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14. ABSTRACT

Mononitrobiuret (MNB) and 1,5-Dinitrobiuret (DNB) are, tetrazole-free, nitrogen-rich compounds, which have been reported as powerful new explosives. The initiation of thermal decomposition of MNB and DNB was found to involve an intra-molecular transfer of the H-atom from the central NH group to one of the adjacent nitro oxygens to eliminate the unstable intermediate, HNNO2H, which undergoes further decomposition. In this work, we have investigated the thermal decomposition of HNNO2H using multi-reference second-order perturbation theory and coupled-cluster theory. The following HNNO2H decomposition pathways were found to be important. First, a direct N−OH bond fission occurs with a loose saddle point to form OH and cis-HNNO radicals. Second, an inversion of the aminylene H-atom elongates the N−OH bond due to repulsion between the aminylene H-atom and the hydroxyl H-atom, and this leads to N−OH bond fission to form OH and trans-HNNO radicals. Third, the thermodynamically stable products, N2O + H2O, are formed by a complex mechanism, which involves rotation of the N−OH bond, an H-atom shift from the hydroxyl H-atom to the nitric oxygen, and then migration of the aminylene H-atom to the hydroxyl O-atom, resulting in H2O elimination with 50.4 kcal/mol of exothermicity.

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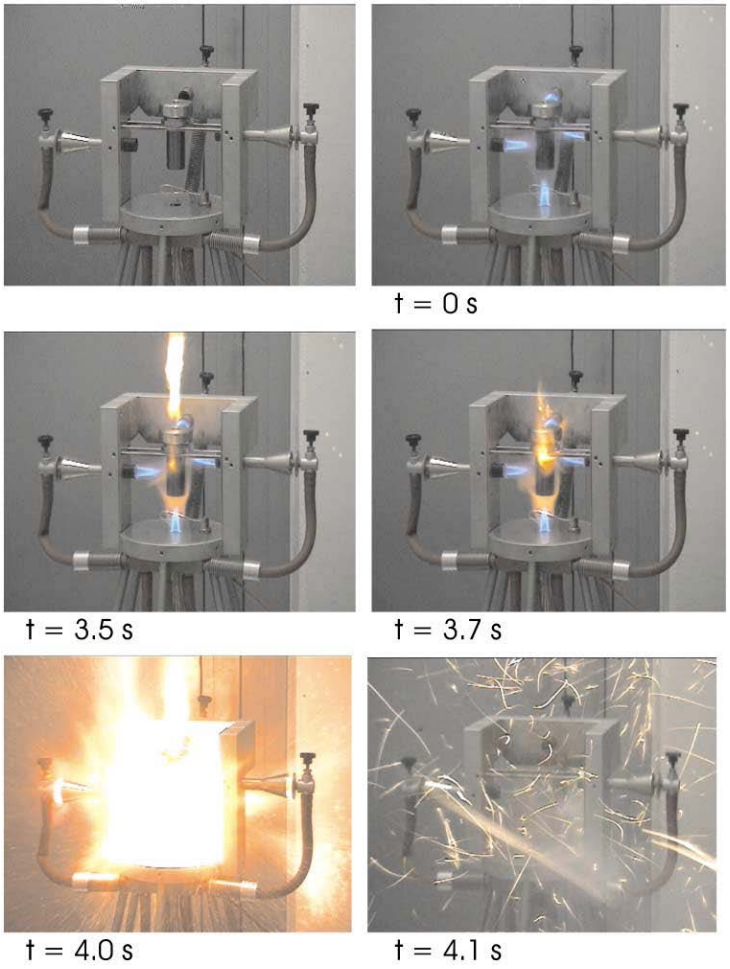
Thermal Decomposition Mechanism of $HNNO_2H$ Dissociated from Mononitrobiuret and 1,5-Dinitrobiuret

Spring 2014 Technical Meeting, Western States Section of the Combustion Institute, March 24-25, 2014
California Institute of Technology

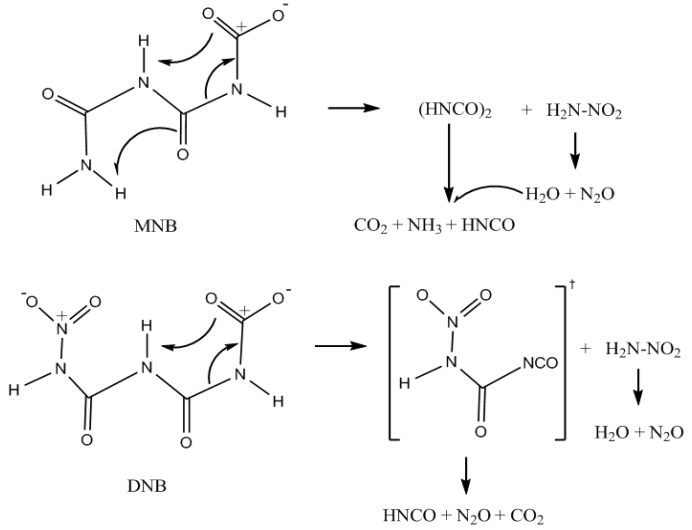
Hongyan Sun
Ghanshyam L. Vaghjiani

Energetic Materials: MNB & DNB

DNB detonates strongly without oxidizer in the steel sleeve test after 4 seconds



- MNB & DNB: tetrazole-free, nitrogen-rich molecules
- High energy density: 1.859 g/cm^3 (DNB)
- Thermal decomposition mechanism of MNB and DNB was proposed by Klapötke et al. (*Combust. Flame* **2004**) as below:



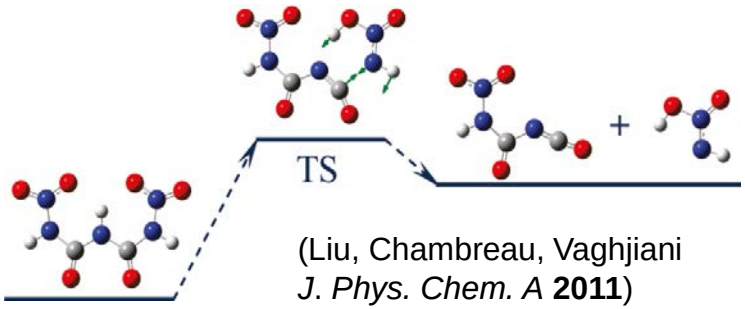
- The decomposition is initiated by elimination of $HNNO_2H$ intermediate, which was confirmed by direct dynamics trajectory simulations as the only dominant channel below 1500 K (Liu, Chambreau, Vaghjiani, *J. Phys. Chem. A* **2011**)

(Klapötke et al., *Propellants, Explosives, Pyrotechnics,* **2004**)

New Ignition Mechanism of MNB & DNB

- The thermal decomposition of MNB and DNB occurs through a multistep reaction process

1. Initiated by an intramolecular H-atom transfer from the central NH group to an adjacent nitro oxygen of NO_2 group to form the $HNNO_2H$ intermediate



(Liu, Chambreau, Vaghjiani *J. Phys. Chem. A* **2011**)

