Kinetics Studies of Radical-Radical Reactions (I): The NO₂ + N₂H₃ System

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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: NO₂ + N₂H₃, 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.
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The NO₂ + N₂H₃ System

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N$_2$H$_4$ + NTO Hypergolic Ignition

• N$_2$H$_3$ and NO$_2$: major components of N$_2$H$_4$ + NTO earlier ignition

• NTO consists of structural conformers:
  NO$_2$, sym-N$_2$O$_4$ (D$_{2h}$), cis-ONONO$_2$, trans-ONONO$_2$

• Hypergolicity of hydrazine/N$_2$O$_4$:

  \[
  \begin{align*}
  N_2H_4 + cis-ONONO_2 & \rightarrow HONO_2 + H_2NN(H)NO \quad (k_{1a}) \\
  N_2H_4 + trans-ONONO_2 & \rightarrow HONO_2 + H_2NN(H)NO \quad (k_{1b}) \\
  H_2NN(H)NO & \rightarrow N_2H_3 + NO \quad (k_2)
  \end{align*}
  \]

\[
\begin{align*}
  k_1 &= 4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (\geq 250 \text{ K}) \\
  k_2 &= 1 \times 10^7 \text{ s}^{-1} \quad (1000 \text{ K})
  \end{align*}
\]


• Fast exothermic reactions:
  N$_2$H$_3$ + NO$_2$ (Radical + Radical) $\rightarrow$ addition $\rightarrow$ products
  N$_2$H$_3$ + N$_2$O$_4$ (Radical + Stable) $\rightarrow$ abstraction $\rightarrow$ products
Motivation: NO$_2$ + N$_2$H$_3$

- **Practically**
  - Occurs with negative energy barrier and large exothermicity, significant importance in N$_2$H$_4$ + NTO ignition

- **Theoretically**
  - Occurs via a complex reaction mechanism
  - Multireference characters of wavefunction are significant due to the electron repulsion between electronegative O and N atoms
  - Quantitatively correct description of the electron correlation in presence of configurational quasi-degeneracy effects
  - Chemically accurate representation of exact molecular wave function, and exact energy for prediction of accurate rate coefficient
Theoretical Approach

Electronic Structure Calculations

- Geometries optimization and ro-vibrational frequencies by multireference second-order perturbation theory (CASPT2) with aug-cc-pVDZ or aug-cc-pVTZ basis sets
- For R + R addition and abstraction, the energies were extrapolated to the CBS limit from those of CASPT2/aug-cc-pVQZ and CASPT2/aug-cc-pVTZ
- For dissociation of addition adducts, the energies were extrapolated to the CBS limit from those of CCSD(T)/cc-pVQZ and CCSD(T)/cc-pVTZ

Kinetic Rate Coefficients

- Two transition state theory for submerged energy barriers
- Microcanonical TST at E/J resolved level
  - rigid-rotor harmonic-oscillator assumptions
  - tunneling correction with asymmetric Eckart potentials
  - Master equation analysis via an eigenvector based approach
  - Exponential down energy transfer models
  - Lennard-Jones collision rates
$N_2H_3 + NO_2$ (Abstraction)

Unit: kcal/mol

CASPT2/CBS
RCCSD(T)/CBS//CASPT2
TSA2 $\rightarrow$ NNH$_2$-cisHONO

Optimized at the CASPT2(4e,3o)/aug-cc-pVTZ level
TSA4 $\rightarrow$ NNH$_2$-HNO$_2$

Optimized at the CASPT2(8e,6o)/aug-cc-pVDZ level
Rate Coefficients: Abstraction

- Inner TS
  - Covalent bond formation
  - Energy barriers: CASPT2/CBS
  - Rigid rotor harmonic oscillator

