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***Ab initio* Quantum Chemical Reaction Kinetics: Recent Applications in Combustion Chemistry**

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**9th ICCK
June 28, 2015**

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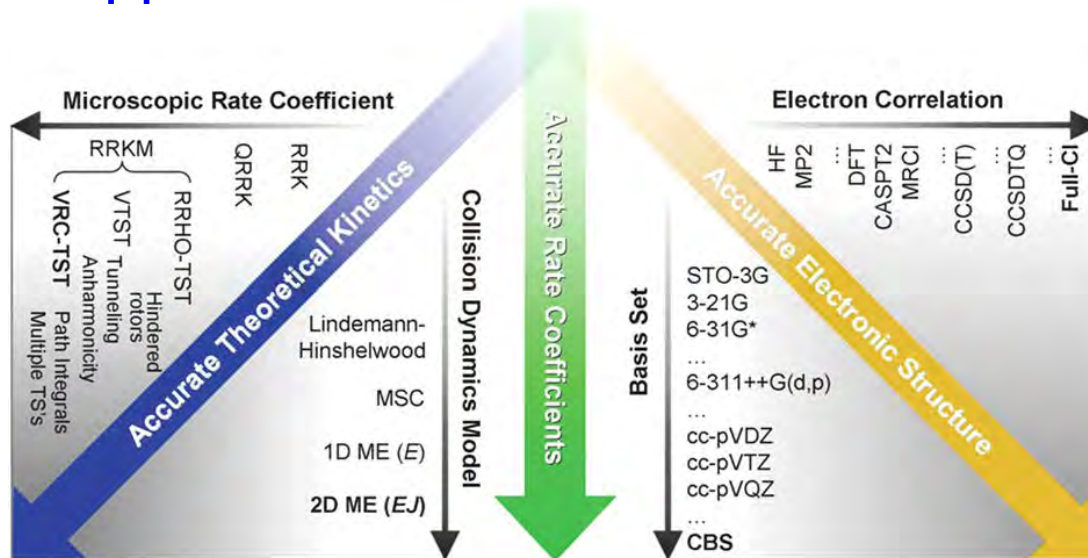
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Why Quantum Chemical Reaction Kinetics Studies?



- Only Option When Experiments are not Possible or Limited
 - Combustion Conditions of P & T too Extreme to Probe
- Accuracy (E_a) can be as Good or Better Than Experiments
 - Thermochemical Accuracy Possible
 - Ideal for Branching Ratio Predictions for Closely Competing Reactions
- Can be a Cost Effective Alternate to Experiments
 - Hardware & Software Efficiencies Improving Constantly
- A Balanced Approach to Kinetics Calculations Recommended

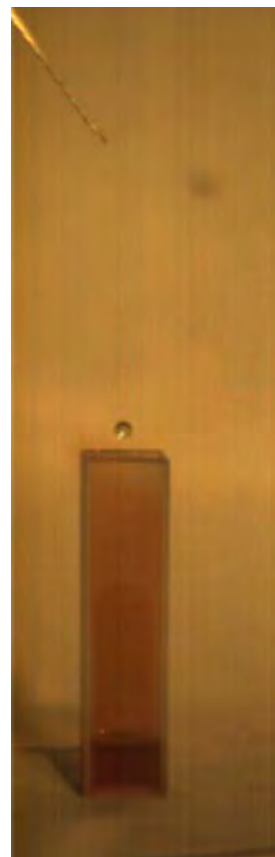




Our Interest in Combustion Chemistry



- Autoignition Chemistry
 - Low Temperature/Low Pressure Conditions
 - Bi-propellants



- Decomposition Chemistry
 - Emerging Energetic Materials
 - Explosives
 - Ionic Liquid Propellants



$\text{N}_2\text{H}_3 + \text{NO}_2$ Reaction Kinetics Perspective



- Radical Chemistry Modelling

- $\text{N}_2\text{H}_4/\text{NO}_2$ Autoignition

- Recent Works

- Only Theoretical Studies

- See Raghunath *et al.*, Adv. Quantum Chem., **69**, 253 (2014)..... $k_{298\text{ K}, 1\text{ atm}} = (2.3 \times 10^{-11})$
- See Daimon *et al.*, Sci. Tech. Energetic Materials, **74**, 17 (2013)..... $k_{298\text{ K}, 1\text{ atm}} = (1.6 \times 10^{-14})$?
- See Daimon *et al.*, J. Propul. Power, **30**, 707 (2014)..... $k_{298\text{ K}, 1\text{ atm}} = (1.9 \times 10^{-11})$
- Also, See Kanno *et al.*, DOI: 10.1021/acs.jpca.5b00987 (2015)