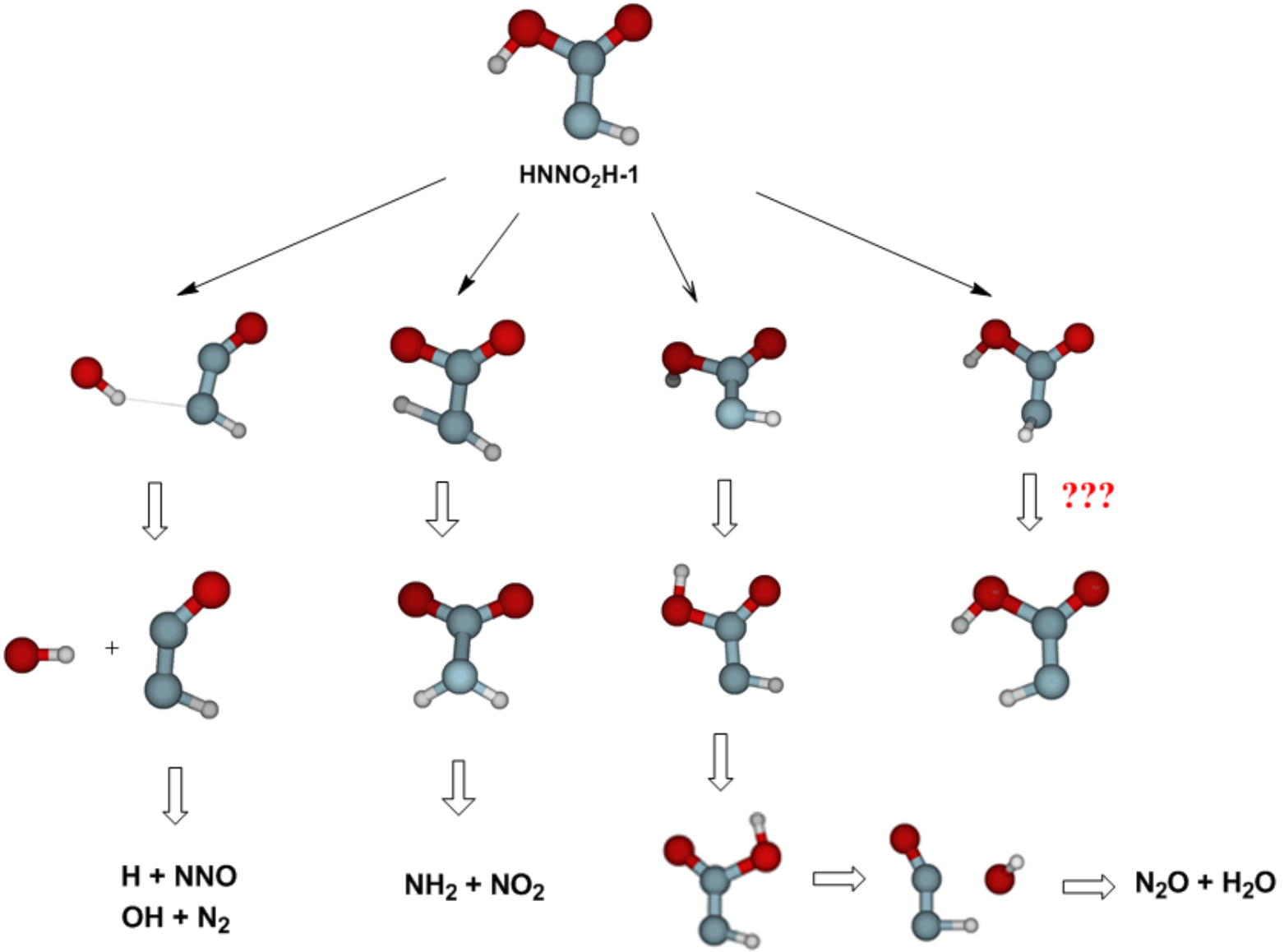
1. The $HNNO_2H$ rapidly dissociates to OH, H, cis-HNNO, trans-HNNO, NO, NO_2, NH_2, N_2O, and H_2O

2. The H-abstraction from unburned MNB and DNB by active radicals such as OH produces corresponding MNB and DNB radicals

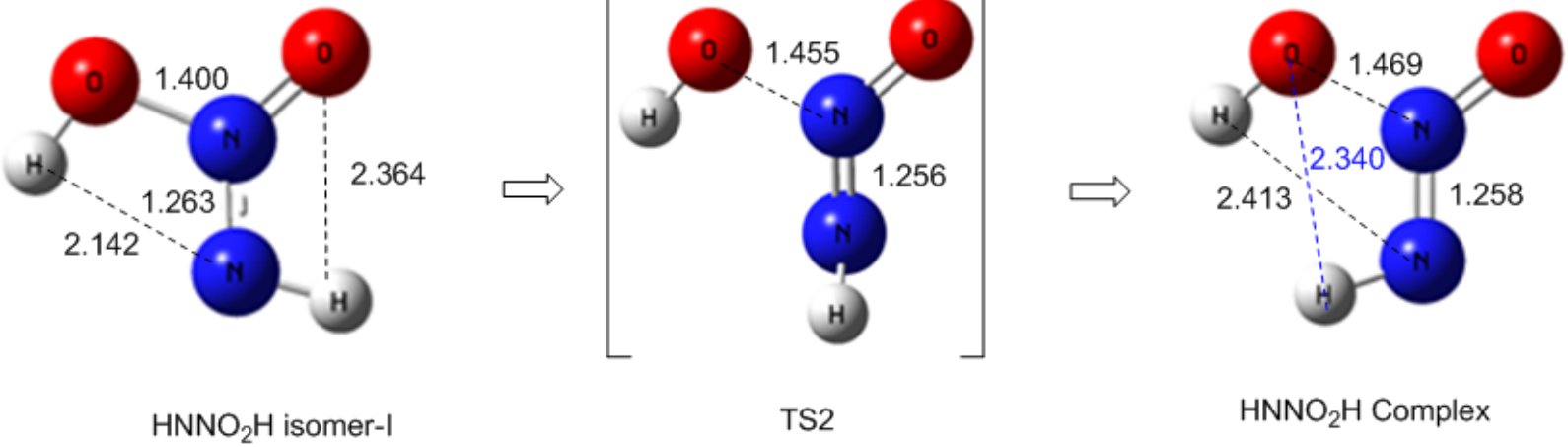
3. MNB and DNB radicals subsequently decompose to low-molecular weight intermediates

