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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 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 complex of these, the roaming mediated mechanism for conversion of CH3NHNO2 to CH2NH + 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
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(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. Jasper 2 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):

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TOTAL:

	Peer-Reviewed Conference Proceeding publications (other than abstracts):
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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) CH₃NO₂, which is the smallest nitrite containing molecule to show the effects of roaming,¹ (ii) (CH₃)₂NNH₂ (UDMH, for unsymmetrical dimethyl hydrazine), which is used as a bipropellant (with N_2O_4) in hypergolic rocket fuels,^{2,3} and (iii) CH₃NHNO₂, 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. (CH₃)₂NNH₂ 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 CH₃NO₂ we focused on the CN fission and for CH₃NHNO₂ 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.

CH₃NO₂

Our collaborative theory-experiment study on CH₃NO₂ 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. А high-level -1 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 CH₃NO₂ decomposition in a shock tube for pressures of 30, 60, and 120 Torr at temperatures ranging from 1200 to 1860 K.

The analysis focused on the roaming dynamics in a reduced dimensional space⁶ consisting of the rigid-body motions of the



Figure 1: Plot of the (70,10e)-CASPT2/adz interaction potential between CH₃ and NO₂ (relative to CH₃ + NO₂) at a fixed CN distance of 3.0 Å (approximately the separation at the roaming saddle point).

CH₃ and NO₂ 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 CH₃NO₂ and CH₃ONO 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



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.

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.

Our thermal kinetic analysis exponential down employed an 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 NH₂ group or the other CH₃ 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 CH₄ + CH₃NNH. Meanwhile, the most direct pathway from UDMH to CH₄ + CH₂NNH₂ must proceed through at least three distinct transition states (TSs). There is also a separate three TS path connecting UDMH to CH₄ + CH₃NNH. 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



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

describing these mechanistic explorations will soon be submited for publication.²

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 NH₃ + CH₃N=CH₂ 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 CH₃NO₂, suggest that the high pressures of relevance to propellant usage will generally negate the importance of the roaming channels.

CH₃NHNO₂

For methylnitroamine we have $NO_2 + C\overline{H_3NH}$ completed our exploration of the potential energy surface⁴ and are in the process of exploring the kinetics.⁵ This was chosen because molecule it of represents one 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.

The analysis began with an dominate bond fission channel is to the

 $CH_3NH + NO_2$ products. There is also a low energy H transfer TS yielding CH₃NN(O)OH, but the lowest energy decompositions from there are higher than the bond fission from CH₃NHNO₂. From CH₃NHNO₂ 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

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



Figure 7: Schematic ANLO PES diagram for the decomposition of CH₃NHNO₂.

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



Figure 8: Schematic CASPT2/CBS PES for the roaming region of the NO₂...CH₃NH PES.

complexity of the NO₂ 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 CH₃NHONO, (ii) roaming mediated H abstraction by the N end of the NO₂ group to form ONHO + CH₂NH, and (iii) roaming mediated abstraction by the O end of the NO₂ group to form HONO + CH₂NH. Interestingly, the latter two channels share the first roaming TS, and then branch out from the CH₃NH...NO₂ 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, (CH₃)₂NNH₂, *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 (CH₃)₂NNH₂, unpublished (2017).

⁴ A. Landera, L. B. Harding, S. J. Klippenstein, Decomposition Mechanism for CH₃NHNO₂, *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 CH₃NHNO₂, 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 + O₂ 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 CH₃NO₂ 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 CH₃NO₂. *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).