

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE (DD-MM-YYYY) August 2013		2. REPORT TYPE Technical Paper		3. DATES COVERED (From - To) August 2013-October 2013	
4. TITLE AND SUBTITLE Kinetics Studies of Radical-Radical Reactions (I): The NO ₂ + N ₂ H ₃ System				5a. CONTRACT NUMBER FA9550-12-D-0001	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) H. Sun, S. D. Chambreau, C. K. Law, A. Schenk, G. L. Vaghjiani				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER QOPX	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQRP 10 E. Saturn Blvd. Edwards AFB CA 93524-7680				8. PERFORMING ORGANIZATION REPORT NO.	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQR 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-RQ-ED-TP-2013-217	
12. DISTRIBUTION / AVAILABILITY STATEMENT Distribution A: Approved for Public Release; Distribution Unlimited. PA#13474					
13. SUPPLEMENTARY NOTES Conference paper for the WSS-Combustion Meeting, Fort Collins, CO, 7-8 October 2013.					
14. ABSTRACT The state-of-the-art hypergol combination currently used in the US for many space propulsion applications consists of monomethyl hydrazine, as the fuel, and nitrogen tetroxide, as the oxidizer. The Air Force Research Laboratory is developing new hypergolic fuels which will provide enhanced performance capabilities as well as improved affordability and efficiency. Furthermore, handling of these new hypergolic fuels is also expected to have a much smaller logistical footprint due to the fact that they are being designed to be environmentally benign. However, practical realization of these hypergols in spacecraft propulsion systems will only come after attaining a satisfactory understanding of how to optimize their combustion characteristics in relevant operating environments. Here we report theoretical results obtained on the prototypical radical-radical reaction: NO ₂ + N ₂ H ₃ , and the progress made towards building an apparatus consisting of laser photolysis/fast flow-tube reactor coupled to a mass spectrometer for investigating the kinetics of this elementary reaction.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE	SAR	8	G. Vaghjiani
Unclassified	Unclassified	Unclassified			19b. TELEPHONE NO (include area code) 661-525-5657

Fall 2013 Technical Meeting of the Western States Section of the Combustion Institute
Hosted by Colorado State University, October 7-8, 2013

Kinetics Studies of Radical-Radical Reactions (I): The $\text{NO}_2 + \text{N}_2\text{H}_3$ System

Hongyan Sun, Ghanshyam L. Vaghjiani*, Steven D. Chambreau, and Adam Schenk
*Propellants Branch, Aerospace Systems Directorate, Air Force Research Laboratory, AFRL/RQRP
Edwards AFB, California 93524, USA*

Chung K. Law
*Department of Mechanical and Aerospace Engineering, Princeton University
Princeton, New Jersey 08544, USA*

The state-of-the-art hypergolic combination currently used in the US for many space propulsion applications consists of monomethyl hydrazine, as the fuel, and nitrogen tetroxide, as the oxidizer. The Air Force Research Laboratory is developing new hypergolic fuels which will provide enhanced performance capabilities as well as improved affordability and efficiency. Furthermore, handling of these new hypergolic fuels is also expected to have a much smaller logistical footprint due to the fact that they are being designed to be environmentally benign. However, practical realization of these hypergols in spacecraft propulsion systems will only come after attaining a satisfactory understanding of how to optimize their combustion characteristics in relevant operating environments. Here we report theoretical results obtained on the prototypical radical-radical reaction: $\text{NO}_2 + \text{N}_2\text{H}_3$, and the progress made towards building an apparatus consisting of laser photolysis/fast flow-tube reactor coupled to a mass spectrometer for investigating the kinetics of this elementary reaction.

Keywords: Hypergolic, Propellants, N_2H_3 , Kinetics, Mechanism.