4. Decomposition/oxidation of the intermediates form final stable products

$HNNO_2H$ Decomposition Paths

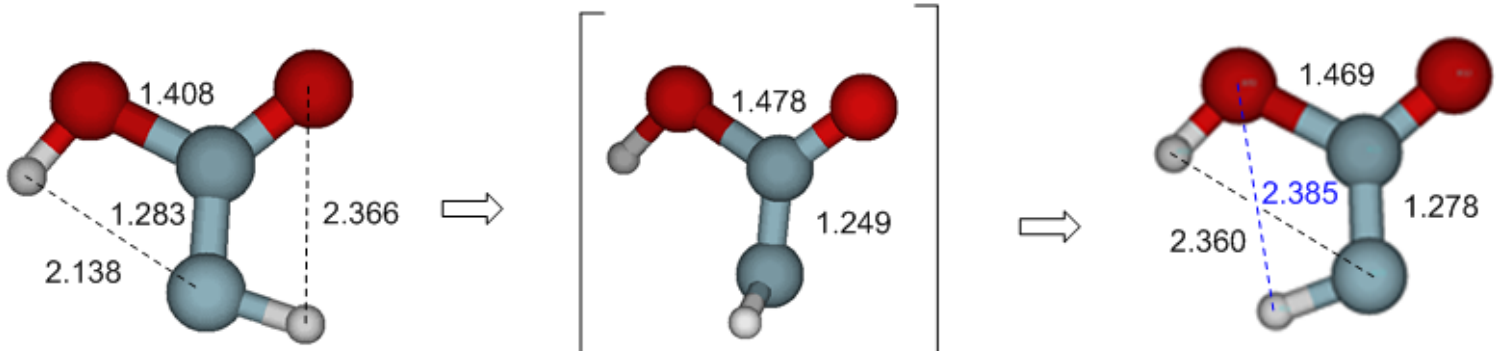


Rotation of N−N bond in $HNNO_2H$



$HNNO_2H$ isomer-I | TS2 | $HNNO_2H$ Complex

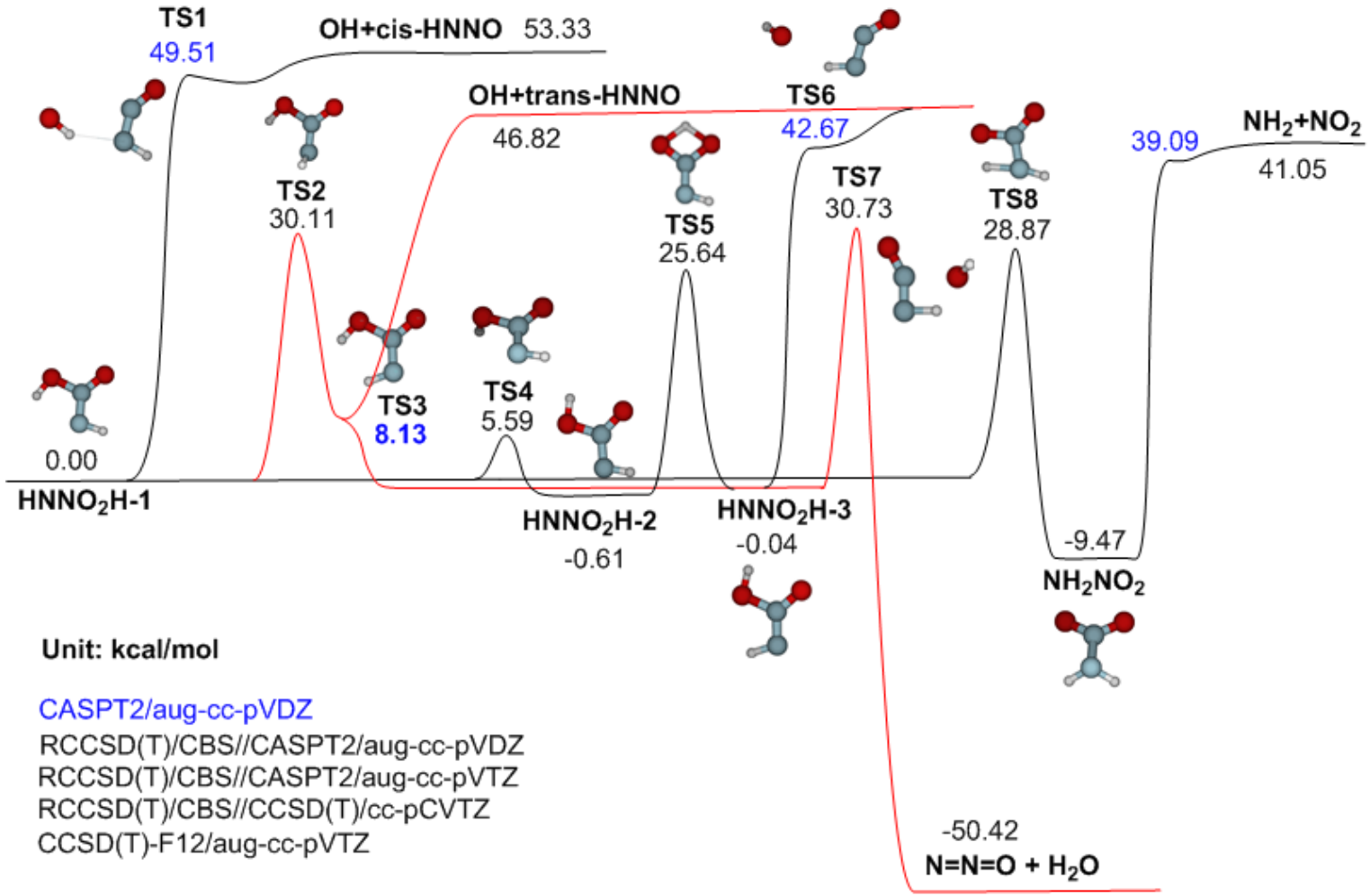
Optimized at the B3LYP/6-311++G(d,p) level



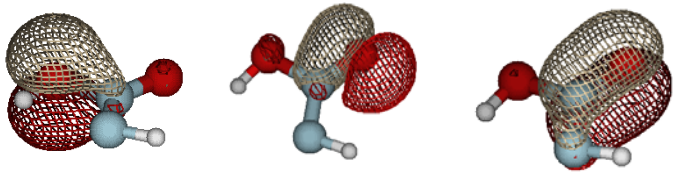
$HNNO_2H$ isomer-I (Cs) | TS2 | TS3 (Cs symmetry)

Optimized at the CASPT2(12e,9o)/aug-cc-pVDZ level

PES of $HNNO_2H$ Decomposition



$HNNO_2H \rightarrow TS8 \rightarrow H_2NNO_2$



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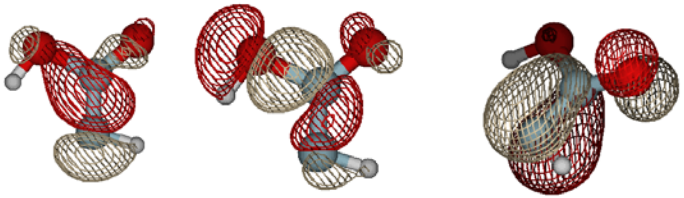

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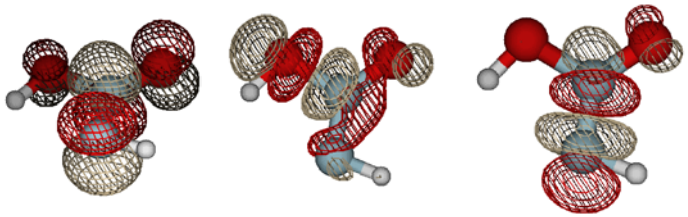

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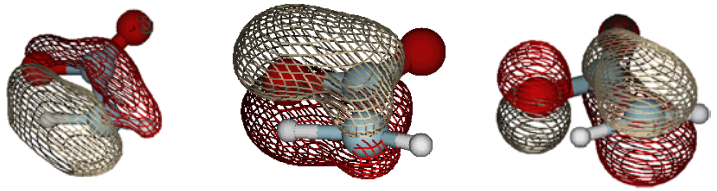
$HNNO_2H$



