role of the roaming radical mechanism in the thermal decomposition of such compounds we studied the decomposition kinetics for three small molecules that contain representative nitrate and amine groups: (i) CH_3NO_2, which is the smallest nitrite containing molecule to show the effects of roaming,[1] (ii) $(CH_3)_2NNH_2$ (UDMH, for unsymmetrical dimethyl hydrazine), which is used as a bipropellant (with N_2O_4) in hypergolic rocket fuels,[2,3] and (iii) CH_3NHNO_2, which is one of the smallest propellants with both amine and nitrite groups.[4,5] For each system we performed detailed and wide-ranging high-level multireference wavefunction based explorations of the long-range (van der Waals region) portion of the potential energy surface for the lowest energy bond fissions. These roaming radical potential energy surfaces were found to be remarkably complex, exhibiting a wide variety of kinetic behaviors. $(CH_3)_2NNH_2$ is interesting in that it contains nearly isoenergetic N-N and C-N fission channels, and we studied the related roaming dynamics for both channels. Meanwhile, for CH_3NO_2 we focused on the CN fission and for CH_3NHNO_2 we focused on the NN fission channel since the CN fission was found to be considerably higher lying. Overall, we discovered and explicated a wide variety of roaming radical behavior, much of which is novel.

CH_3NO_2

Our collaborative theory-experiment study on CH_3NO_2 decomposition was published in J. Phys. Chem. A as part of the special issue honoring the 100 Years of Combustion Kinetics at Argonne by Larry Harding, Joe Michael, and Al Wagner.[1] This decomposition provides a classic example of the competition between roaming mediated isomerization (RMI) and simple bond fission. A high-level theoretical analysis provided a quantitative exploration of the effects of roaming on the thermal decomposition kinetics. Meanwhile, laser schlieren densitometry was used to explore the effect of roaming on the density gradients for CH_3NO_2 decomposition in a shock tube for pressures of 30, 60, and 120 Torr at temperatures ranging from 1200 to 1860 K.

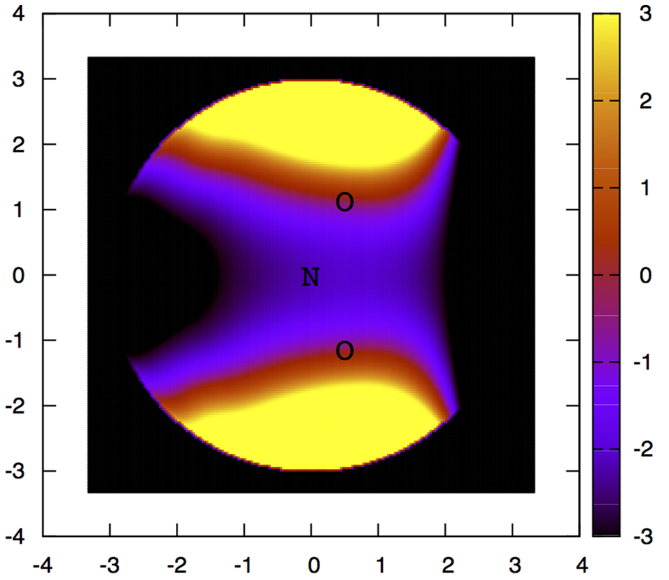

Figure 1: Plot of the (7o,10e)-CASPT2/adz interaction potential between CH_3 and NO_2 (relative to CH_3 + NO_2) at a fixed CN distance of 3.0 Å (approximately the separation at the roaming saddle point).

The analysis focused on the roaming dynamics in a reduced dimensional space[6] consisting of the rigid-body motions of the

CH_3 and NO_2 radicals. A high-level reduced-dimensionality potential energy surface (PES) was developed from fits to large-scale multi-reference *ab initio* calculations. The plot in Fig. 1 illustrates this interaction potential in the roaming region of configuration space. The saddle point for roaming lies at roughly (0.5,0.0), while the minima to the left and right of this point relax to the CH_3NO_2 and CH_3ONO complexes, respectively. A combination of CASPT2, Davidson corrected MRCI, and CCSD(T) calculations [each extrapolated to the complete basis set limit (CBS) from explicit calculations for the aug-cc-pVTZ and aug-cc-pVQZ bases] indicate that the fully relaxed zero-point corrected saddle point energy is -0.78 +/- 0.15 kcal/mol. These calculations, which make use of our recently developed spin-splitting based analysis approach,[7,8] provide the most definitive analysis to date of roaming saddle point energies.

