

This document is confidential and is proprietary to the American Chemical Society and its authors. Do not copy or disclose without written permission. If you have received this item in error, notify the sender and delete all copies.

**Large Intermediates in Hydrazine Decomposition: A
Theoretical Study of the N₃H₅ and N₄H₆ Potential Energy
Surfaces**

Journal:	<i>The Journal of Physical Chemistry</i>
Manuscript ID	jp-2019-02217p.R1
Manuscript Type:	Article
Date Submitted by the Author:	n/a
Complete List of Authors:	Grinberg Dana, Alon; Massachusetts Institute of Technology, Chemical Engineering Moore, Kevin; Argonne National Laboratory, Gas Phase Chemical Dynamics Jasper, Ahren; Argonne National Laboratory, Gas Phase Chemical Dynamics Green, William; Massachusetts Institute of Technology, Chemical Engineering

SCHOLARONE™
Manuscripts

1
2
3
4 **Large Intermediates in Hydrazine Decomposition: A Theoretical Study of the**
5
6 **N₃H₅ and N₄H₆ Potential Energy Surfaces**
7
8

9 Alon Grinberg Dana¹, Kevin B. Moore III,² Ahren W. Jasper,² William H. Green^{1*}
10
11

12
13 ¹ Department of Chemical Engineering, Massachusetts Institute of Technology,
14 Cambridge, MA 02139, United States
15

16
17 ² Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL
18 60439, United States
19

20 * Corresponding author. Email: whgreen@mit.edu; Fax: +1-617-324-0066; Tel: +1-617-253-4580
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57

Abstract

Large complex formation involved in the thermal decomposition of hydrazine (N_2H_4) is studied using transition state theory based theoretical kinetics. A comprehensive analysis of the N_3H_5 and N_4H_6 potential energy surfaces was performed at the CCSD(T)-F12a/aug-cc-pVTZ// ω B97x-D3/6-311++G(3df,3pd) level of theory, and pressure-dependent rate coefficients were determined. There are no low-barrier unimolecular decomposition pathways for triazane (n - N_3H_5), and its formation becomes more significant as the pressure increases; it is the primary product of $N_2H_3 + NH_2$ below 550, 800, 1150, and 1600 K at 0.1, 1, 10, and 100 bar, respectively. The N_4H_6 surface has two important entry channels, $N_2H_4 + H_2NN$ and $N_2H_3 + N_2H_3$, each with different primary products. Interestingly, $N_2H_4 + H_2NN$ primarily form $N_2H_3 + N_2H_3$, while disproportionation of $N_2H_3 + N_3H_3$ predominantly leads to the other N_2H_2 isomer, HNNH. Stabilized tetrazane (n - N_4H_6) formation from $N_2H_3 + N_2H_3$ becomes significant only at relatively high pressures and low temperatures due to fall-off back into $N_2H_3 + N_2H_3$. Pressure-dependent rate coefficients for all considered reactions as well as thermodynamic properties of triazane and tetrazane, which should be considered for kinetic modeling of chemical processes involving nitrogen- and hydrogen-containing species, are reported.

1. Introduction

Hydrazine (N_2H_4), the main component of diamine-based rocket fuels, is an excellent propellant: using oxygen as the oxidizer, it is only second to hydrogen in terms of the specific impulse (thrust developed per fuel mass per unit time) it generates.¹ Its decomposition could lead to auto-ignition and detonation,²⁻⁴ and it is sometimes used as a monopropellant, usually by decomposing over a catalyst.¹ Hydrazine and hydrazine-based fuels such as monomethyl hydrazine are more commonly used as bipropellants with N_2O_5 as the oxidizer. Hydrazine is used in thruster engines for attitude and in-orbit control of satellites and spacecraft,¹ where it is being stored and utilized at a maximal pressure of about 25 bar.⁵⁻⁷

No detailed kinetic models for hydrazine-based fuels combustion in N_2O_5 exist in the current literature; a step towards this goal is understanding hydrazine decomposition better. Detailed kinetic models for hydrazine decomposition were previously suggested by Halat-Augier et al.⁸ as well as by Konnov and De Ruyck.⁹ More recently, however, computations of the N_2H_2 ,^{10,11} N_2H_3 ,¹¹ and N_2H_4 ¹⁰⁻¹² potential energy surfaces determined updated kinetics. Interestingly, none of the previous works on hydrazine decomposition has considered species containing more than two nitrogen atoms. In the absence of an oxidizer, a monopropellant's decomposition could be thought of as an extreme case of fuel-rich combustion, a chemistry region in which fuel-radical recombination reactions often play a significant role. At low pressures, chemically-activated isomerization and decompositions are often important. As the working pressure increases, radical recombination reactions, leading to formation of relatively large complexes, become more significant due to collisional stabilization.