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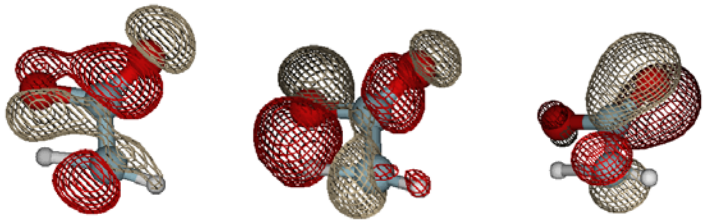

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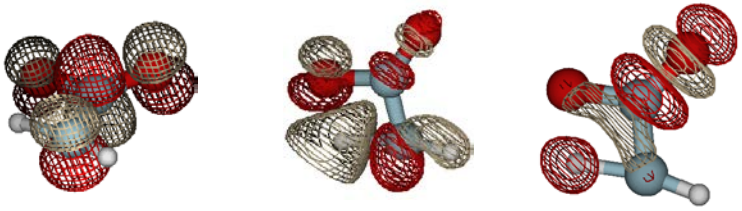


17.1 18.1 19.1

TS3

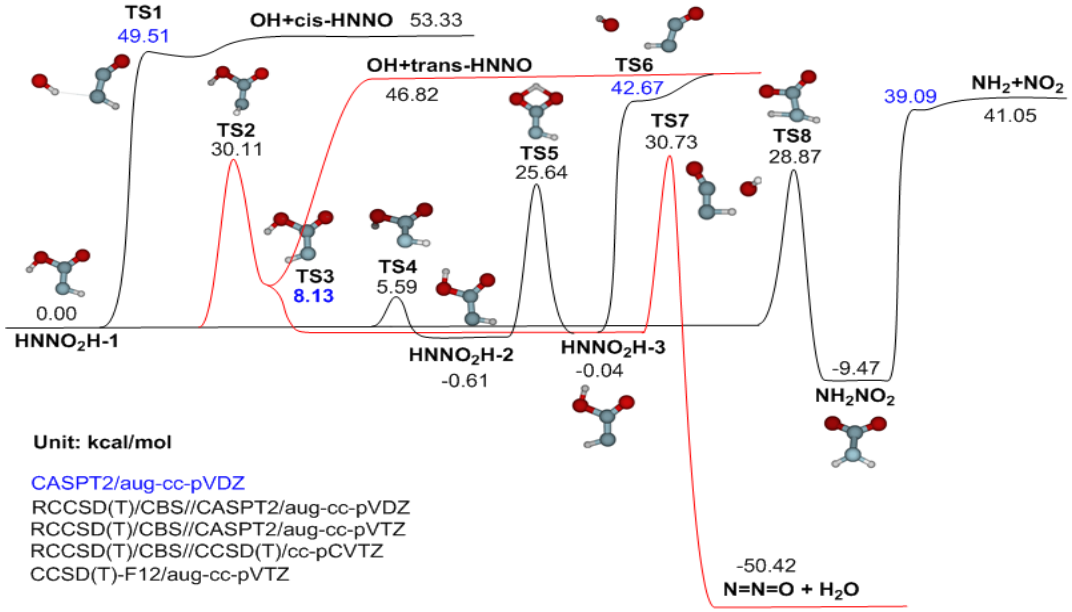
Optimized at the CASPT2(12e,9o)/aug-cc-pVDZ level

Active space was selected to describe the bond breaking/making process

High-Accuracy Potential Energy Surface

Comparison of Calculated Energy Difference with Literature Data

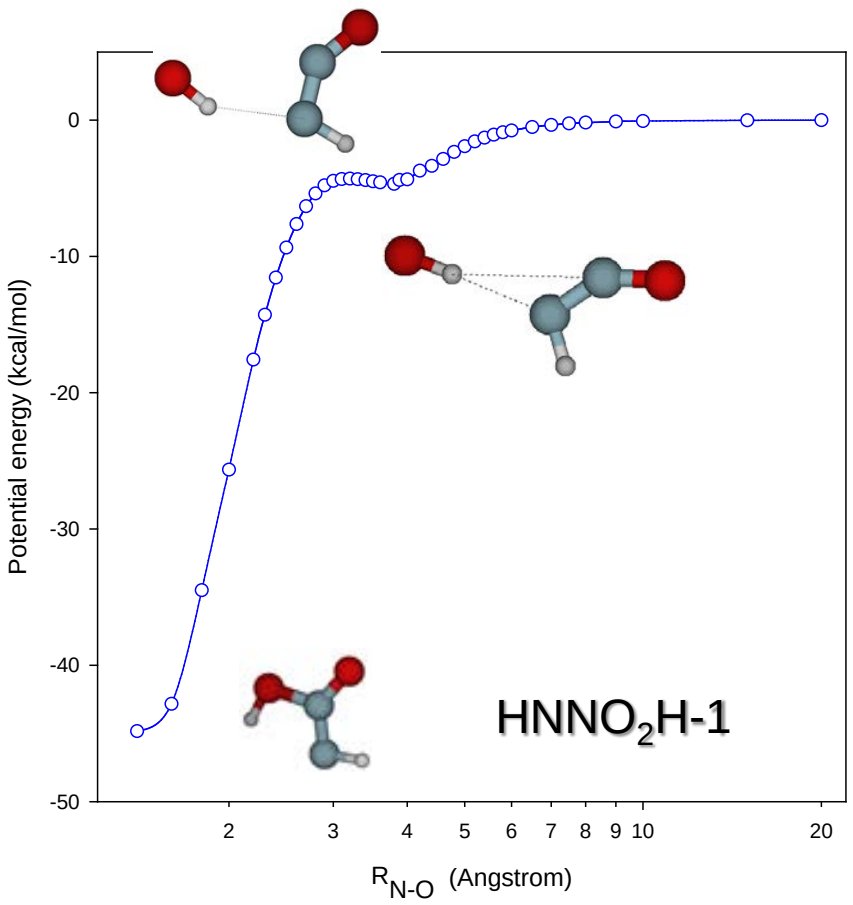
E(cis-HNNO) - E(trans-HNNO)	**6.51**	this work
	6.41	K. A. Peterson & J. S. Francisco, J. Chem. Phys. (2011), calculated at the R/UCCSD(T)/CBS + ΔRel + ΔCV + ΔT + ΔQ level of theory
E(OH) + E(trans-HNNO) - E(N_2O) - E(H_2O)	**97.34**	this work
	97.58	determined from $\Delta_f H°$ listed on NIST Gas phase thermochemistry database
E(NH_2) + E(NO_2) - E(N_2O) - E(H_2O)	**91.47**	this work
	91.60	determined from $\Delta_f H°$ listed on NIST Gas phase thermochemistry database