Rigid body trajectory (RBT) simulations coupled with master equation kinetics calculations were used to obtain high-level *a priori* predictions for the microcanonical and thermal branching between RMI and dissociation. These predictions differ quite strongly from those of earlier classical trajectory and statistical theory simulations (cf. Fig. 2).[9,10] Our focus on dynamics within the roaming subspace, coupled with our careful analysis of the PES, yields more quantitative results. A statistical model [11] provided a qualitatively useful physical description that is even semiquantitatively correct.

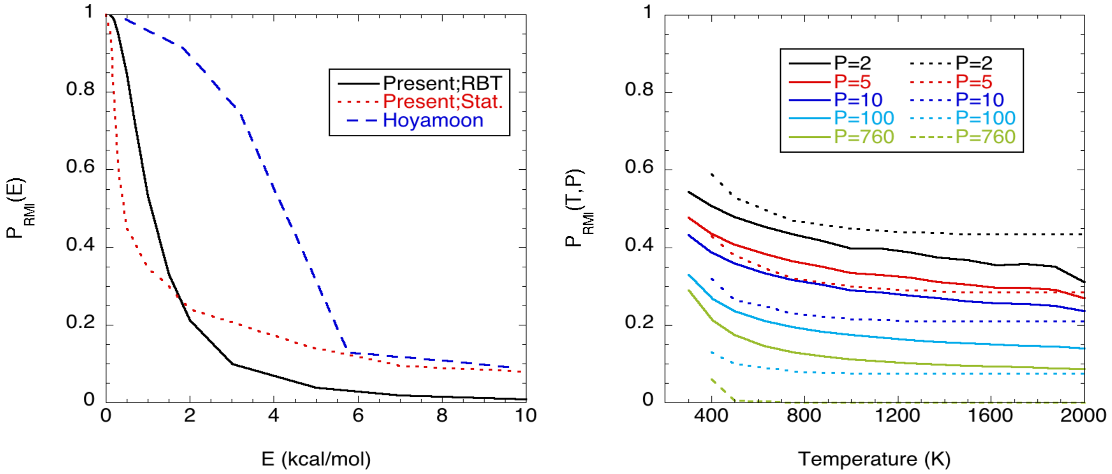

Figure 2: Plot of the predicted RMI probability as a function of (i) the energy relative to CH_3 + NO_2 (plot on the left) and (ii) the temperature and pressure (Torr) in an Ar bath gas. For the latter plot the solid lines denote the present approach and the dashed lines from Zhu and Lin.

Our thermal kinetic analysis employed an exponential down energy transfer model together with Lennard Jones collision rates. Appropriate adjustment of the energy transfer parameter α (approximately the average energy transferred in downwards colliions, $<\Delta E_{down}>$)

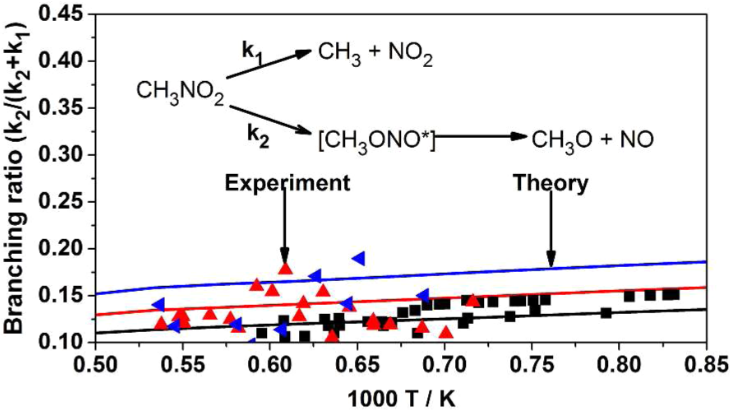

Figure 3. Comparison of theory and experiment for the roaming branching fraction for decomposition of CH_3NO_2 at 30 (blue), 60 (red) and 120 (blue) Torr.

yielded quantitative agreement with both the present and previous experimental observed dissociation rate constants. More interestingly, the predicted roaming branching fractions were also consistent with the experimental observations, as illustrated in Fig. 3.