1
2
3 Unlike carbon, nitrogen does not normally form the major elemental backbone of large
4 molecules. For example, an experimental study of tetrazene (linear unsaturated N_4H_4)
5
6 determined that its thermolysis in the solid phase begins at room temperature, while in the gas
7
8 phase it is metastable.¹³ Moreover, cyclic nitrogenous rings, and specifically tetrazetidene (cyclic
9
10 N_4H_4), were determined to have relatively high ring strain energies.^{14–16} However, a theoretical
11
12 study of triazane (N_3H_5) concluded that it is kinetically stable.¹⁷ Tetrazane (saturated N_4H_6) was
13
14 also studied theoretically, and its most stable stereoisomer was determined,¹⁸ yet its overall
15
16 kinetic stability was not assessed. A sub-atmospheric room temperature experimental
17
18 observation of N_2H_3 self-reaction concluded that the disproportionation reaction yielding $N_2H_4 +$
19
20 N_2H_2 is approximately four times faster than a recombination reaction yielding tetrazane, unlike
21
22 the tendency of the analogous hydrocarbon radical, C_2H_5 .¹⁹ Yet the behavior of the $N_2H_3 + N_2H_3$
23
24 system at high temperatures and different pressure, and specifically the importance of well-
25
26 skipping chemically-activated reactions, has not been reported in the literature.
27
28
29
30
31
32
33
34

35 In the present contribution, we examine the hypothesis that abundant radicals in
36
37 decomposing hydrazine might form relatively large complexes such as triazane and tetrazane,
38
39 becoming more significant as the pressure increases. We therefore explore the $NH_2 + N_2H_3$ and
40
41 $N_2H_3 + N_2H_3$ reactions which lead to pressure-dependent kinetic networks on the N_3H_5 and N_4H_6
42
43 potential energy surfaces, respectively. Specifically, collisional-stabilized formation of the
44
45 complexes along with well-skipping reactions are considered, and pressure-dependent rate
46
47 coefficients are determined.
48
49
50
51
52
53
54
55
56
57
58
59
60

2. Theoretical methods

2.1. Characterizing the Potential Energy Surface

Geometric structures and vibrational frequencies for all wells and saddle points considered here were obtained using density functional theory employing the ω B97x-D3 functional²⁰ and the 6-311++G(3df,3pd) basis set.²¹ The growing string method (GSM)²² was used to provide initial guesses for some of the transition state geometries. Intrinsic reaction coordinate (IRC) calculations²³ were used to verify all transition state configurations by tracking the minimum energy paths leading to adjacent local minima.

Higher level single-point energies were obtained by employing the explicitly correlated coupled-cluster CCSD(T)-F12a method^{24,25} and using an augmented Dunning's correlation consistent, polarized valence triple- ζ (aug-cc-pVTZ) basis set.²⁶ Zero-point energy (ZPE) corrections, incorporated into the final energies reported here, were evaluated at the ω B97x-D3/6-311++G(3df,3pd) level and scaled by a recommended factor of 0.970²⁷ to account for their average overestimation, due in part to anharmonicity. Previously, Hwang and Mebel¹⁰ showed that CCSD(T)/6-311G(d,p) level energies are reliable (do not deviate by more than 2 kcal mol⁻¹ from respective multireference CASSCF calculations using the full valence active space) for similar N/H systems on the N₂H₄ potential. The comparison included the iminoammonium (NH₃NH) species, a zwitterionic compound similar in structure to other zwitterions discussed in the present work. A high value of the T1 diagnostic parameter²⁸ implies that additional dynamic electron correlation retrieved by a multireference method is significant. At the CCSD(T)-F12a/aug-cc-pVTZ level, the T1 value for NH₃NH is 0.0112, similar to the T1 range of the various

1
2
3 stable species reported in the present work (0.0090–0.0151). However, radicals such as N_2H_3 and
4
5 N_3H_4 have higher T1 values in the range of 0.0211 – 0.0247, indicating a larger uncertainty in their
6
7 energies.
8
9