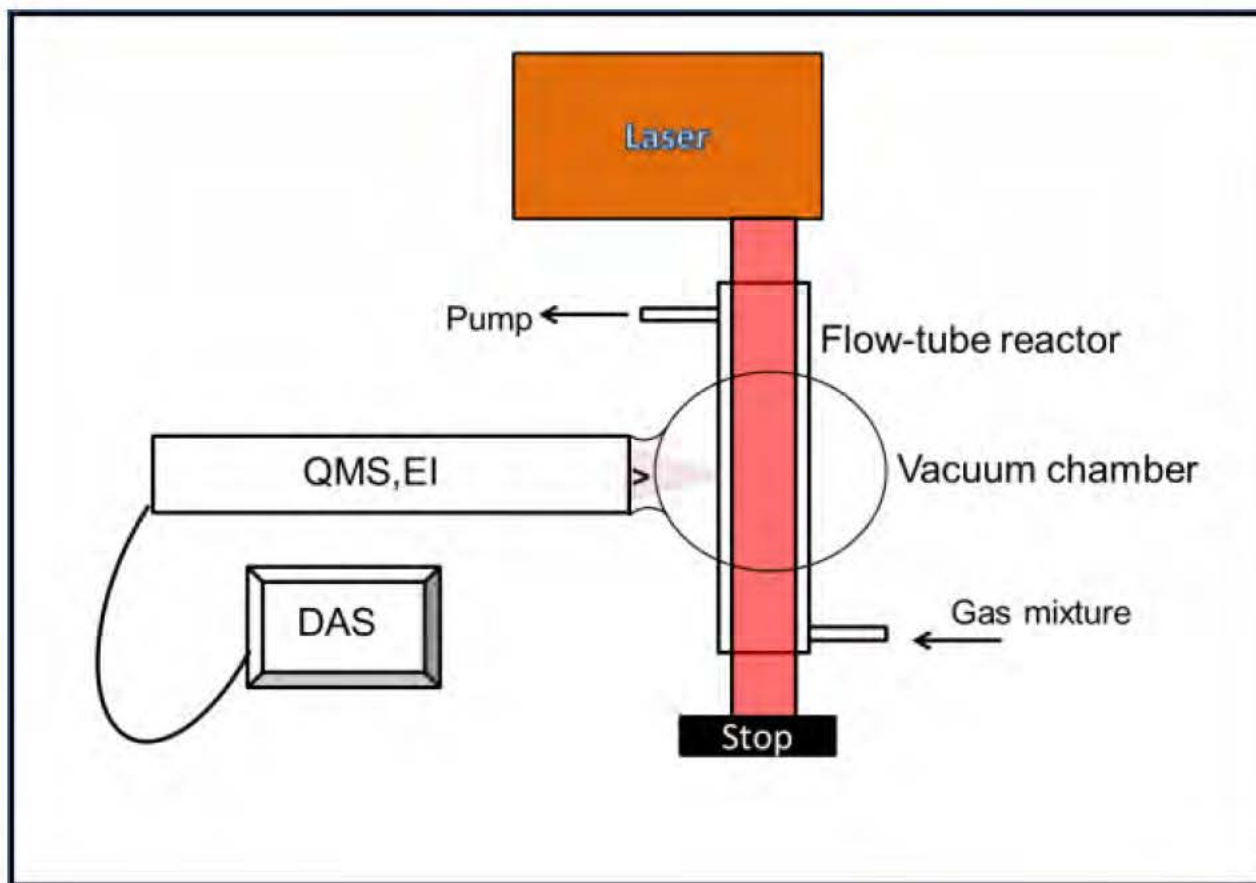


- This work

- Pulsed Laser Photolysis - Flow Tube MS Experiments
 - First Experimental Determination
- *Ab initio* Chemical Kinetics
 - Multi-reference Second-order Perturbation and Coupled-cluster Methods: PES (Potential Energy Surface)
 - RRKM (Rice–Ramsperger–Kassel–Marcus) Theory and Master Equation Simulations: k



Pulsed Laser Photolysis Flow Tube Apparatus





N_2H_3 Source & Flow Tube Chemistry



$\text{N}_2\text{H}_4 + h\nu \rightarrow \text{N}_2\text{H}_3 + \text{H}$	$\sigma_{193 \text{ nm}} = 450 \times 10^{-20} \text{ cm}^2 \text{ molec}^{-1}$	1
$\text{NO}_2 + \text{H} \rightarrow \text{NO} + \text{OH}$	$k_2 = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	2
$\text{N}_2\text{H}_4 + \text{H} \rightarrow \text{N}_2\text{H}_3 + \text{H}_2$	$k_3 = 1.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	3
$\text{N}_2\text{H}_4 + \text{OH} \rightarrow \text{N}_2\text{H}_3 + \text{H}_2\text{O}$	$k_4 = 3.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	4
$\text{N}_2\text{H}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{H}_2 + \text{HONO}$	k_5	5
$\text{N}_2\text{H}_3 + \text{NO}_2 \rightarrow \text{other products}$	k_6	6
$\text{HONO} \rightarrow \text{loss}$	$k_7 = 1 \text{ s}^{-1}$	7
$\text{N}_2\text{H}_3 \rightarrow \text{loss}$	$k_8 = 10 \text{ s}^{-1}$	8
$\text{H} \rightarrow \text{loss}$	$k_9 = 10 \text{ s}^{-1}$	9
$\text{OH} \rightarrow \text{loss}$	$k_{10} = 10 \text{ s}^{-1}$	10

$$[\text{HONO}] = (k_5[\text{NO}_2][\text{N}_2\text{H}_3]_0) \{e^{-k_7 t} - e^{-k' t}\} / (k' - k_7)$$

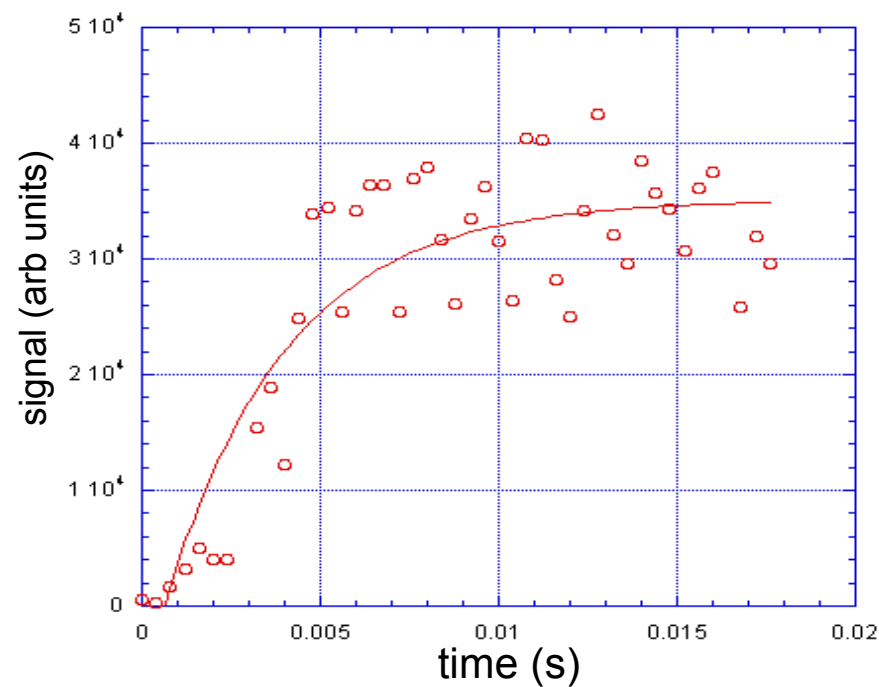
$$k' = (k_5 + k_6)[\text{NO}_2] + k_8$$

$$[\text{N}_2\text{H}_4] = 5 \times 10^{14}, [\text{H}] = 5 \times 10^{12}, [\text{NO}_2] = 1 \times 10^{13} \text{ to } 5 \times 10^{13} \text{ molecule cm}^{-3}$$