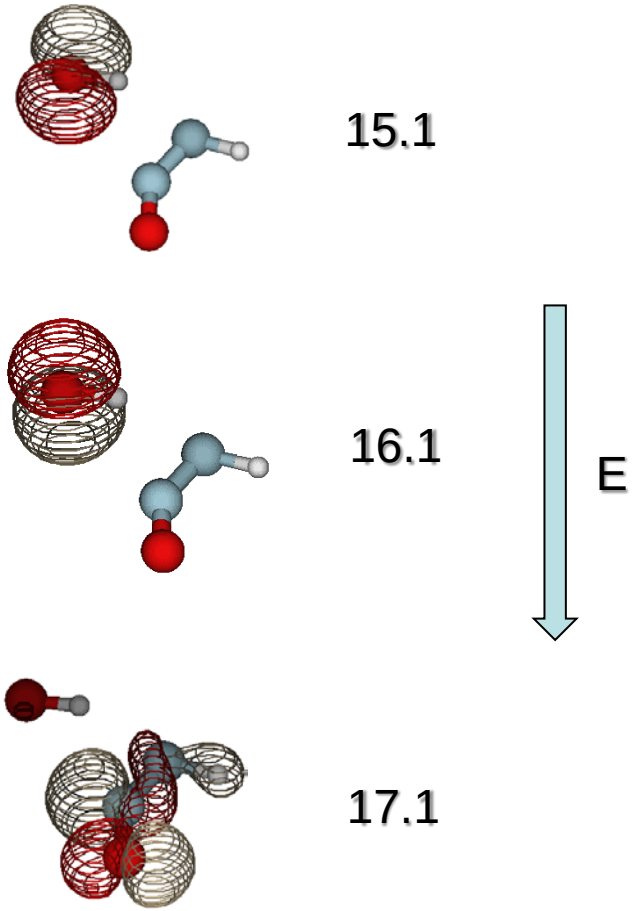


- Theoretical values were determined at 0K with zero-point energy corrections
- They are in excellent agreement with recent data of Peterson & Francisco
- They are in excellent agreement with those determined from experimental enthalpy of formation data

$HNNO_2H \rightarrow OH + cis\text{-}HNNO$

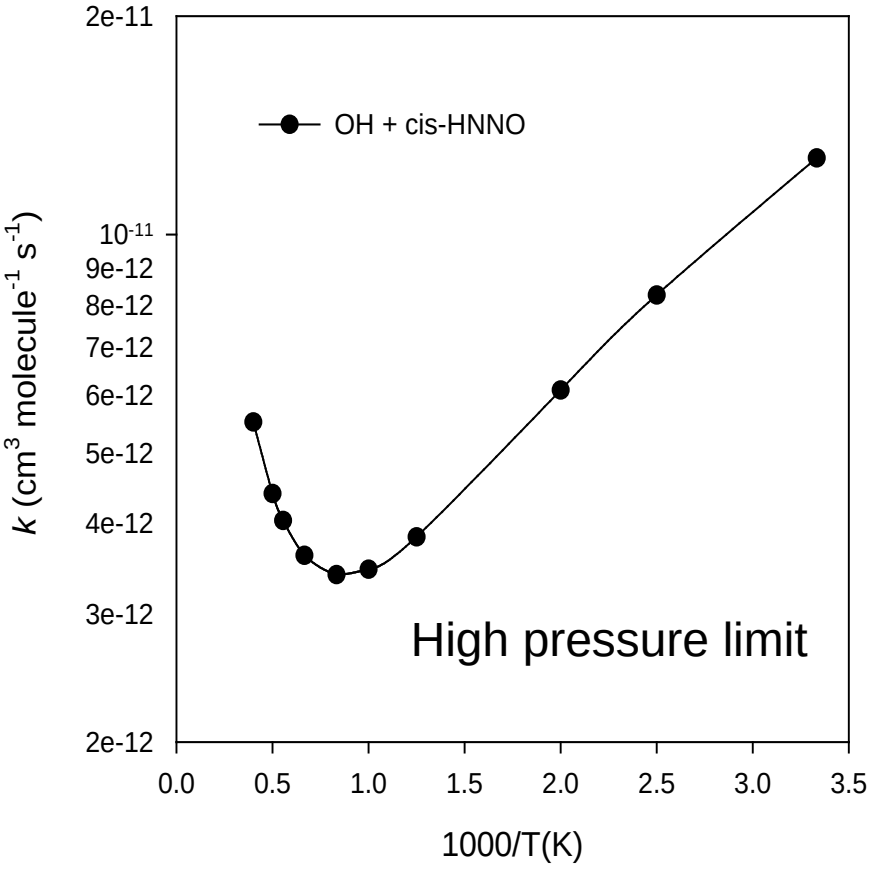
- Computed at the CASPT2/aug-cc-pVDZ level, state-averaged active space (4e,3o) consisting of two degenerated *p* orbitals of the OH and the *p* orbitals of N atoms





OH + cis-HNNO → $HNNO_2H$

- Reactions with submerged energy barriers, high-pressure limit k_∞ was determined by two transition state theory at E, J resolved level
- The low-lying state $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ of the OH radical was included in the electronic partition function



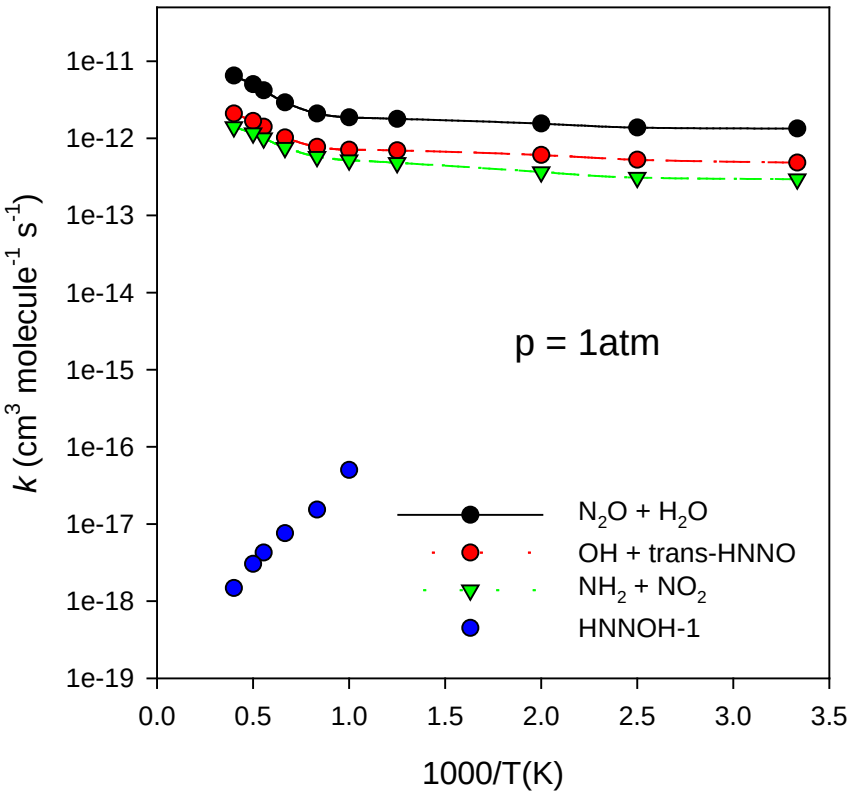
- Inner TS
  - Covalent bond formation
  - Energy barriers: QCISD(T)/CBS
- Outer TS
  - Phase space theory
  - Long range isotropic potential (Georgievskii & Klippenstein, J. Chem. Phys. 2005)
- Effective TS