10 Starting from the optimized geometries, separate relaxed potential energy scans were
11
12 performed as a function of the dihedral angle around each single bond for all stationary points
13
14 on the potential energy surface (PES). All scans had a 10° increment resolution, unless otherwise
15
16 noted. These hindered rotor scans were performed using density functional theory employing
17
18 the Becke-3-Lee-Yang-Parr (B3LYP) functional²⁹ and the 6-311++G(3df,3pd) basis set.²¹ The
19
20 potential energies were fitted to truncated Fourier series, and used as input to Arkane, an open-
21
22 source master equation (ME) transition state theory (TST) solver included within the Reaction
23
24 Mechanism Generator (RMG) suite,^{30,31} to compute the partition functions. The potential scans
25
26 are given in the Supporting Information (Figs S1–S10). The optimized geometry was verified to
27
28 have the lowest energy on these potential scans.
29
30
31
32
33

34 Q-Chem 4.4.0³² was used for geometry optimizations and frequency calculations. Molpro
35
36 2015.1^{33,34} was used for coupled-cluster electronic energy calculations. Gaussian³⁵ was used for
37
38 all dihedral angle rotor scans, IRC, and GSM calculations. Radical species were computed using
39
40 unrestricted methods. IQmol³⁶ was used to plot molecular orbitals generated using the NBO 6.0
41
42 population analysis software³⁷.
43
44
45
46

47 **2.2. Calculating thermodynamic parameters**

48
49 Energies at zero K (E_0) of $n-N_3H_5$, $n-N_3H_4$, $i-N_3H_4$, and $n-N_4H_6$ were compared using three
50
51 computational methods. First, the composite CBS-QB3 method³⁸ was considered; the reported
52
53 error bar of the CBS-QB3 method is 13.0 kJ mol^{-1} .³⁹ A recommended ZPE correction scaling factor
54
55
56
57

1
2
3 of 0.99⁴⁰ was used for this method. The level of theory used throughout this work to characterize
4 the potential energy surfaces and calculate kinetic rate coefficients, CCSD(T)-F12a/aug-cc-
5 pVTZ// ω B97x-D3/6-311++G(3df,3pd), was also used. A ZPE correction scaling factor of 0.970 was
6 adopted for this method.²⁷ A similar method with a different basis set for the single point
7 calculation, CCSD(T)-F12a/cc-pVTZ-F12// ω B97x-D3/6-311++G(3df,3pd), was also implemented.
8 Here, a ZPE correction scaling factor of 0.984 was used.^{41,42} Only the CCSD(T)-F12a/cc-pVTZ-F12
9 method was used for thermodynamic data calculations since it has available bond additivity
10 corrections (BAC) in Arkane.
11
12
13
14
15
16
17
18
19
20
21
22

23 **2.3. Calculating kinetic parameters**

24
25 Both high-pressure (P) limit and P-dependent thermal rate coefficients, $k(T)$ and $k(T,P)$, were
26 calculated at CCSD(T)-F12a/aug-cc-pVTZ// ω B97x-D3/6-311++G(3df,3pd) using Arkane. Values of
27 $k(T)$ for every elementary chemical reaction which has an energy barrier were calculated by a TST
28 analysis⁴³ using the rigid-rotor harmonic oscillator (RRHO) approximation with low-energy (< 40
29 kJ mol⁻¹ barrier) internal rotations modelled as one-dimensional hindered rotors (1D-HR). The
30 effect of internal rotation(s) on the harmonic frequencies was eliminated by projection.⁴⁴ One-
31 dimensional asymmetric tunneling through tight transition states was incorporated by assuming
32 that the reaction path can be described by an Eckart function.⁴⁵ Phenomenological $k(T,P)$'s were
33 computed by applying the microcanonical RRKM (Rice–Ramsperger–Kassel–Marcus) theory to
34 solve the ME⁴⁶ under the modified strong collision (MSC) approximation (RRHO and 1D-HR
35 approximations were also used in calculating densities of states).⁴⁷ Calculations were performed
36 at a mesh of (T_i, P_j) points, and the $k(T_i, P_j)$ fitted to a Chebyshev polynomial suitable for use in
37 Cantera⁴⁸ or the commercial version of Chemkin⁴⁹. The reported rate coefficients incorporate
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