1. Introduction

The hydrazine (N_2H_4) and dinitrogen tetroxide (N_2O_4) reaction system is widely used as liquid propellants for satellite and space propulsion applications.¹ As an oxidizer, the N_2O_4 molecule is known to have several inter-conversion structural conformers: NO_2 monomer, symmetric N_2O_4 dimer with D_{2h} symmetry, asymmetric ONONO_2 with cis- and trans-structures, and the van der Waals complex with C_{2v} symmetry.² Recently, Lai et al.³ theoretically studied the reaction of N_2H_4 with the N_2O_4 isomers and reported that the reaction of N_2H_4 with sym- N_2O_4 (D_{2h}), cis- ONONO_2 (C_s), and NO_2 has to overcome an activation barrier of 14.2, 10.6, and 7.6 kcal/mol, respectively. However, N_2H_4 can spontaneously react with trans- ONONO_2 (C_s) and cis- ONONO_2 (C_1) to produce $\text{HONO}_2 + \text{H}_2\text{NN}(\text{H})\text{NO}$ with a rate constant of $4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 250 K. The intermediate $\text{H}_2\text{NN}(\text{H})\text{NO}$ thus formed can rapidly fragment to produce the reactive radical N_2H_3 with a rate constant of $1 \times 10^7 \text{ s}^{-1}$ at 1000 K, which is fast enough to initiate the hypergolic chain

*Email: ghanshyam.vaghjiani@us.af.mil

reactions of NO_2 and N_2O_4 . Consequently, the kinetics of N_2H_3 with NO_2 is important for understanding the mechanism and the ignition process of the hydrazine and N_2O_4 system. However, the reaction is complicated by multiple radical-radical abstraction, addition and subsequent dissociation pathways. In this work, the reaction of N_2H_3 with NO_2 was studied by *ab initio* multi-reference second-order perturbation theory and quadratic configuration interactions and coupled-cluster theories. It was found that oxidation of the N_2H_3 radical by NO_2 occurs with submerged barriers with relatively large exothermicities. Consequently, the accuracy of the value of the theoretical rate coefficient computed for this reaction will greatly depend on the level of accuracy employed to describe the electron correlation effects for both the outer and multiple inner transition states.⁴ We have accurately characterized the potential energy surface for the $\text{NO}_2 + \text{N}_2\text{H}_3$ system and have established the most likely reaction mechanism. The technique of laser photolysis/fast flow-tube reactor coupled to a mass spectrometer is also being utilized to experimentally investigate the reaction kinetics of this system.

2. Theoretical and Computational Details

Due to electron repulsion between the electronegative oxygen and nitrogen atoms in this reaction system, the multi-reference character of the wavefunction is quite strong. Therefore, we have used multi-reference second-order perturbation theory (CASPT2) with Dunning's augmented correlation consistent basis set, aug-cc-pVDZ to optimize the geometries of the stationary points of the potential energy surface and to calculate the corresponding ro-vibrational frequencies. For the reactants (N_2H_3 and NO_2) and the products (NNH_2 , cis-NH=NH, and trans-NH=NH), the larger basis set, aug-cc-pVTZ was applied, and all of the electrons were included in the active space. The geometries of the products (cis-HONO, trans-HONO, and HNO_2) were optimized at the CASPT2/aug-cc-pVDZ level, with all the electrons included in the active space. For the transition states, the active space was selected to describe adequately the bond breaking/making process of interest with reasonable computational efficiency. Specifically, for H-abstraction from N_2H_3 by NO_2 to form cis-HONO and the NNH_2 diradical, the transition state was optimized using an active space (6e,8o) consisting of σ bonding and anti-bonding pairs of the imidogen-H being abstracted, π bonding and anti-bonding pairs of the N–N bond, *s* orbital of the electron-deficient N atom on NNH_2 , and σ bonding of the O–H bond being formed. For H-abstraction from N_2H_3 by NO_2 to form cis-HONO and trans-NH=NH, the transition state was optimized using an active space (6e,6o) consisting of σ and π bonding and anti-bonding pairs of N–O bond, *p* orbital of the O atom that is interacting with the H being abstracted and its corresponding virtual orbital. Furthermore, the (6e,8o) active space was used for optimization of the addition adducts and H-bonded complexes.

Higher-level stationary point energies were obtained from quadratic configuration interactions and coupled-cluster theories with single and double excitations, and correction for triple excitations. Specifically, the QCISD(T) and CCSD(T) calculations employed the correlation-consistent, polarized-valence, triplet- ξ (cc-pVTZ) and quadruple- ξ (cc-pVQZ) basis sets of Dunning.^{5,6} The energies were then extrapolated to the complete basis set (cc-pV ∞ Z) limit⁷ by the asymptotic form.^{8,9} Electronic structure calculations were performed using the MOLPRO¹⁰ quantum chemistry package.