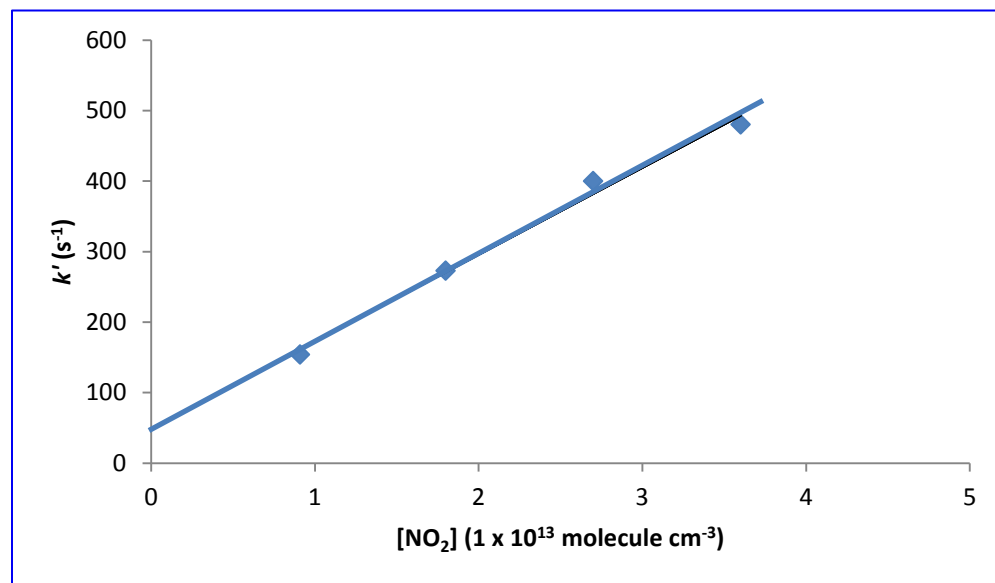


$\text{N}_2\text{H}_3 + \text{NO}_2$ Reaction Kinetics

Typical [HONO] Temporal Profile



Second-order Plot



$$k_{298 \text{ K}, 2 \text{ Torr N}_2} = (1.23 \pm 0.25) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$



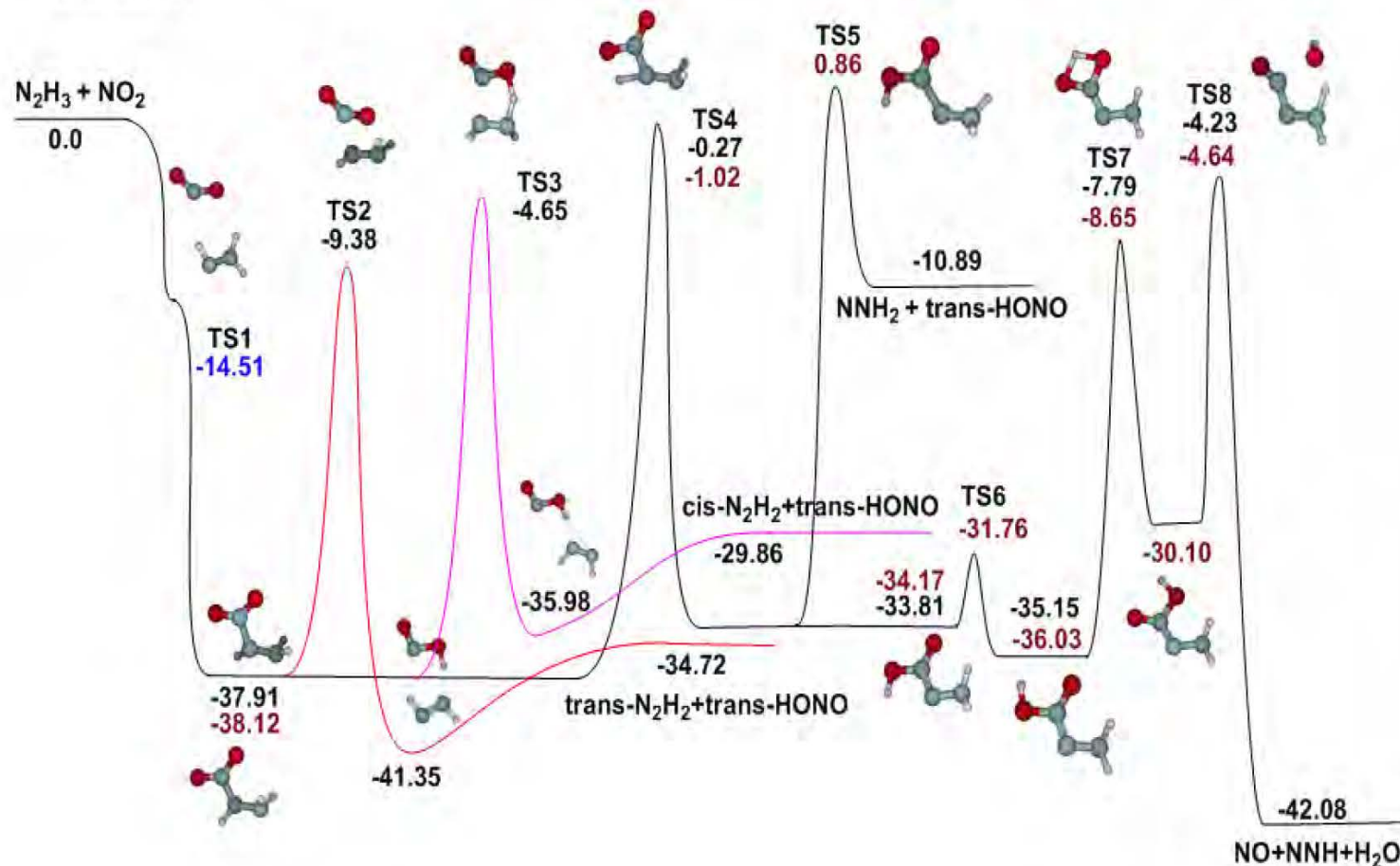
Potential Energy Surface for $\text{N}_2\text{H}_3\text{NO}_2$ Adduct Formation