appropriate degeneracy factors. For barrierless pathways, high-P $k(T)$'s estimates (either using literature data or estimated by the respective RMG template) were input into Arkane and converted into $k(E)$'s for solution of the ME using an inverse Laplace transform.⁴⁷ As is usually done when constructing the ME, the input channel was treated as pseudo-first-order and dissociations into bimolecular products in P-dependent networks were treated as irreversible. The rates of collisional energy transfer (CET) for deactivating collisions were modeled using the "single exponential down" expression:

$$P(E \leftarrow E') \propto \exp\left(-\frac{E' - E}{\langle \Delta E_d \rangle}\right), \quad E' > E$$

where $\langle \Delta E_d \rangle$ is a measure of the collision efficiency. We computed $\langle \Delta E_d \rangle$ for $\text{N}_3\text{H}_5 + \text{N}_2$ and $\text{N}_4\text{H}_6 + \text{N}_2$ at several temperatures using classical trajectory approaches⁵⁰⁻⁵² and potential energy surface construction strategies⁵³ described in detail elsewhere. The trajectory-based results are well-represented (to better than 10%) by the expressions $\langle \Delta E_d \rangle = 175 (T/298 \text{ K})^{0.52} \text{ cm}^{-1}$ and $\langle \Delta E_d \rangle = 250 (T/298 \text{ K})^{0.30} \text{ cm}^{-1}$ from $T = 300$ to 3000 K for $\text{N}_3\text{H}_5 + \text{N}_2$ and $\text{N}_4\text{H}_6 + \text{N}_2$, respectively. The calculated values of $\langle \Delta E_d \rangle$ for the two systems are similar at high T , while $\langle \Delta E_d \rangle$ is larger for N_4H_6 than for N_3H_5 at low T . These trends are consistent with those reported previously for hydrocarbons and several bath gases,⁵⁴ where we also showed that trajectory-based values of $\langle \Delta E_d \rangle$ often have a weaker temperature dependence than the $T^{0.85}$ appearing in the empirical standard expression.⁵⁵ In addition to uncertainties arising from the value of $\langle \Delta E_d \rangle$, errors in the present collision model may be attributed to simplifications in the expression for $P(E \leftarrow E')$ given above and to the neglect of rovibrational anharmonicity when evaluating the density of states near threshold.⁵² Altogether, we often find empirically (e.g., for methane,⁵⁶ propargyl radical,⁵⁷ and 2-methyl-allyl radical⁵⁸) that the use of the single exponential down model

1
2
3 along with trajectory-based values of $\langle \Delta E_d \rangle$ predicts k_0 with errors of a factor of two or less,
4
5 thanks in part to a cancellation of errors when rovibrational anharmonicity is neglected.
6

7
8 Transport parameters (Lennard-Jones parameters, dipole moment, and polarizability) were
9
10 calculated using the OneDMin code,⁵⁹ Molpro, and Gaussian. These Lennard-Jones parameters
11
12 (well depth and collision diameter) are also necessary for pressure-dependent rate calculations,
13
14 specifically for the collision frequency calculation. Lennard-Jones parameters were calculated
15
16 using a DF-MP2/aug-cc-pVDZ potential energy surface with N₂ as the collider. Similar calculations
17
18 (MP2/aug-cc-pVDZ) were previously shown to be within 10% of the more accurate MP2/CBS and
19
20 QCISD(T)/CBS computations;⁵⁹ similar errors were found in tests of this approach against
21
22 experimental and higher-level theoretical diffusion coefficients.⁶⁰ The dipole moment and
23
24 polarizability parameters were computed at the B2PLYPD3/cc-pVTZ level. All transport
25
26 parameters are given in the Supporting Information (Table S1).
27
28
29
30

31
32 Network sensitivity analysis was conducted using Arkane by perturbing each of the relevant wells
33
34 and transition states in the potential energy surface, and determining the effect on the calculated
35
36 pressure-dependent rates.
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57

3. Results and Discussion

3.1. The N_3H_5 system

An N3 isomer with the empirical chemical formula N_3H_5 could be generated in systems with relatively high concentrations of N_2H_3 and NH_2 radicals. This N_3H_5 potential energy diagram describes several ammonia-forming pathways (Fig. 1). It consists of a pressure-dependent network on the singlet surface (Fig. 1) with two isomers, n- N_3H_5 (triazane, NH_2NHNH_2) and 1,2-z- N_3H_5 (NH_2NH_2NH) (Fig. 2), as well as bimolecular pathways on both the singlet and triplet surfaces. The 'n' and 'z' in the species names above stand for normal and zwitterion, respectively. Geometric representations of relevant species and saddle points are given in Figs. 2 and 3, respectively. Table 1 lists point groups, rotational constants, and unscaled harmonic frequencies for all relevant species and transition states.