$(CH_3)_2NNH_2$

The decomposition of UDMH is particularly interesting as it shows two separate sets of roaming mediated reactions, related to partial N-N and C-N bond fissions, that are separated by only 4.1 kcal/mol. Furthermore, the roaming pathways for the partial C-N fission are remarkably complex. Taken together, the two sets of decomposition pathways (cf. Figs. 4 and 5) illustrate the widely variable nature of roaming mediated mechanisms.

The structures, energies, and frequencies for the long range stationary points for these two partial bond fissions were calculated at the CASPT2(2e,2o)/CBS//CASPT2(2e,2o)/aVTZ level of theory. The key roaming saddle point energies were also evaluated with the spin-splitting approach and with the Davidson corrected MRCI method. These calculations show reasonable consistency, suggesting that the predictions are again accurate to within about 0.2 kcal/mol. For kinetic evaluation purposes, the other stationary points on the potential energy surface were again explored with the high level ANL-0 method (cf. discussion in the proposed work below).[12] The energies reported here are all relative to the corresponding bond fission products and include ZPE corrections.

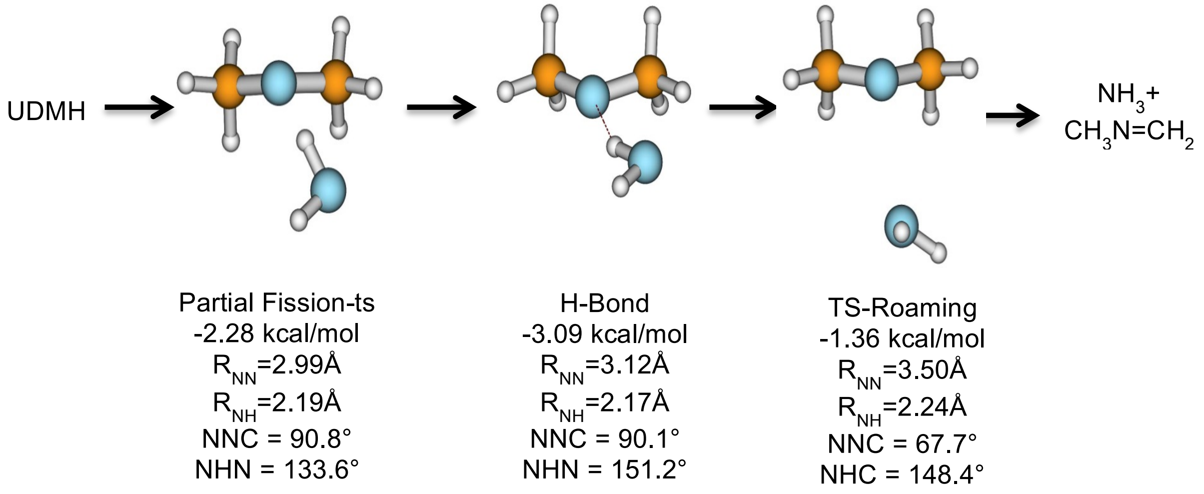

Figure 4: Schematic diagram of the stationary points on the roaming mediated abstraction pathway for partial NN fission in UDMH.

The partial NN fission pathway (Fig. 4) differs from classic roaming mediated pathways[6,13] in that there are two saddle-points for the transition from bound complex to abstraction products. The partial CN fission pathways (Fig. 5) are even more complex. In this case, the departing methyl radical may roam around to abstract an H from either the NH_2 group or the other CH_3 group. Furthermore, there are at least 4 distinct minima in the long-range region of PES, with a multitude of connections between them. A classic roaming pathway directly connects UDMH with CH_4 + CH_3NNH. Meanwhile, the most direct pathway from UDMH to CH_4 + CH_2NNH_2 must proceed through at least three distinct transition states (TSs). There is also a separate three TS path connecting UDMH to CH_4 + CH_3NNH. These three TS roaming paths appear to be more complex than any previously published roaming pathways. Generally, the presence of stronger dipoles, nitrogen lone-pairs, and hydrogen bonding is expected to lead to considerably more complex roaming dynamics.