CASPT2/CBS

RCCSD(T)/CBS//CASPT2

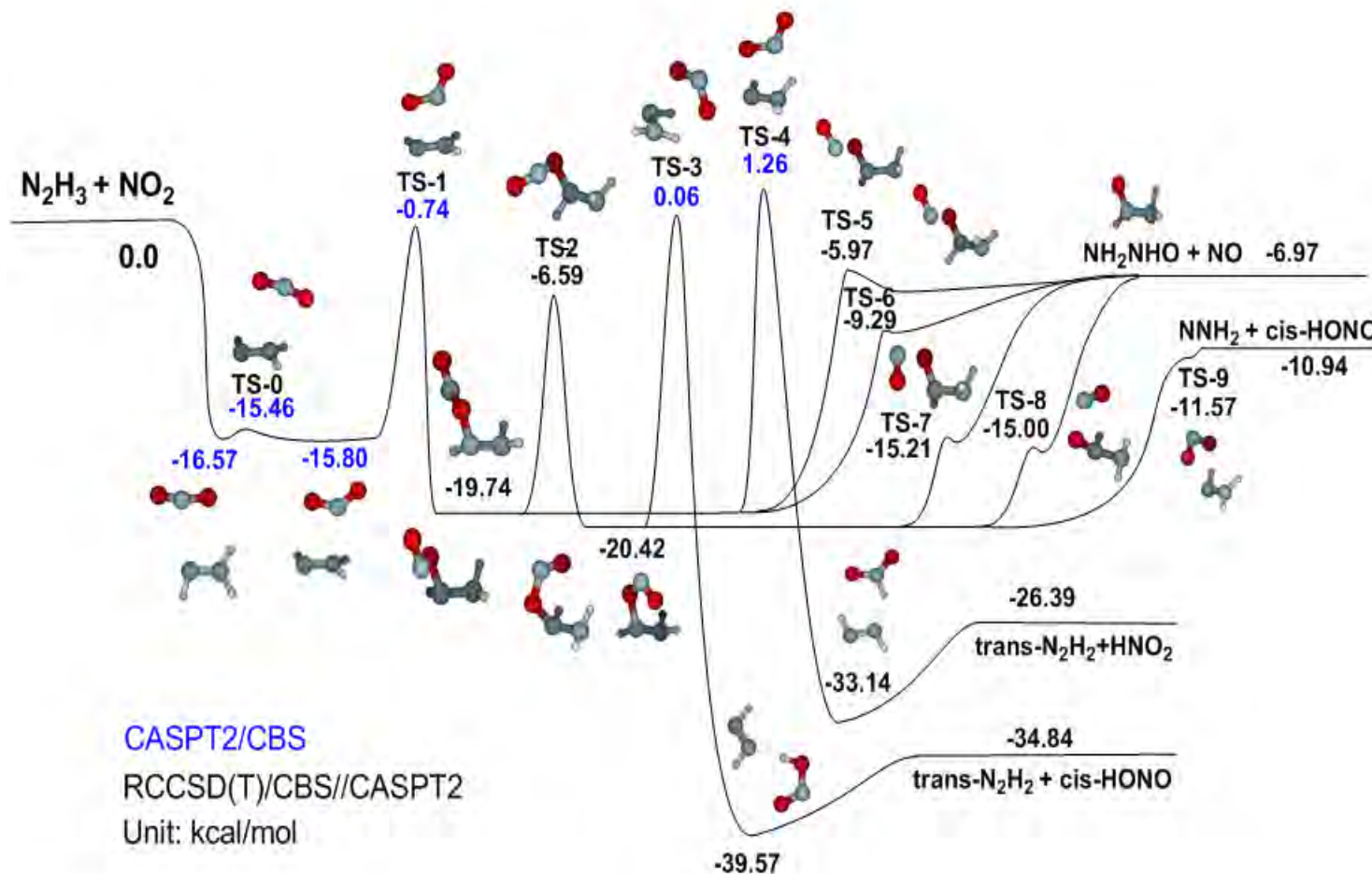
RCCSD(T)/CBS//B3LYP

Unit: kcal/mol



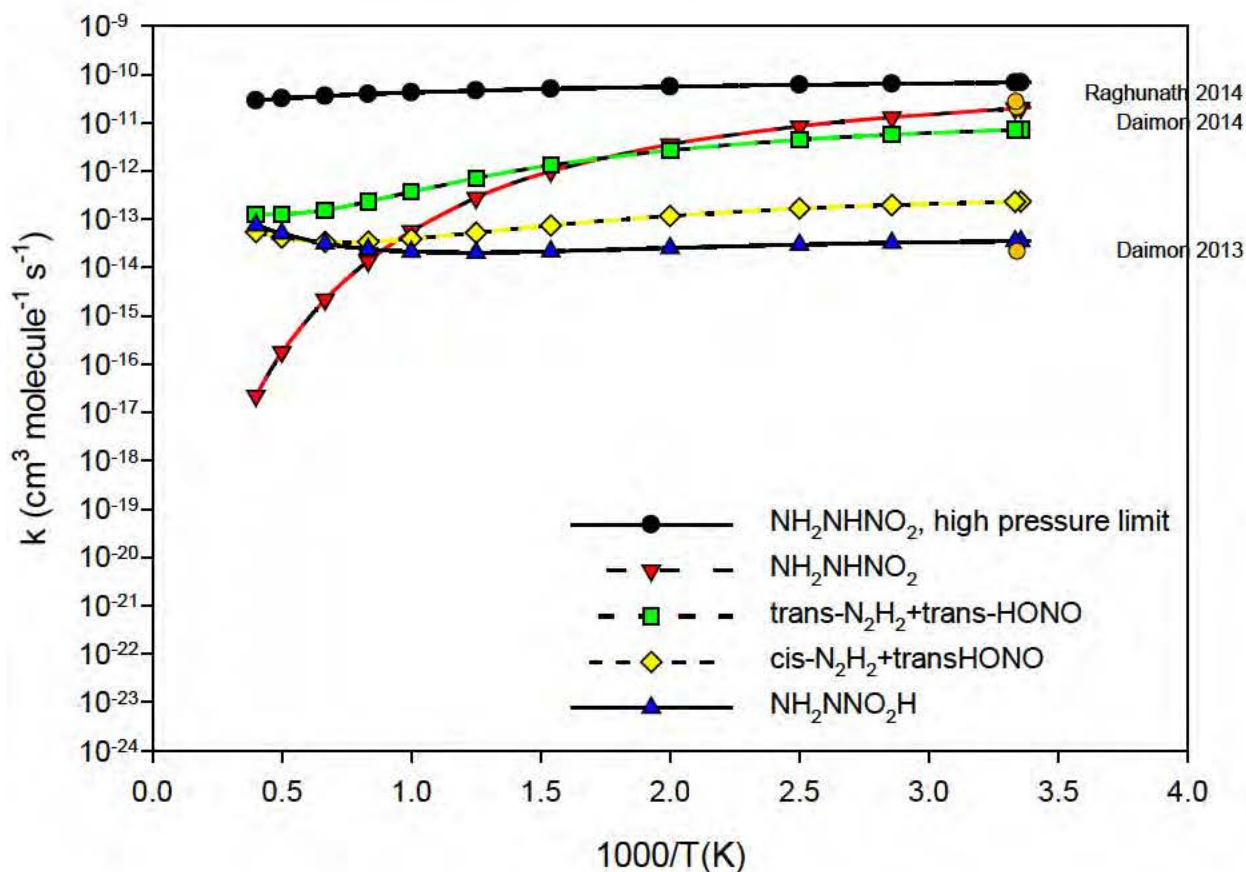


Potential Energy Surface for $\text{N}_2\text{H}_3\text{ONO}$ Adduct Formation





Branching Rate Coefficients (2 Torr N_2) & High Pressure Limit Versus T



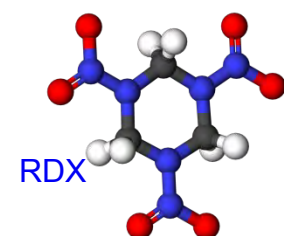
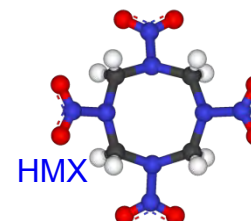


MNB & DNB Energetic Materials Perspective



■ MNB & DNB

- Mononitrobiuret & 1,5-dinitrobiuret (less stable)
 - promising explosives



■ Recent Works

- See Geith *et al.*, *Propellants, Explosives, Pyrotechnics*, **29**, 3 (2004)
 - $\Delta H_{\text{comb}}(\text{DNB}) = (5195 \pm 300) \text{ kJ kg}^{-1}$ (bomb calorimetry and MP2/cc-pVTZ ΔH_f) cf HMX 9435 & RDX 9560 kJ kg^{-1}
 - $V_d = 8660 \text{ ms}^{-1}$, cf HMX 9100 & RDX 8750 ms^{-1}
- See Geith *et al.*, *Combust and Flame*, **139**, 358 (2004)
 - Recent synthesis (known since 1898 by Thiele) & decomposition mechanism studies
 - Initially NH_2NO_2 released, followed by residues decomposing to give HNCO
- See Liu *et al.*, *J. Phys. Chem. A* **115**, 8064 (2011) & Sun *et al.*, *J. Phys. Chem. A* **118**, 2228 (2013)
 - Quasi-classical direct dynamics trajectory simulations to understand DNB decomposition
 - Elimination of HNN(O)OH intermediate identified
- See Suntsova *et al.*, *Struct. Chem.*, **24**, 745 (2013)
 - Electronic structure of DNB was studied by two-dimensional B3LYP potential energy scans
 - Solid- and gas-phase conformers differ

■ This work

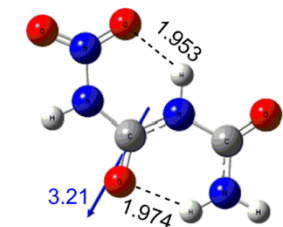