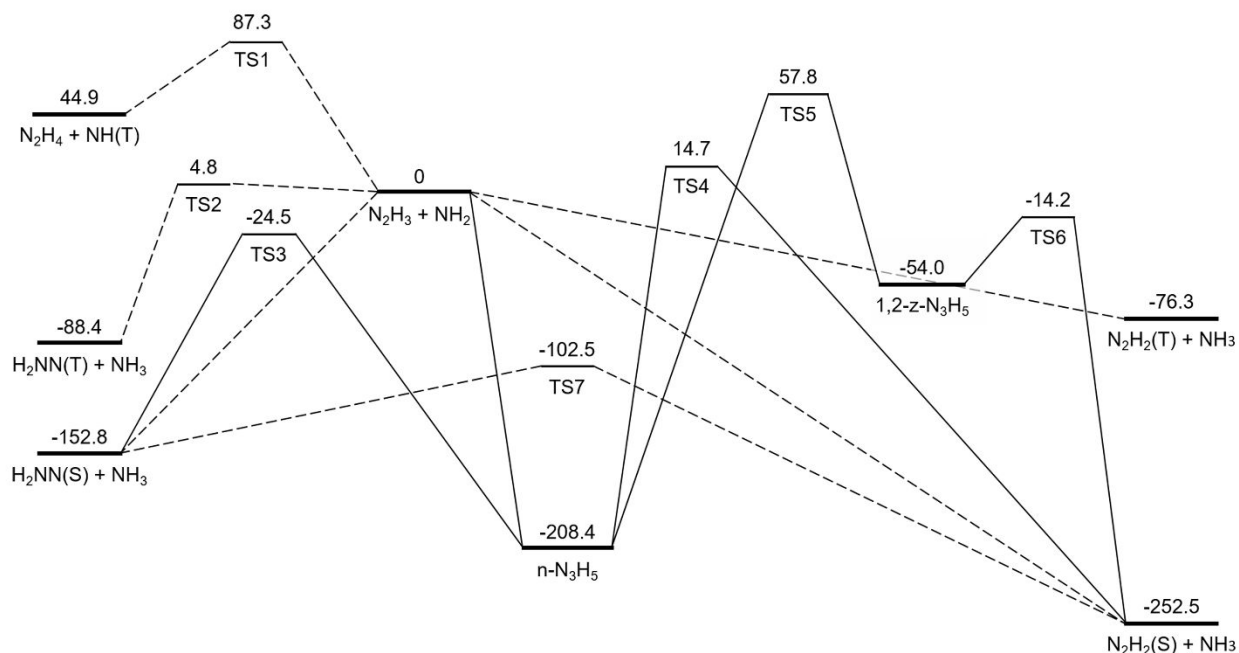


Figure 1. Reaction path diagram for the N_3H_5 PES. Dashed lines represent non-pressure-dependent pathways. (S) and (T) represent singlet or triplet multiplicities, respectively. Energies are in kJ mol^{-1} , and scaled relative to the $N_2H_3 + NH_2$ entry channel, which was set at zero.

The entry channel of the pressure-dependent network, $N_2H_3 + NH_2$, leads via the $n-N_3H_5$ intermediate to two lower-energy bimolecular exit channels, each consists of an N_2H_2 isomer and ammonia. The barrierless high pressure limit rate for the complex formation reaction, $N_2H_3 + NH_2 \leftrightarrow n-N_3H_5$ (Reaction B1, Table 2), was assumed to equal the rate of a similar reaction, $CH_3NH + NH_2 \leftrightarrow CH_3NHNH_2$, calculated at the CASPT2/aug-cc-pVDZ level.⁶¹ For simplicity, highly energetic wells were excluded from the PES. For example, $N_2H_2 + NH(S)$ formed barrierlessly from 1,2-z- N_3H_5 is 192.0 kJ mol⁻¹ above the $N_2H_3 + NH_2$ entry channel.