3. Experimental Details

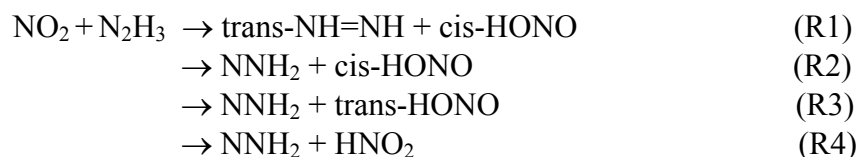
A halo-carbon wax coated Pyrex flow-tube reactor which was 100 cm long with internal diameter of 2.54 cm was used. N_2H_4 vapor and gaseous NO_2 were carried into the flow-tube using excess nitrogen gas. The N_2H_4 was photolyzed under optically thin conditions by sending a 193-nm laser beam along the axis of the flow-tube which had been fitted with appropriate quartz optical ports at both ends to produce N_2H_3 radicals under excess NO_2 conditions. The pressure of the flow-tube was typically held at ~ 2 Torr and the linear flow velocity of the gas mixture adjusted to attain plug-flow conditions that gave reaction lengths ranging from 40 to 70 msec. The reaction kinetics of the N_2H_3 radicals was followed in real-time by sampling the gas mixture through a small pin hole at the mid-point down the flow-tube axis using a skimmer that was attached to a differentially pumped chamber containing an electron impact ionization quadrupole mass spectrometer.