- Outer TS
  - Phase space theory
  - Long range isotropic potential

- Effective TS

\[
\frac{1}{N_{\text{eff}}^{+}} = \frac{1}{N_{\text{inner}}^{+}} + \frac{1}{N_{\text{outer}}^{+}}
\]

\[
k^{\infty}(T) = \frac{1}{h Q_R} \int N_{\text{eff}}^{+}(E,J) e^{-E/k_b T} dE dJ
\]
N–N Addition Potential

\[ \Delta H^o_{f, \text{NHNH}_2} = 55.3 \text{ kcal/mol} \]

\[ \Delta H^o_{f, \text{NO}_2} = 7.9 \text{ kcal/mol} \]
Addition of $\text{N}_2\text{H}_3 + \text{NO}_2$

Ground state destabilization: orbital splitting ($p_{\pi} - p_{\pi}$ repulsion) on $\text{NO}_2$

Optimized at the CASPT2(2e,2o)/aug-cc-pVDZ level
PES of N₂H₃ + NO₂ (Addition)

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

Unit: kcal/mol
N$_2$H$_3$-NO$_2$ Adduct Decomposition

Electron transfer for N-N bond breaking
Thermodynamic product stability

Adduct-1 $\rightarrow$ TS3

i$1067.05$ cm$^{-1}$

CASPT2(8e,6o)/aug-cc-pVDZ
PES of $\text{N}_2\text{H}_3 + \text{NO}_2$ (Addition)

Cas: $\text{N}_2\text{H}_3 + \text{NO}_2$

TS-1c: 7.25 kcal/mol

TS-1a: 3.79 kcal/mol

TS-1b: -11.31 kcal/mol

TS-2: -15.18 kcal/mol

TS-3: -9.72 kcal/mol

NH$_2$NHO + NO:

-6.94 kcal/mol

trans-NH=NH + cis-HONO:

-34.81 kcal/mol

CASPT2/aug-cc-pVDZ

CASPT2/aug-cc-pVTZ

RCCSD(T)/CBS//CASPT2

T1 diagnostic: RCCSD(T)/cc-pVQZ//CASPT2
Rate Coefficients: Addition

\[ k_1, \text{NO}_2 + \text{N}_2\text{H}_3 \rightarrow \text{NH}_2\text{NHNO}_2 \]

\[ k_2, \text{NO}_2 + \text{N}_2\text{H}_3 \rightarrow \text{NH}_2\text{NHONO} \]

**Graph:**
- **$k_1$, N-N addition, Ea=-11.73 kcal/mol**
- **$k_2$, N-O addition, Ea=-11.61 kcal/mol**
Rate Coefficients: Dissociation

- Microcanonical TST at the E/J resolved level employing rigid-rotor harmonic-oscillator assumptions
- The pressure-dependent kinetics analysis using single-well master equation for irreversible dissociation at the E/J resolved level
- The collisional energy transfer probability was approximated by:
  \[ \Delta E_{\text{down}} = 200 \times (T/300)^{0.85} \, \text{cm}^{-1} \]
- The Lennard-Jones parameters for collision rates were estimated to be \( \sigma = 4.84 \, \text{Å} \) and \( \varepsilon = 441 \, \text{cm}^{-1} \)
Concluding Remarks

- Four abstraction channels were found with the negative energy barriers up to 12 kcal/mol, and product H-bonded complexes have 5 - 12 kcal/mol energies stable than the dissociation products.

- Abstraction by the nucleophilic O atom forming trans-$\text{N}_2\text{H}_2$ + cis-$\text{HONO}$ is exothermic to 34.8 kcal/mol, forming $\text{NNH}_2$ + cis-$\text{HONO}$ is the dominant channel.

- The NO$_2$ addition to the N$_2$H$_3$ radical proceeds via a complex mechanism. The N–N addition is more favorable than the N–O addition.

- The predominant channel for the dissociation of the N–N addition adduct is an intramolecular H-transfer to form the trans-$\text{HONO}$ + trans-$\text{N}_2\text{H}_2$ products.
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