The $N_2H_2(S) + NH_3$ product well is the most stable product channel in Fig. 1, yet the pathway forming the $H_2NN(S) + NH_3$ product well has a lower barrier (Fig. 1). Nevertheless, all barriers surrounding $n-N_3H_5$ are relatively high; consequently, even moderate pressures would be enough for the excited complex to be stabilized as $n-N_3H_5$.

Table 1. Point Groups, Rotational Constants and Unscaled Vibrational Frequencies Calculated at the $\omega B97x-D3/6-311++G(3df,3pd)$ Level of Theory for Stationary Points on the N_3H_5 PES

stationary point	point group	rotational constants (cm ⁻¹)	harmonic frequencies (cm ⁻¹)
NH(T)	C _{∞v}	16.66	3326.8
NH ₂	C _{2v}	23.77, 12.93, 8.37	1519.9, 3418.0, 3510.4
NH ₃	C _{3v}	10.02, 10.02, 6.31	1030.0, 1664.9, 1677.8, 3518.4, 3644.2, 3644.2
H ₂ NN(S)	C _{2v}	11.18, 1.34, 1.18	1016.2, 1342.2, 1642.3, 1735.5, 3154.9, 3165.2
H ₂ NN(T)	C _s	10.02, 1.13, 1.05	727.2, 1102.3, 1265.6, 1587.7, 3448.1, 3555.2
N ₂ H ₂ (S)	C _{2h}	10.25, 1.34, 1.18	1351.8, 1355.3, 1601.8, 1701.2, 3309.3, 3335.2
N ₂ H ₂ (T)	C ₂	11.72, 1.17, 1.16	783.5, 1079.8, 1088.7, 1509.7, 3363.1, 3384.5
N ₂ H ₃	C ₁	6.91, 1.04, 0.91	519.0, 710.8, 1154.5, 1293.8, 1496.0, 1668.8, 3485.1, 3549.2, 3687.8
N ₂ H ₄	C ₂	4.89, 0.82, 0.82	444.4, 829.7, 973.6, 1154.1, 1311.8, 1342.6, 1681.1, 1693.0, 3515.3, 3524.0, 3619.1, 3623.6
$n-N_3H_5$	C ₁	1.37, 0.34, 0.30	334.5, 449.9, 493.8, 824.4, 850.8, 962.2, 1160.4, 1183.5, 1253.9, 1361.3, 1532.8, 1669.9, 1697.6, 3447.3, 3462.0, 3584.0, 3599.0, 3610.7
1,2-z- N_3H_5	C ₁	1.35, 0.33, 0.30	241.6, 452.6, 482.2, 820.8, 936.0, 982.5, 1169.0, 1203.3, 1403.5, 1457.6, 1504.8, 1645.9, 1671.8, 3357.0, 3466.1, 3482.1, 3520.1, 3559.7
TS1	C ₁	1.09, 0.19, 0.17	1900.0i, 25.3, 163.7, 244.1, 463.5, 660.1, 748.7, 844.3, 1163.5, 1175.4, 1363.4, 1443.2, 1557.7, 1667.4, 3380.8, 3520.4, 3561.1, 3661.9

TS2	C ₁	1.11, 0.21, 0.18	1229.9i, 164.8, 191.2, 379.7, 542.4, 608.6, 673.5, 878.7, 1079.1, 1262.4, 1297.9, 1498.5, 1553.4, 1632.0, 3444.4, 3499.3, 3535.9, 3655.8
TS3	C ₁	1.33, 0.25, 0.22	1409.4i, 232.8, 293.8, 415.5, 557.1, 644.0, 767.8, 812.5, 1221.3, 1346.0, 1515.4, 1569.9, 1690.0, 2568.3, 3503.0, 3522.2, 3619.1, 3627.1
TS4	C ₁	1.19, 0.37, 0.31	1194.1i, 286.9, 543.7, 656.7, 847.9, 977.5, 985.2, 1127.7, 1196.8, 1418.5, 1483.3, 1547.7, 1607.4, 2262.6, 3432.7, 3469.5, 3490.7, 3574.8
TS5	C ₁	1.37, 0.32, 0.28	1603.4i, 317.7, 362.8, 429.3, 811.7, 914.5, 976.4, 1136.5, 1243.4, 1392.0, 1472.9, 1533.3, 1680.1, 2751.3, 3439.8, 3452.8, 3594.0, 3622.4
TS6	C ₁	1.48, 0.22, 0.20	870.5i, 184.6, 284.0, 478.1, 546.1, 632.8, 712.6, 987.4, 1178.4, 1459.8, 1540.9, 1545.8, 1705.5, 3325.9, 3469.7, 3476.7, 3566.4, 3624.4
TS7	C ₁	1.18, 0.25, 0.21	1358.0i, 393.8, 453.4, 476.6, 722.7, 752.5, 769.0, 1178.8, 1460.0, 1557.1, 1559.4, 1642.2, 1657.3, 1749.3, 2375.8, 3156.2, 3610.3, 3706.0