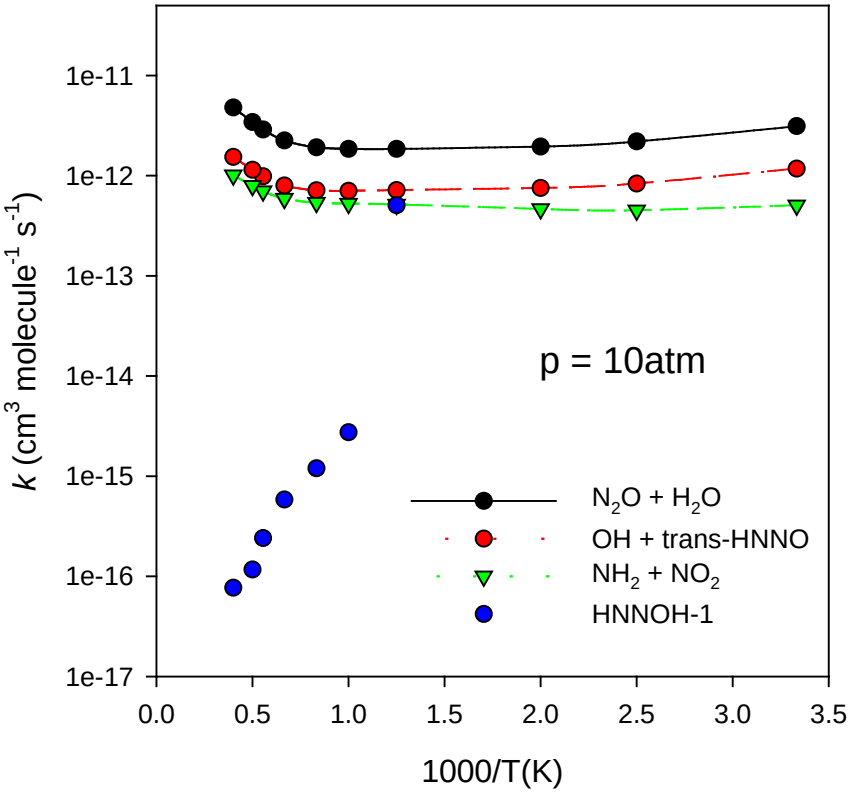
$$\frac{1}{N_{eff}^{\dagger}} = \frac{1}{N_{inner}^{\dagger}} + \frac{1}{N_{outer}^{\dagger}}$$

$$k^{\infty}(T) = \frac{1}{hQ_R}\int N_{eff}^{\dagger}(E,J)e^{-E/k_bT}dEdJ$$

Decomposition to bimolecular Products

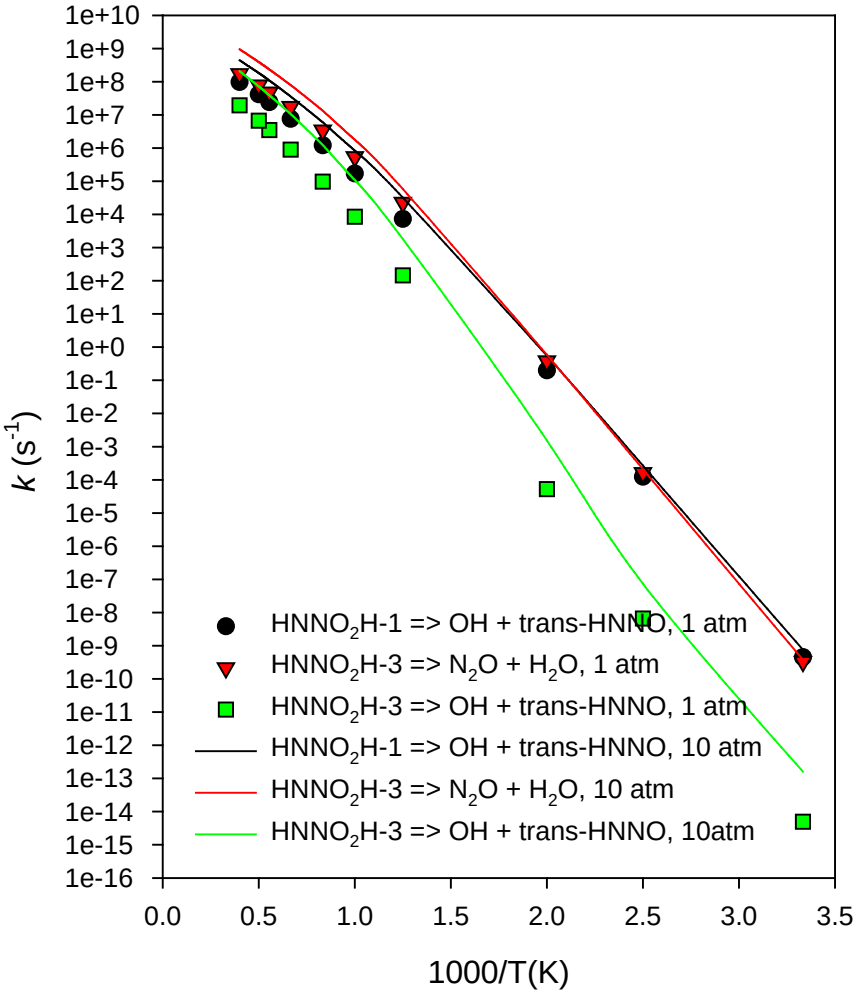
- Pressure dependent rate coefficients were determined by Rice–Ramsperger–Kassel–Marcus (RRKM) theory with Multi-Well Master Equation simulations at E, J resolved level
- Exponential down energy transfer model: $\Delta E_{down} = 200 \times (T/300)^{0.85}\ cm^{-1}$
- Lennard-Jones parameters: σ = 4.45 Å and ε = 379.3 cm^{-1}
- Tunneling correction with asymmetric Eckart potentials