- PESs for the thermal decomposition of MNB and DNB investigated
- Temperature and pressure-dependent rate coefficients were calculated using micro-canonical transition state theory with master equation simulations



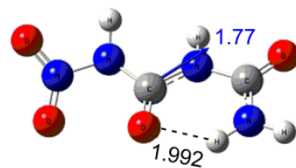
MNB & DNB Structures (M06-2X/aug-cc-pVTZ level)

■ H-bond Stabilized Conformers

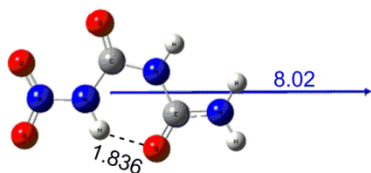
- MNB(C_s) 0
- MNB(trans) +4.82
- MNB(C_1) +6.38
- MNB(cis) +7.95 kcal/mol



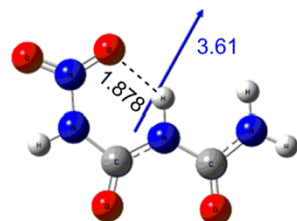
MNB (C_s)



MNB (C_1)



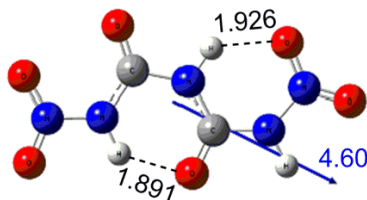
MNB (trans)



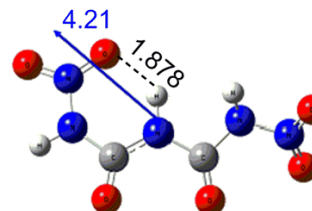
MNB (cis)

■ Double H-bond Stabilized Conformers

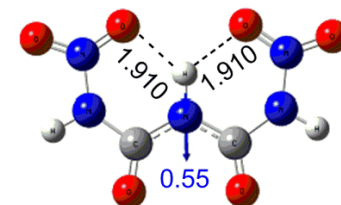
- DNB(C_s) 0
- DNB(C_{2v}) +1.22
- DNB(C_1) +7.82 kcal/mol



DNB (C_s)



DNB (C_1)



DNB (C_{2v})



Stationary Point Energies for MNB Thermal Decomposition



Species	M06-2X /aug-cc-pVDZ	M06-2X /aug-cc-pVTZ	RCCSD(T)/cc-pV ∞ Z //M06-2X/aug-cc-pVTZ
MNB (C _s)	0.00	0.00	0.00
TS1	33.86	33.18	33.99
HBC-P1	18.50	20.51	19.43
IM1 + HNN(O)OH	29.42	26.85	27.08
TS2	34.58	33.73	34.66
HBC-P2	27.75	26.20	26.41
IM2 + HNCO	30.43	32.17	32.95
trans-biuret radical + NO ₂	51.41	51.34	52.75
MNB (C ₁)	6.41	6.38	5.86
TS3	41.05	40.35	41.00
HBC-P3	34.23	32.65	32.47
IM3 + HNCO	40.33	38.46	38.77
TS4	53.77	54.71	53.71
NH ₂ C(O)NH ₂ + NO ₂ , NCO	34.38	32.53	30.68
iso-trans-biuret radical + NO ₂	57.25	56.99	58.43
TS5	7.84	8.29	7.32

All energies include zero-point corrections and are in kcal/mol relative to the global energy minimum of MNB (C_s).