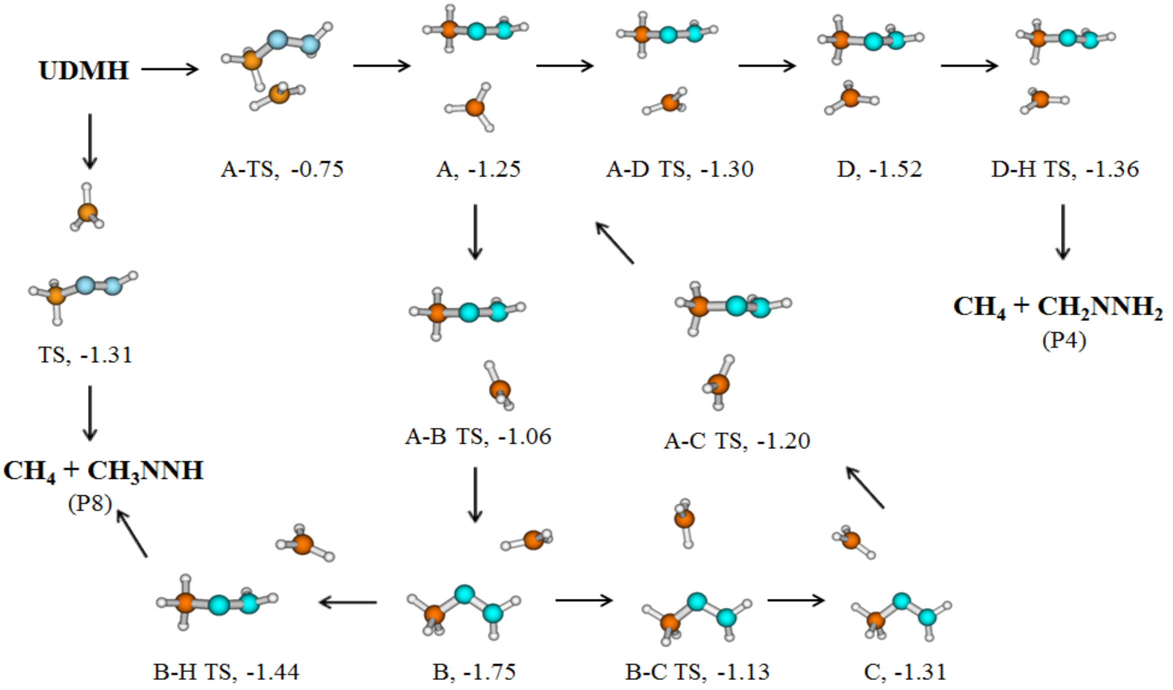

Figure 5: Schematic diagram of the stationary points on the roaming mediated pathways for the partial CC fission of UDMH.

The complexity of the roaming for this partial C-N fission case led us to develop new methods for visualizing the potential energy surface. Limited features of one of these visualization methods are illustrated in Fig. 6. To make this plot we generated contours of the orientation dependent interactions on a sphere of fixed CN separation. With advanced graphical plotting software we are able to rotate these spheres by hand (i.e., with a mouse), which allows us to obtain a good physical sense of the connections between the various minima. Unfortunately, it is difficult to convey the beauty and utility of this software on the printed page. A manuscript describing these mechanistic explorations will soon be submited for publication.[2]

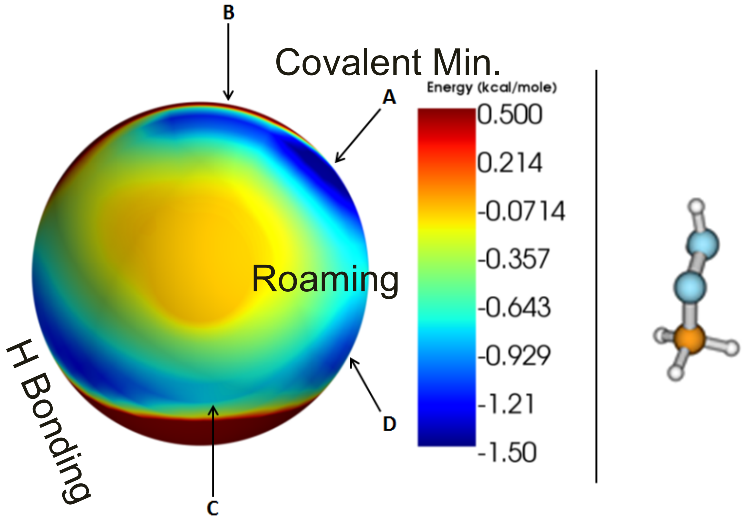

Figure 6: 3-Dimensional contours of the fixed CN interaction potential.