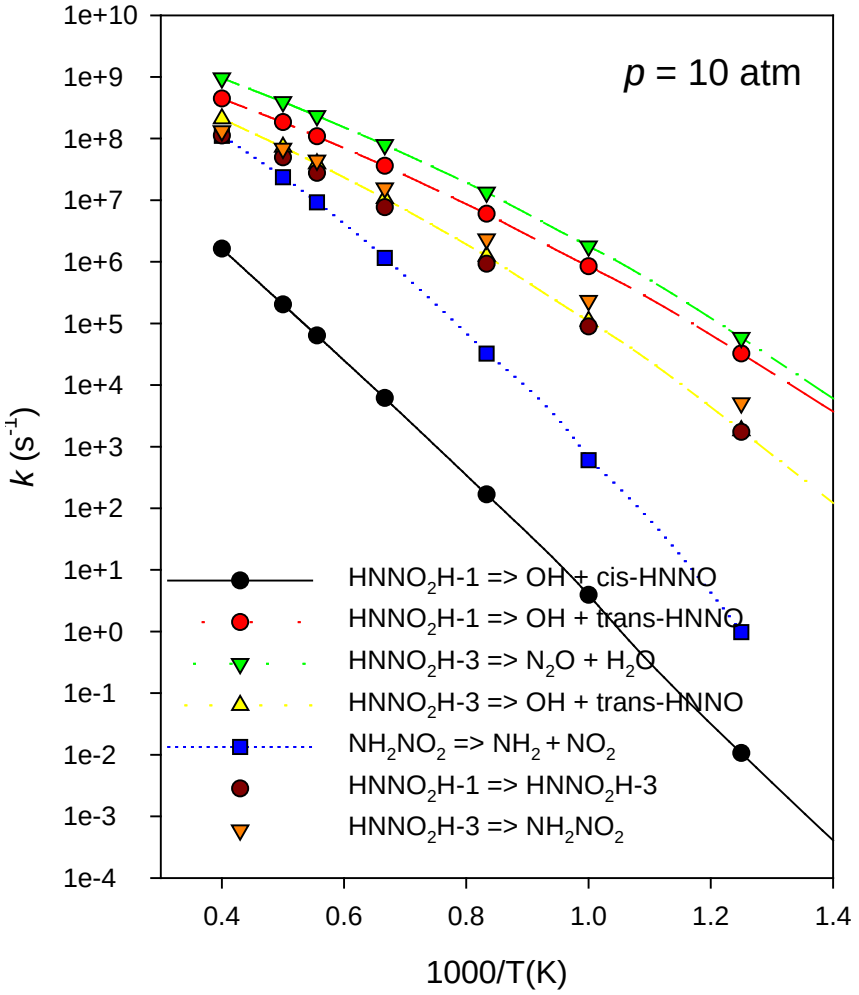




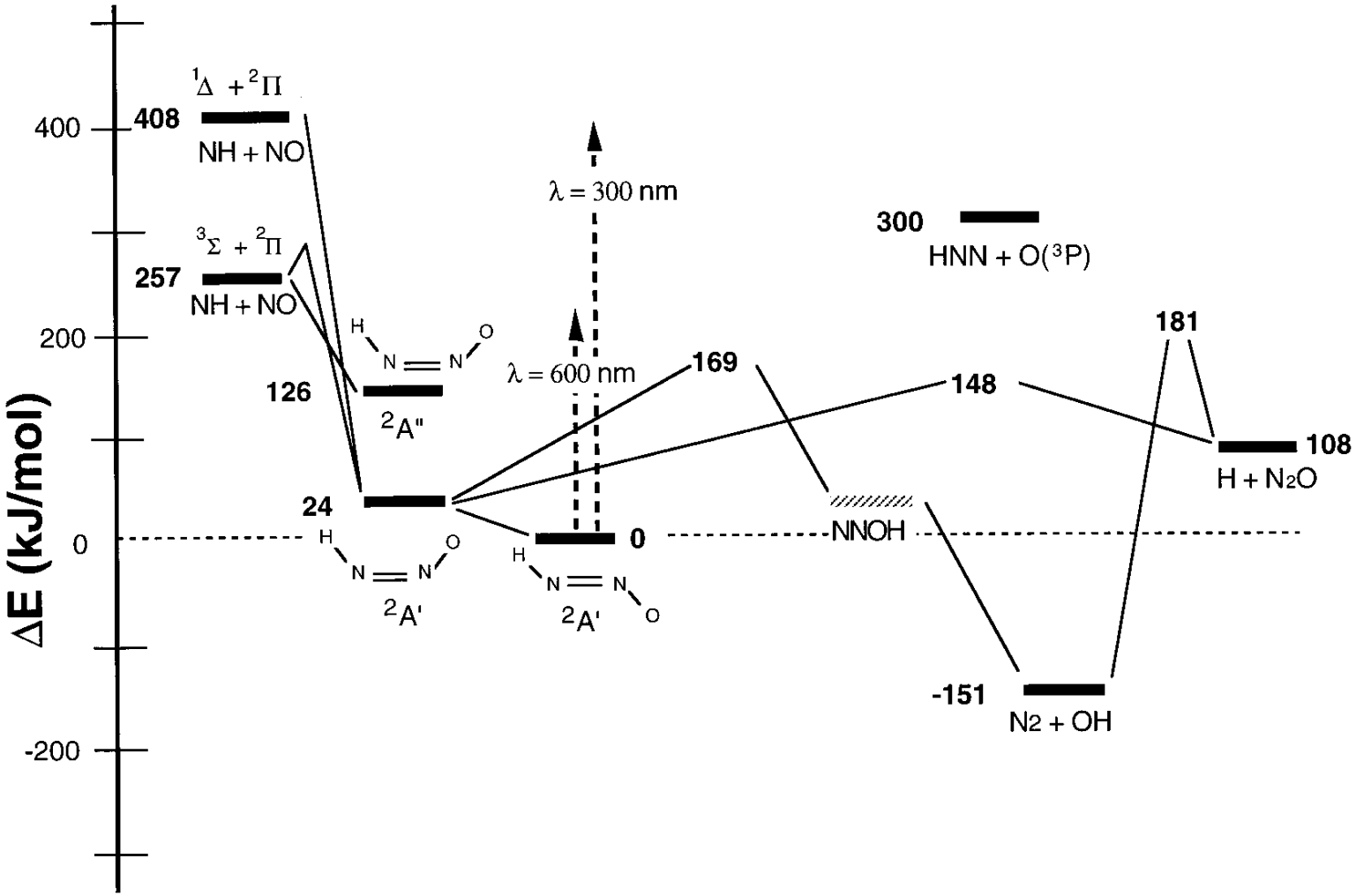
Unimolecular Decomposition of $HNNO_2H$

- Pressure dependent $k(E,J)$ was determined by Rice–Ramsperger–Kassel–Marcus (RRKM) theory with Multi-Well Master Equation simulations