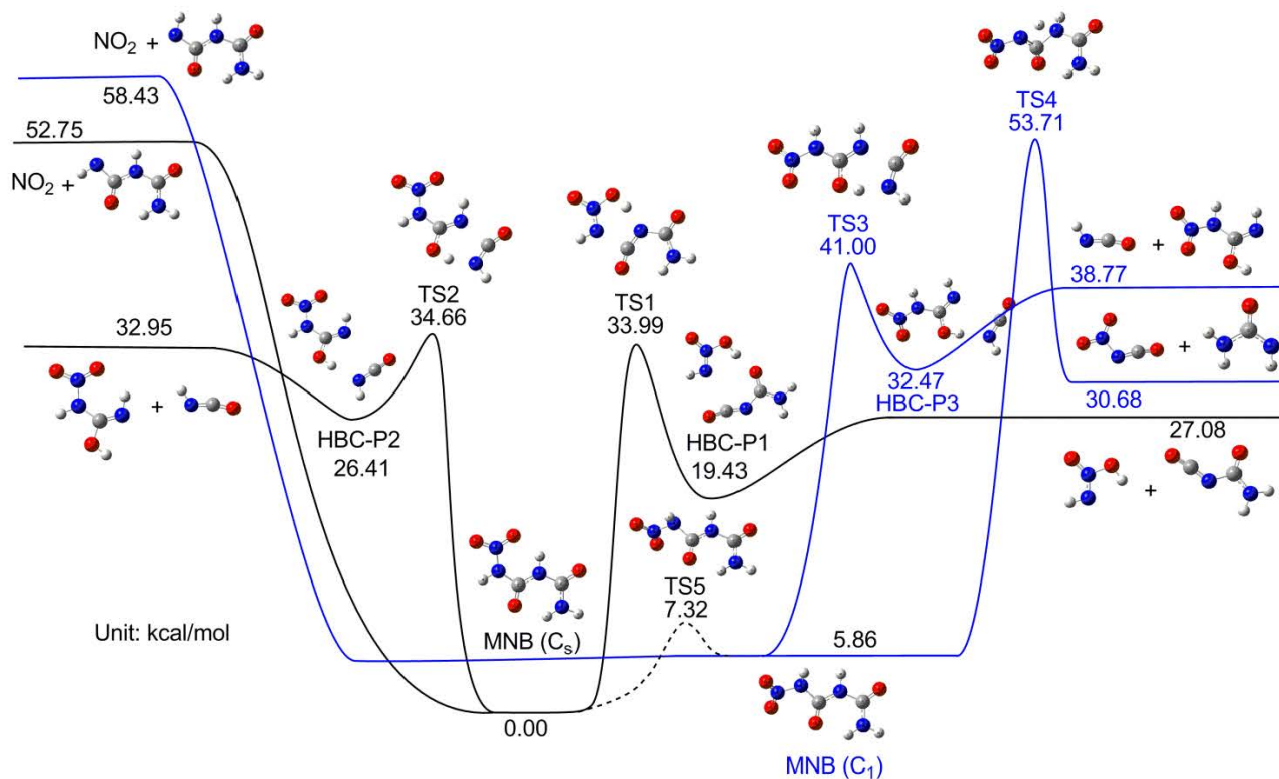
Within 1.0 kcal/mol for the barrier heights, and 1.8 kcal/mol for endothermicities compared to RCCSD(T)/cc-pV ∞ Z//M06-2X/aug-cc-pVTZ, implying that the M06-2X/aug-cc-pVTZ energies are good for larger analogous systems.



Potential Energy Surface for MNB Decomposition

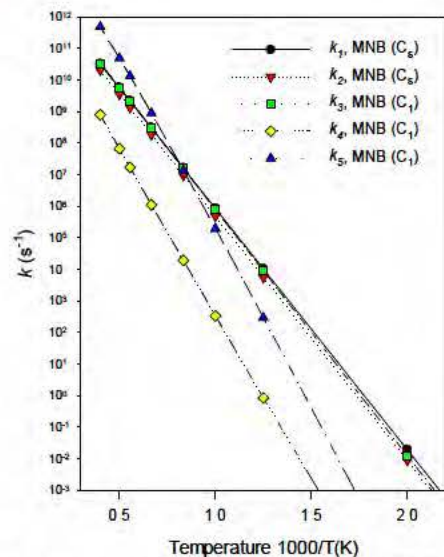


RCCSD(T)/cc-pV ∞ Z//M06-2X/aug-cc-pVTZ





Ab initio Kinetics of MNB Thermal Decomposition

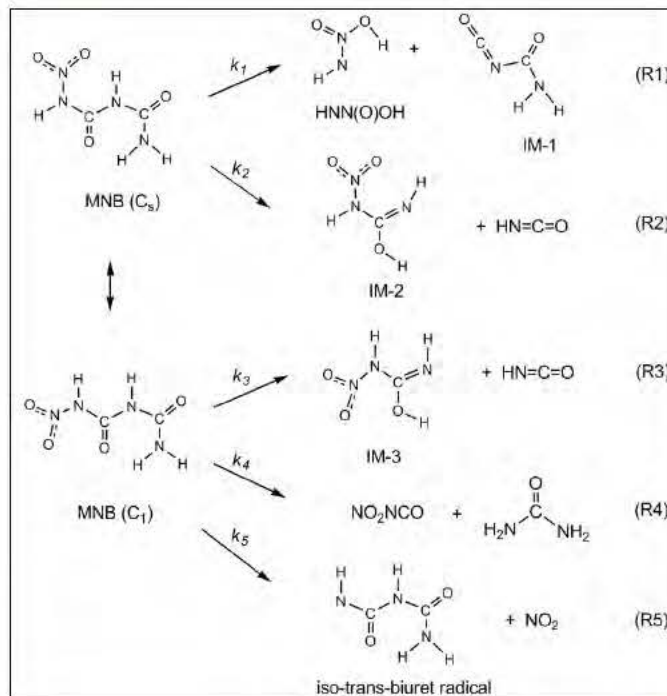


High-pressure rate limit for MNB (C_6) and MNB (C_1) primary thermal decomposition channels