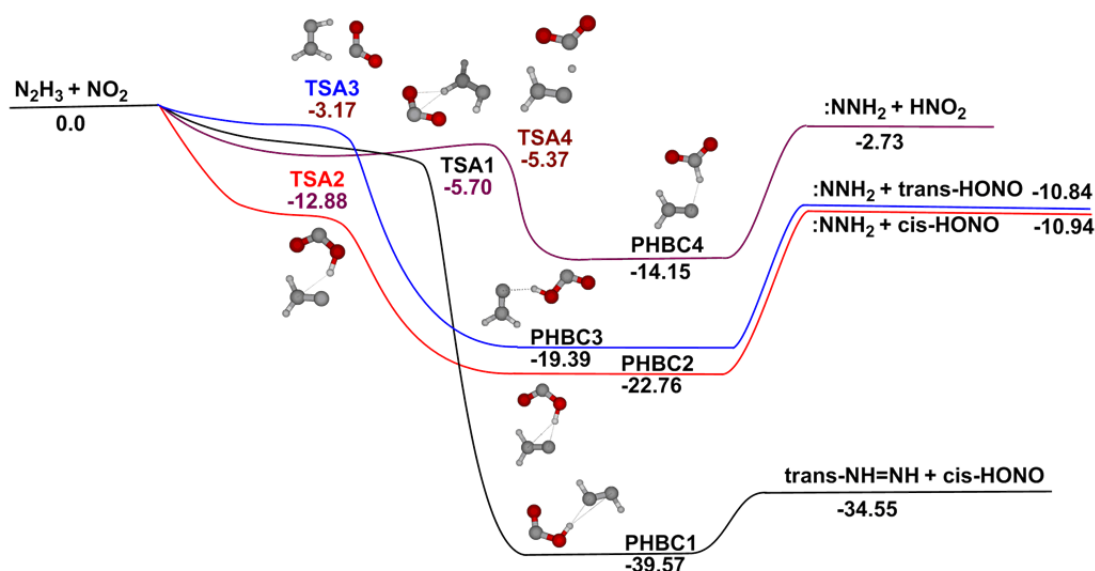
4. Results and Discussion

To our knowledge, experimental and/or theoretical studies on the kinetics of the reaction $\text{NO}_2 + \text{N}_2\text{H}_3$ has not been reported in the literature. Recently, Liu et al.¹¹ studied the gas-phase chemistry of the hypergolic system, monomethyl hydrazine (MMH) with $\text{NO}_2/\text{N}_2\text{O}_4$ at room temperature, and proposed that the oxidation of MMH by $\text{NO}_2/\text{N}_2\text{O}_4$ at atmospheric pressure occurs via two mechanisms: (1) sequential H-abstraction and HONO formation, and (2) reaction of MMH with asymmetric ONONO₂, leading to the formation of methyl nitrate. Furthermore, they reported that all of the intermediates observed experimentally could be successfully explained by the above mechanisms. Furthermore, Catoire et al.¹² suggested that the addition products $\text{CH}_3\text{N}(\text{NO}_2)\text{NH}_2$ and $\text{CH}_3\text{N}(\text{ONO})\text{NH}_2$ are the major stable pre-ignition products which account for the formation of the white-yellow condensate.¹³ However, in the study of Liu et al.,¹¹ these species were not identified as the major early species and the only major product observed is methyldiazene, $\text{CH}_3\text{N}=\text{NH}$. This indicates that the direct H-abstraction reaction from the methylhydrazyl radical by NO_2 leading to the formation of $\text{CH}_3\text{N}=\text{NH}$ might be a more dominant path compared to the radical-radical addition path followed by subsequent decomposition of addition products. Consequently, this would suggest that this might also be the case for the analog reaction between NO_2 and N_2H_3 . In this work, the reaction pathways for both abstraction and addition in $\text{NO}_2 + \text{N}_2\text{H}_3$ were theoretically explored at the CCSD(T)/cc-pV ∞ Z//CASP2/aug-cc-pVDZ level.

(I). Direct H-abstraction Reactions

The ground state of NO_2 ($^2\text{A}_1$) has C_{2v} symmetry. For direct abstraction of hydrogen from N_2H_3 , hydrogen bonding plays an important role in the transition state geometries. It was determined that direct abstraction occurs via four different transition states, all with negative barriers (see Figure 1), to form the following products:





CASPT2/aug-cc-pVDZ
RCCSD(T)/CBS//CASPT2/aug-cc-pVDZ

Figure 1: Potential energy surface of $\text{NO}_2 + \text{N}_2\text{H}_3$ (abstraction) calculated at the RCCSD(T)/cc-pV ∞ Z//CASPT2/aug-cc-pVDZ level. Energies are zero-point corrected and relative to that of entrance channel at 0 K.

The most exothermic abstraction channel is reaction (R1), which has a submerged barrier of -5.70 kcal/mol via TSA1, forming an H-bonded product complex (PHBC1) with an energy of -39.57 kcal/mol. It then dissociates to the products trans-NH=NH and cis-HONO with an overall reaction energy of -34.55 kcal/mol. The abstraction of imidogen-H (R2) was found to have the lowest energy barrier of -12.88 kcal/mol via TSA2, which is due to electron donation from the N atom to the forming O—H bond. The reaction forms an H-bonded product complex (PHBC2) with an energy of -22.76 kcal/mol, which then dissociates to the products NNH_2 plus cis-HONO with an overall reaction energy of -10.94 kcal/mol. Reaction (R3) has an energy barrier of -3.17 kcal/mol via TSA3 and it forms an H-bonded product complex (PHBC3) with energy of -19.39 kcal/mol, which then dissociates to the products NNH_2 plus trans-HONO with overall reaction energy of -10.84 kcal/mol. The abstraction reaction by the less nucleophilic nitrogen of NO_2 was found to be almost thermal-neutral, with energy of reaction of -2.73 kcal/mol. Even though the nitrogen is less nucleophilic than the oxygen in NO_2 , the H-abstraction by the nitrogen of NO_2 still has a negative energy barrier of -5.37 kcal/mol via TSA4 due to electron donation from the N atom to the forming N—H bond. The formed H-bonded product complex (PHBC4) from this channel has an energy of -14.15 kcal/mol. Overall, the four H-bonded product complexes are 5 to 12 kcal/mol more stable than the corresponding dissociation products, and it is noted that, at low and intermediate pressures, cis-HONO, trans-HONO, trans-NH=NH, and NNH_2 are the favorable products.

(II). N-N Addition Reactions

It was found that both the nitrogen and the oxygen of the NO₂ can be added to the N₂H₃ radical. For the case of nitrogen addition to the radical site in N₂H₃ (N-N addition), as shown in Figure 2, two adducts are formed, which are optical isomers with energy of -37.9 kcal/mol.