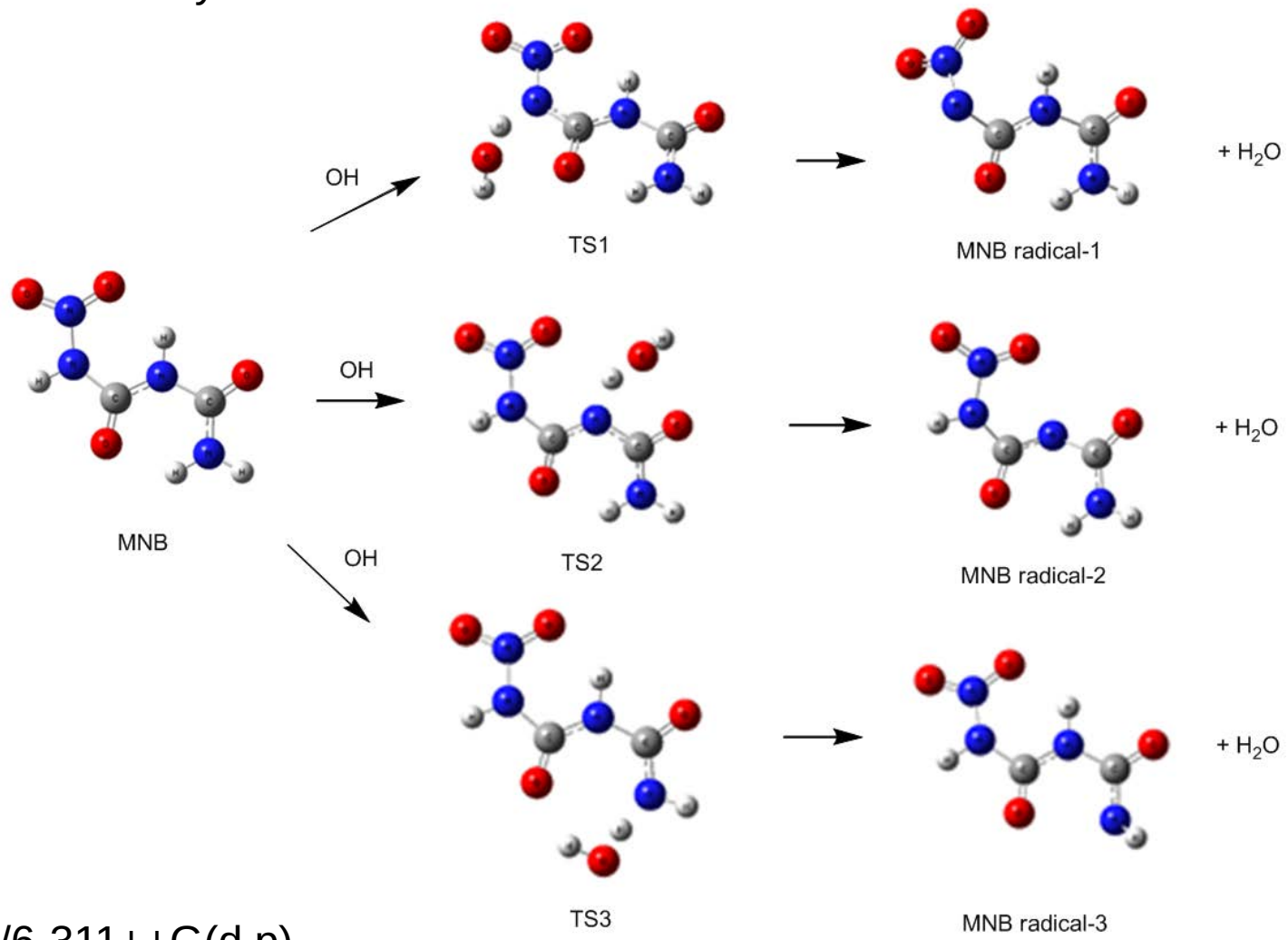
Decomposition of HNNO Radical



Laursen et al., J. Phys. Chem. A **2000,** *104,* 3681-3692

H-Abstraction from MNB by OH

H-abstraction Pathways:

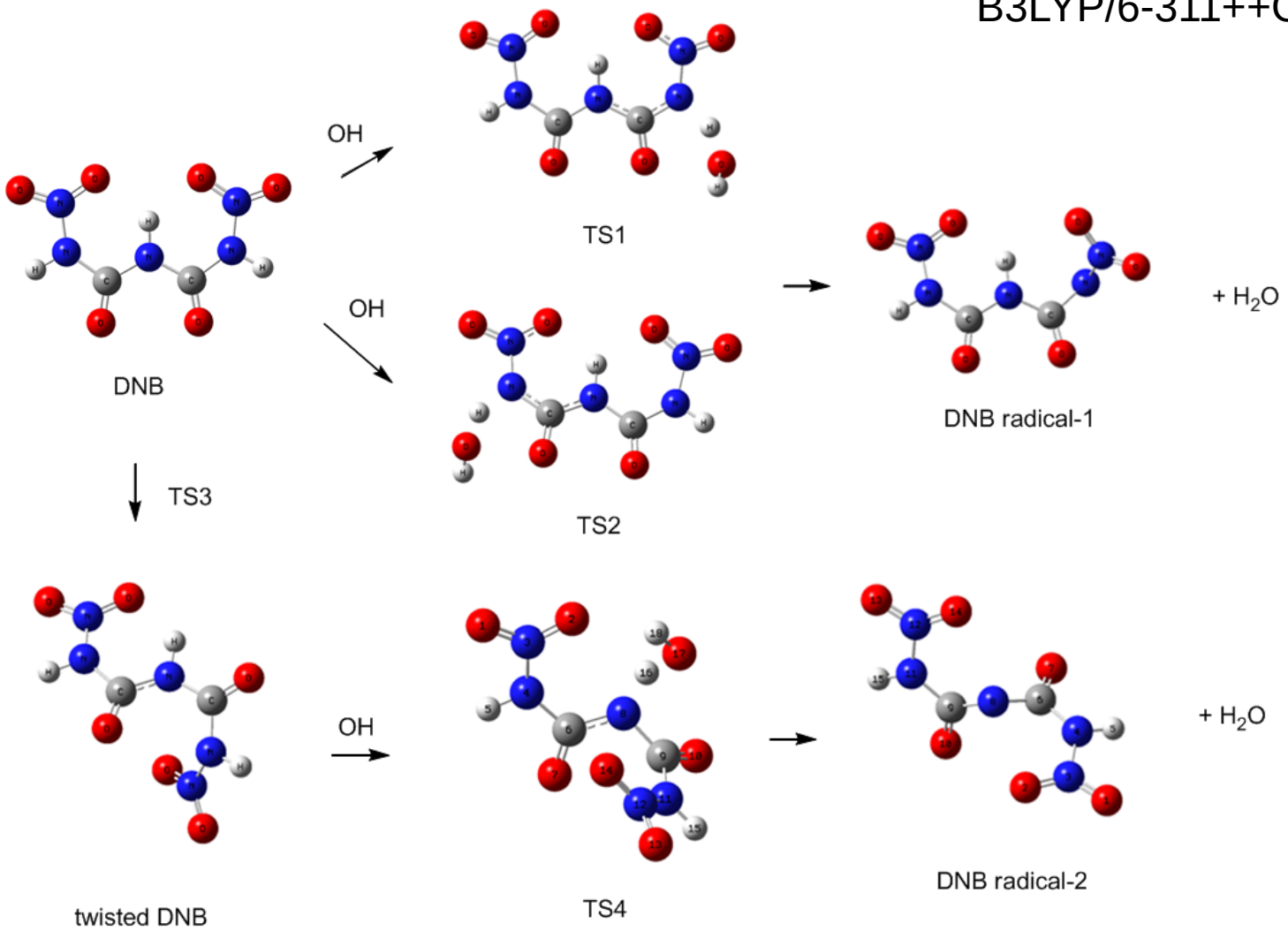


B3LYP/6-311++G(d,p)

H-Abstraction from DNB by OH

H-abstraction Pathways:

B3LYP/6-311++G(d,p)



Concluding Remarks

- New ignition chemistry mechanism for MNB and DNB has been proposed/verified
- The PES for thermal decomposition of $HNNO_2H$ intermediate was characterized by high-accuracy *ab initio* CASPT2 and CCSD(T) theories
- N_2O, H_2O, OH and trans-HNNO radicals are predicted to be major species from $HNNO_2H$ decomposition
- Temperature and pressure-dependent rate coefficients for $HNNO_2H$ decomposition were determined by two-transition state theory, RRKM theory and Multi-Well Master equation analysis at E,J resolved level
- Transition states for H-abstraction from MNB and DNB by OH radical were located with approximate energy barriers of 10 kcal/mol. H-abstraction reactions by active radicals generated from $HNNO_2H$ decomposition can further induce ignition of MNB and DNB

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