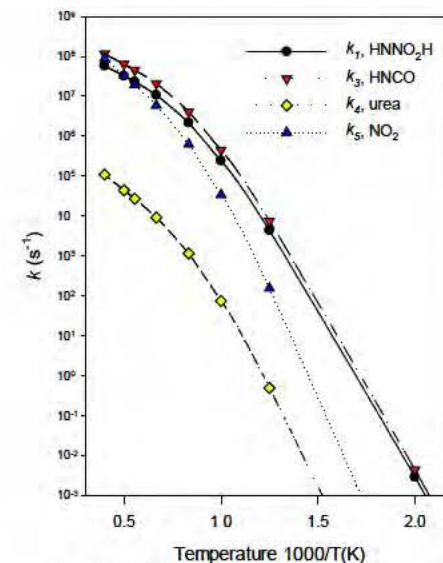
$$\begin{aligned}
 k_{1,\infty} &= 1.32 \times 10^{13} T^{0.131} \exp(-17474.7/T) \\
 k_{2,\infty} &= 1.05 \times 10^{13} T^{0.112} \exp(-17692.1/T) \\
 k_{3,\infty} &= 1.15 \times 10^{14} T^{-0.117} \exp(-18011.4/T) \\
 k_{4,\infty} &= 1.26 \times 10^4 T^{2.539} \exp(-21375.5/T) \\
 k_{5,\infty} &= 2.07 \times 10^{23} T^{-2.002} \exp(-27714.8/T)
 \end{aligned}$$

Below 1200 K, HNCO & HNN(O)OH eliminations dominate, consistent with experimental work of Gieth *et al.* 2004

Above 1200 K, NO_2 elimination dominates



MNB (C_6) and MNB (C_1) primary thermal decomposition channels



Rate coefficients at pressure of 1 atm for MNB (C_6) and MNB (C_1) primary thermal decomposition channels

Pressure dependence of unimolecular decomposition evaluated using $\Delta E_{\text{down}} = 200 \times (T/300)^{0.85} \text{ cm}^{-1}$ energy transfer probability model

Strong pressure dependences observed

HNCO & HNN(O)OH eliminations are competitive & dominate below 2500 K

NO_2 elimination becomes competitive only above 2500 K

R2 & R3 (HNCO) & R1 (HNN(O)OH) are primary (product) channels at ignition temperatures



Stationary Point Energies for DNB Thermal Decomposition



Species	M06-2X/aug-cc-pVDZ	M06-2X/aug-cc-pVTZ
DNB (C_s)	0.00	0.00
TS6	34.17	33.77
HBC-P6	21.58	20.30
HNN(O)OH + NO ₂ NHC(O)NCO	28.68	26.79
TS7	31.72	31.21
HBC-P7	30.70	29.98
IM2 + NO ₂ NCO	34.79	36.91
C ₁ -MNB radical + NO ₂	50.20	49.79
trans-MNB radical + NO ₂	50.89	51.09
DNB (C_{2v})	1.16	1.22
TS8	28.64	28.61
HBC-P8	22.35	21.70
HNN(O)OH + iso-NO ₂ NHC(O)NCO	29.08	27.26
cis-MNB radical + NO ₂	52.54	52.84
DNB (C_1)	7.45	7.82
TS9	9.42	10.32
TS10	10.79	11.20

All energies include zero-point corrections and are in kcal/mol relative to the global energy minimum of DNB (C_s).

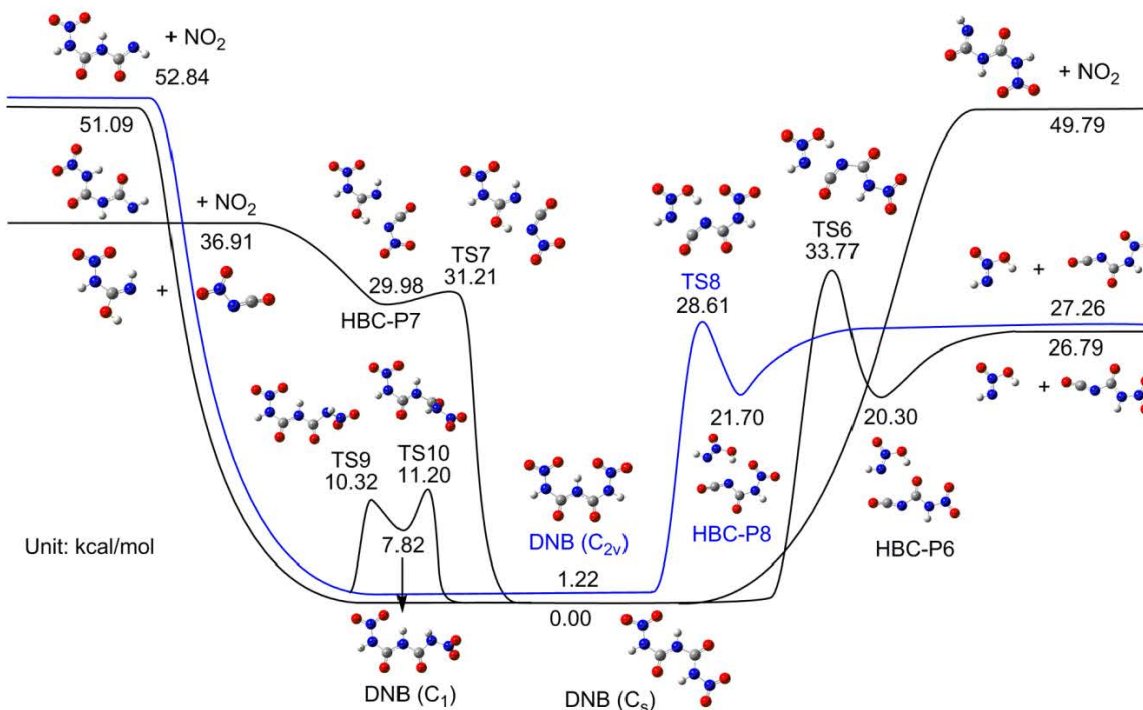
Predicted energy barrier heights from these two levels of calculation show excellent agreement, but discrepancy reaches to 2.1 kcal/mol for reaction endothermicities. Consequently, the M06-2X/aug-cc-pVTZ energies were used for carrying out the kinetics analysis for DNB decomposition.