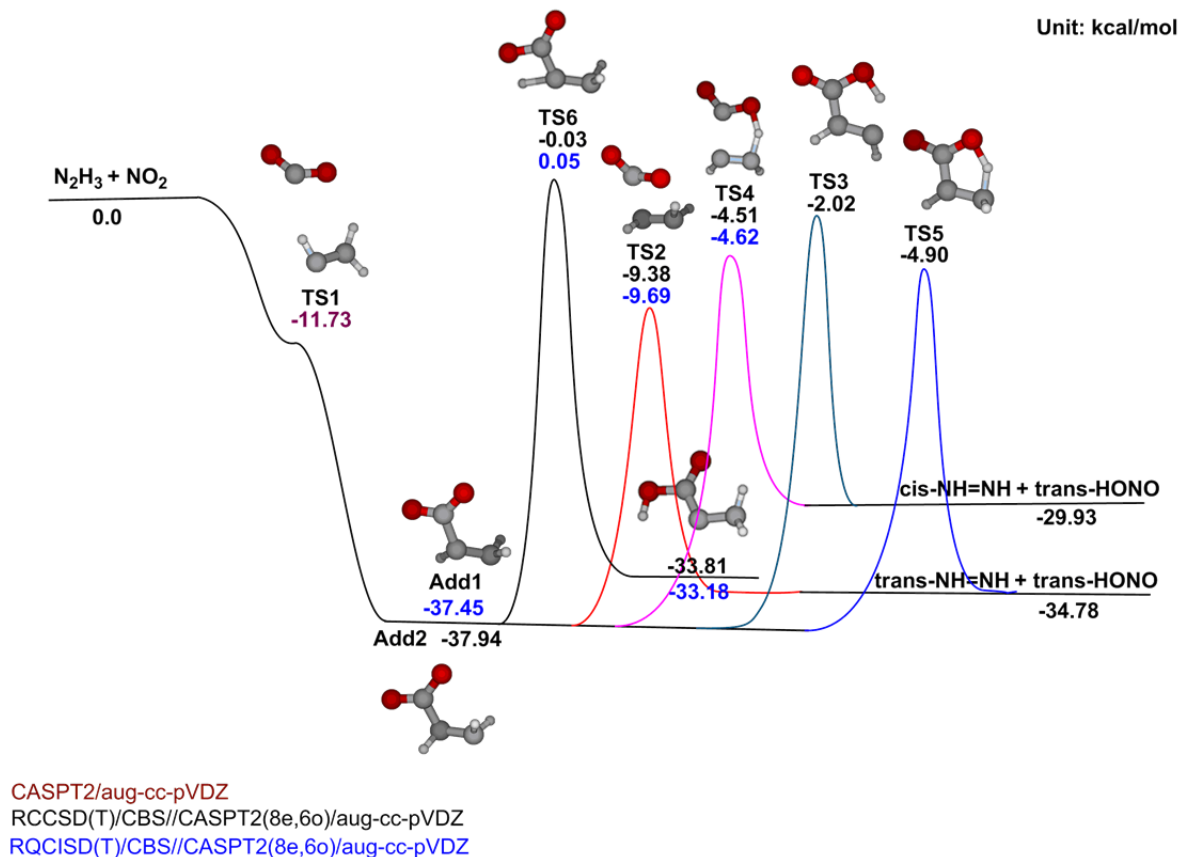


Figure 2: Potential Energy surface of NO₂ + N₂H₃ (addition) calculated at the RCCSD(T)/cc-pV ∞ Z//CASPT2/aug-cc-pVDZ level. Energies are zero-point corrected and relative to that of entrance channel at 0 K.

In Figure 2, adduct Add1 is formed with the imidogen-H in the front of the pseudo N-N-N-O plane, and Add2 is formed with the imidogen-H in the back of the pseudo N-N-N-O plane. By intrinsic reaction coordinate (IRC) analysis, it was found that the two isomeric adducts are formed via one saddle point, TS1, which has a planar structure with an energy barrier of -11.73 kcal/mol. Furthermore, no pre-reactive H-bonded complex is formed before the saddle point due to the presence of the strong nucleophilic O atom in NO₂. It was also found that each of the optical isomer adducts, NH₂NHNO₂ have distinct transition states corresponding to intramolecular H-abstraction from the NH₂ group to form trans- and cis-NH=NH, and trans-HONO products. The Add1 adduct undergoes intramolecular H-abstraction via TS2 with an energy barrier of -9.38 kcal/mol to form trans-NH=NH + trans-HONO products, and it also undergoes an intramolecular H-abstraction via TS3 with an energy barrier of -2.02 kcal/mol to form cis-NH=NH + trans-HONO products. Similarly, the Add2 adduct undergoes intramolecular H-abstraction via TS4 with an energy barrier of