A high-level reduced-dimensionality potential energy surface (PES) for the lower energy partial N-N fission channel was developed from fits to large-scale multi-reference *ab initio* calculations. This potential energy surface was employed in rigid body trajectory simulations of the flux to both the radical loss channel and the $NH_3 + CH_3N{=}CH_2$ channel. The predicted fluxes were then incorporated in kinetic models for the decomposition of UDMH. The predicted rate constants were found to be in satisfactory agreement with the experimental data.[8] Preliminary results for the roaming branching fraction indicate that roaming is very significant at low pressures (up to 50% roaming at 1000 K), but that this significance decays rapidly with increasing pressure (by 1 atm, the branching is only a few % at 1000 K).[3] These observations, which are similar to what was observed for CH_3NO_2, suggest that the high pressures of relevance to propellant usage will generally negate the importance of the roaming channels.

CH_3NHNO_2

For methylnitroamine we have completed our exploration of the potential energy surface[4] and are in the process of exploring the kinetics.[5] This molecule was chosen because it represents one of the smallest bipropellants with both an amine and nitro group. The presence of both amine and nitro groups was expected to yield interesting effects for the long-range interactions.

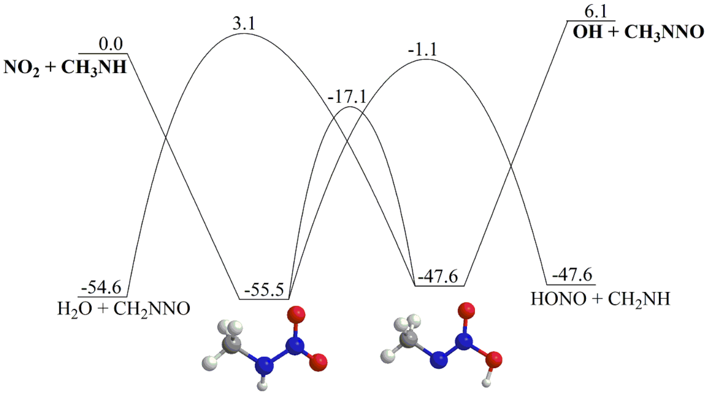

Figure 7: Schematic ANL0 PES diagram for the decomposition of CH_3NHNO_2.

The analysis began with an exploration of the minima and tight TSs on the thermal decomposition PES, beginning with a slightly modified version of the ANL0 method (cf. Fig. 7). The calculations indicate that the dominate bond fission channel is to the $CH_3NH + NO_2$ products. There is also a low energy H transfer TS yielding $CH_3NN(O)OH$, but the lowest energy decompositions from there are higher than the bond fission from CH_3NHNO_2. From CH_3NHNO_2 there is also a four-center tight TS for loss of HONO that lies slightly below the threshold for the bond-fission channel. This tight TS will compete with the formation of the same products through roaming as is the case for aldehyde roaming reactions.[13]

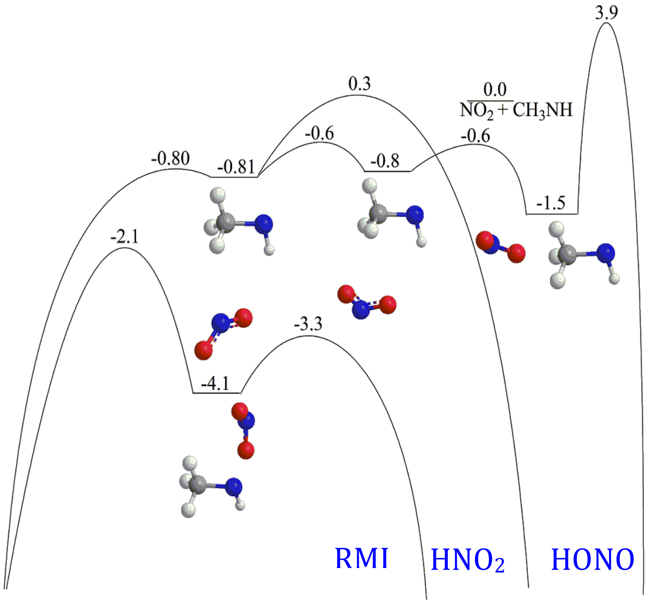

Figure 8: Schematic CASPT2/CBS PES for the roaming region of the $NO_2 \ldots CH_3NH$ PES.