Potential Energy Surface for DNB Decomposition

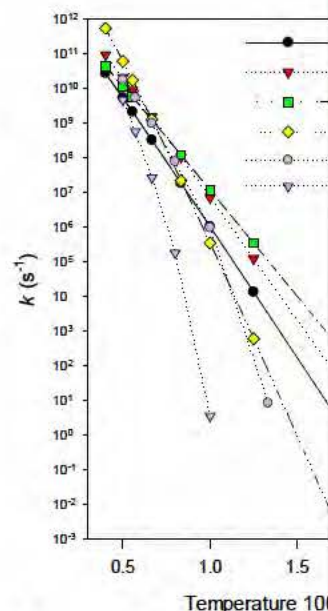


M06-2X/aug-cc-pVTZ





Ab initio Kinetics of DNB Thermal Decomposition



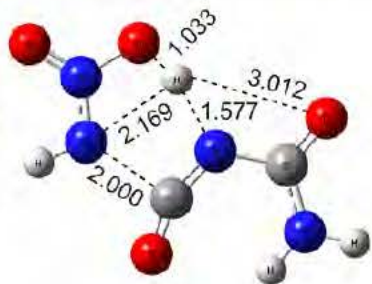
High-pressure rate limit for DNB (primary thermal decomposition)

$$k_{6,\infty} = 3.22 \times 10^{14} T^{-0.289} \exp(-27200.5/T)$$

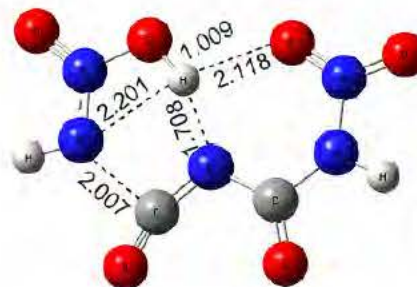
$$k_{7,\infty} = 8.49 \times 10^{16} T^{-0.882} \exp(-27200.5/T)$$

$$k_{8,\infty} = 9.72 \times 10^{13} T^{-0.248} \exp(-27200.5/T)$$

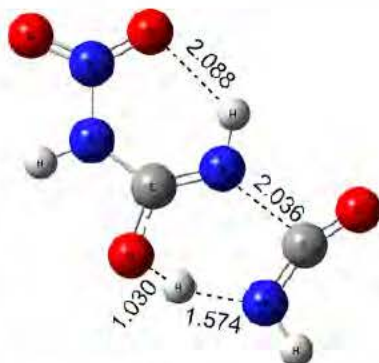
$$k_{9,\infty} = 9.96 \times 10^{23} T^{-2.205} \exp(-27200.5/T)$$



MNB (TS1)



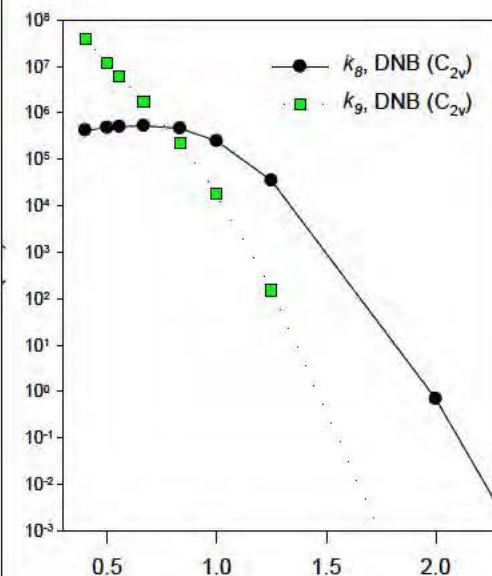
DNB (TS8)



MNB (TS2)



DNB (TS7)



Rate coefficients at pressure of 1 atm for DNB (C_{2v}) primary thermal decomposition channels

ng pressure dependences observed

w 1200 K, HNN(O)OH elimination dominates

Below 1500 K, HNN(O)OH elimination dominates from DNB (C_{2v})

Above 1500 K, NO_2 elimination dominates from DNB (C_{2v})

Similar trend seen in Liu *et al.*, 2011, and good agreement above 1500 K

k_8 for HNN(O)OH elimination from DNB is much larger than k_1 for HNN(O)OH from MNB below 800 K

Consistent with TS1 (and TS3) energy higher than TS8 (Also, TS2 higher than TS7)

TS8 is stabilized by additional intramolecular H-bonding (Also, TS7 is a late transition state)

DNB is less stable than MNB

Present quantitative interpretations are consistent with experimental work of Gieth *et al.* 2004



Conclusions & Acknowledgements



- $\text{N}_2\text{H}_3 + \text{NO}_2$ addition reaction is fast
 - $\text{trans-N}_2\text{H}_2 + \text{trans-HONO}$ main products
- PES surface characterized
 - Calculated reaction rate coefficients in agreement with experiments
- MNB & DNB stabilized via 6-member-ring moieties involving intramolecular H-bonding
 - Solid state conformers have smallest dipole moment
- Energy barriers and endothermicities at the M06-2X/aug-cc-pVTZ level of theory show remarkable agreement with the values obtained from RCCSD(T)/cc-pV ∞ Z//M06-2X/aug-cc-pVTZ computations
 - Former level of theory should be applicable to larger analogous systems
- MNB decomposition initiated by the elimination of HNCO and HNN(O)OH, the latter is also released in DNB (C_{2v}) decomposition
- Energy barrier for HNN(O)OH elimination in DNB is 6.60 kcal/mol lower than that in MNB due to an extra hydrogen bond in the transition state for the former
 - DNB less stable than MNB (as previously shown by experiments)



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