-4.51 kcal/mol to form cis-NH=NH + trans-HONO products, and it also undergoes intramolecular H-abstraction via TS5 with an energy barrier of -4.90 kcal/mol to form trans-NH=NH + trans-HONO products. For the intramolecular abstraction of imidogen-H, both adducts share the same four-member-ring transition state TS6 which has an energy barrier nearly identical to that of the entrance channel. This reaction channel forms NH₂NNO₂H as the intermediate with energy of -33.81 kcal/mol, which is stabilized by two internal H-bonds. The predominant channel in Figure 2 is the dissociation of Add1 via TS2, with an energy barrier of -9.38 kcal/mol, which forms trans-HONO + trans-NH=NH as the products.

For the case of oxygen addition to the N₂H₃ radical, two adducts NH(ONO)NH₂ and NHNH₂(ONO) are formed, which undergo further decomposition reactions. The potential energy profiles for oxygen addition pathways are currently under investigation.

(III). Experimental Reaction Kinetics

Preliminary experimentations are currently underway to measure the rate of HONO production under pseudo-first-order conditions of [N₂H₃] in [NO₂].

5. Conclusions

The potential energy profile of the NO₂ + N₂H₃ reaction was investigated by *ab initio* multi-reference second-order perturbation theory and quadratic configuration interactions and coupled-cluster theories. For direct abstraction reactions, it was found that the most exothermic channel involves the formation of the trans-NH=NH plus cis-HONO products with reaction exothermicity of 34.55 kcal/mol. The abstraction of the imidogen-H of N₂H₃ has the lowest energy barrier of -12.88 kcal/mol, forming the NNH₂ plus trans-HONO products. For the addition of NO₂ to the N₂H₃ radical, it was found that the reaction proceeds via a complex mechanism. Specifically, both the nitrogen and the oxygen atoms of the NO₂ can add to the N₂H₃ radical. The N–N addition adducts were found to have an energy of -37.7 kcal/mol, which undergo further dissociation reactions by intramolecular H transfer. The predominant channel for the dissociation of the N–N addition adduct has an energy barrier of -9.5 kcal/mol, forming the trans-HONO plus trans-NH=NH products.

The major products of the reaction system are the trans- and cis- forms of HONO and NH=NH, and NNH₂. The negative energy barriers and large exothermicities of the reaction channels implicate significant importance in the early stages of hypergolic ignition of hydrazine and its derivatives.

Acknowledgements

The National Research Council is thanked for the Senior Research Associateship Award to H. Sun at the Air Force Research Laboratory, Edwards AFB under Contract No. FA9550-12-d-0001. This research was performed using resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

References

- (1) Schmidt, E. W. *Hydrazine and its derivatives: preparation, properties, applications* 2nd ed.; John Wiley & Sons, Inc., New York, **2001**.
- (2) Liu, W.-G.; Goddard, W. A. *J. Am. Chem. Soc.* **2012**, *134*, 12970-12978.
- (3) Lai, K.-Y.; Zhu, R.; Lin, M. C. *Chem. Phys. Lett.* **2012**, *537*, 33-37.
- (4) Greenwald, E. E.; North, S. W.; Georgievskii, Y.; Klippenstein, S. J. *J. Phys. Chem. A* **2005**, *109*, 6031-6044.
- (5) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007-1023.
- (6) Kendall, R. A.; Thom H. Dunning, J.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796-6806.
- (7) Martin, J. M. L.; Uzan, O. *Chem. Phys. Lett.* **1998**, *282*, 16-24.
- (8) Martin, J. M. L. *Chem. Phys. Lett.* **1996**, *259*, 669-678.
- (9) Feller, D.; Dixon, D. A. *J. Chem. Phys.* **2001**, *115*, 3484-3495.
- (10) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M. and others, MOLPRO, version 2010.1, a package of ab initio programs, see <http://www.molpro.net>.
- (11) Liu, W.-G.; Wang, S.; Dasgupta, S.; Thynell, S. T.; Goddard Iii, W. A.; Zybin, S.; Yetter, R. A. *Combust. Flame* **2013**, *160*, 970-981.
- (12) Catoire, L.; Chaumeix, N.; Paillard, C. *J. Propul. Power* **2004**, *20*, 87-92.
- (13) Catoire, L.; Chaumeix, N.; Pichon, S.; Paillard, C. *J. Propul. Power* **2006**, *22*, 120-126.