The roaming region of the PES was again explored with a combination of CASPT2/CBS, Davidson corrected MRCI/CBS, and CCSD(T)/CBS calculations. In this case, a large (10e,7o) active space was required, due to the complexity of the NO_2 wavefunction. The observed consistency in the roaming related stationary point energies again suggests our results are accurate to within about 0.2 kcal/mol. Interestingly, this PES demonstrates a new type of complexity for the roaming interactions. Now there are three separate roaming possibilities: (i) roaming mediate isomerization, via two saddle points, to form CH_3NHONO, (ii) roaming mediated H abstraction by the N end of the NO_2 group to form ONHO + CH_2NH, and (iii) roaming mediated abstraction by the O end of the NO_2 group to form HONO + CH_2NH. Interestingly, the latter two channels share the first roaming TS, and then branch out from the $CH_3NH\ldots NO_2$ intermediate, with the ONHO forming pathway passing through just one more TS, while the HONO forming pathway encounters three additional saddle points, for a total of 4 saddle points along its roaming pathway. This pathway is the most complex roaming mechanism that we have observed to date.

References

---

[1] C. J. Annesley, J. B. Randazzo, S. J. Klippenstein, L. B. Harding, A. W. Jasper, Y. Georgievskii, B. Ruscic, R. S. Tranter, Thermal Dissociation and Roaming Isomerization of Nitromethane: Experiment and Theory*, J. Phys. Chem. A* **119**, 7872-7893 (2015).

[2] A. Landera, L. B. Harding, S. J. Klippenstein, Roaming Radical Pathways in NN and CN Fissions of Unsymmetrical Dimethylhydrazine, $(CH_3)_2NNH_2$, *J. Phys. Chem. A* to be submitted (2017).

[3] A. Landera, Y. Georgievskii, L. B. Harding, A. W. Jasper, S. J. Klippenstein, Ab Initio Kinetics for the Decomposition of Unsymmetrical Dimethylhydrazine $(CH_3)_2NNH_2$, unpublished (2017).

[4] A. Landera, L. B. Harding, S. J. Klippenstein, Decomposition Mechanism for CH_3NHNO_2, *J. Phys. Chem. A* to be submitted (2017).

[5] A. Landera, Y. Georgievskii, L. B. Harding, A. W. Jasper, S. J. Klippenstein, Ab Initio Kinetics for the Decomposition of for CH_3NHNO_2, work in progress (2017).

[6] L. B. Harding, Y. Georgievskii, S. J. Klippenstein, Roaming Radical Kinetics in the Decomposition of Acetaldehyde, *J. Phys. Chem. A* **114,** 765-777 (2010).

[7] C. P. Moradi, A. M. Morrison, S. J. Klippenstein, C. F. Goldsmith, G. E. Douberly, Propargyl + O_2 Reaction in Helium Droplets: Entrance Channel Barrier or Not? *J. Phys. Chem. A* **117***,* 13626-13635 (2013).

[8] C. F. Goldsmith, L. B. Harding, Y. Georgievskii, J. A. Miller, S. J. Klippenstein, Temperature and Pressure-Dependent Rate Coefficients for the Reaction of Vinyl Radical with Molecular Oxygen, *J. Phys. Chem. A* **119,** 7766-7779 (2015).

[9] Homayoon, Z.; Bowman, J. M. Quasiclassical Trajectory Study of CH_3NO_2 Decomposition via Roaming Mediated Isomerization Using a Global Potential Energy Surface. *J. Phys. Chem*. A **2013**, *117*, 11665-11672.

[10] Zhu, R. S.; Raghunath, P.; Lin, M. C. Effect of Roaming Transition States upon Product Branching in the Thermal Decomposition of CH_3NO_2. *J. Phys. Chem*. A **2013**, *117*, 7308-7313.

[11] S. J. Klippenstein, Y. Georgievskii, L. B. Harding, Statistical Theory for the Kinetics and Dynamics of Roaming Reactions, *J. Phys. Chem. A*, **115,** 14370-14381 (2011).

[12] S. J. Klippenstein, L. B. Harding, B. Ruscic Ab Initio Computations and Active Thermochemical Tables Hand in Hand: Heats of Formation of Core Combustion Species, *J. Phys. Chem. A*, in preparation (2017).

[13] L. B. Harding, S. J. Klippenstein, Roaming Radical Pathways for the Decomposition of Alkanes, *J. Phys. Chem. Lett.* **1**, 3016-3020 (2010).