Iminoammonium (NH₃NH) and H₂NNHN were previously shown to be important intermediates in hydrazine decomposition^{10,12} and triazene (N₃H₃) rearrangements,⁶² respectively. Three similar nitrenes on the N₃H₅ surface could potentially exist, namely NH₂NH₂NH, NH₃NNH₂, and NH₃NHNH, resulting from all possible intra-hydrogen transfers in the system. Nevertheless, only NH₂NH₂NH (referred to herein as 1,2-z-N₃H₅, Fig. 2) is unimolecularly connected to the entry channel, whereas rearrangements of n-N₃H₅ into NH₃NNH₂ and NH₃NHNH immediately lead to bimolecular products (e.g., via TS3 and TS4 in 1,2- and 1,3-NH₃ elimination reactions, respectively).

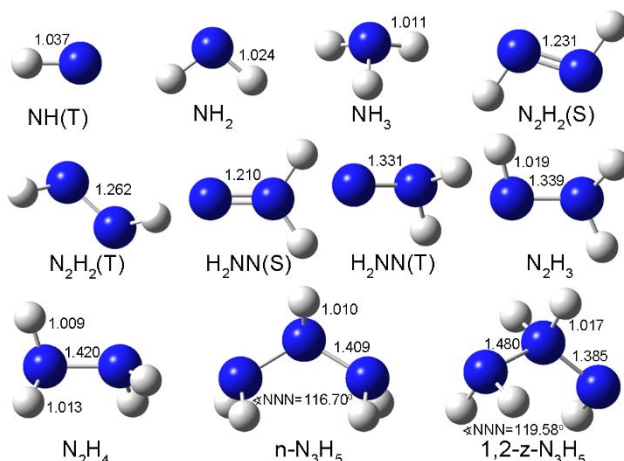


Figure 2. Geometric representation of species on the N_3H_5 PES optimized at the $\omega B97X-D3/6-311++G(3df,3pd)$ level of theory. Bond orders shown for illustration purpose only. Bond lengths are in Å and angles in degrees. Quantitative geometric data was added where it benefits the discussion; geometric coordinates for all species are available in the Supporting Information.

In addition to recombining to form $n-N_3H_5$, $N_2H_3 + NH_2$ can also react to directly form bimolecular products without going through the $n-N_3H_5$ well (see dashed lines in Fig. 1). On the singlet surface, disproportionation reactions proceed barrierlessly, forming either $N_2H_2(S) + NH_3$ or $H_2NN(S) + NH_3$. The triplet surface accommodates two hydrogen abstraction reactions via TS1 and TS2, forming $N_2H_4 + NH(T)$, and $H_2NN(T) + NH_3$, respectively, as well as a barrierless reaction forming $N_2H_2(T) + NH_3$. The rate of the barrierless disproportionation reaction $N_2H_3 + NH_2 \leftrightarrow H_2NN(S) + NH_3$ (Reaction B2 in Table 2) was estimated by ascribing an activation energy of zero to the rate of the respective non-barrierless triplet reaction; in this estimation the rate of the latter was refitted, constraining its temperature exponent to be 0.5 to obey the collision theory. The rate of $N_2H_3 + NH_2 \leftrightarrow N_2H_2(S) + NH_3$ was adopted from Dean and Bozzelli⁶³ (Table 2). No rate was assigned for the $N_2H_3 + NH_2 \leftrightarrow N_2H_2(T) + NH_3$ reaction, which leads to the least stable product channel in the system.

We note that optimization efforts of $N_3H_5(T)$ at the $\omega B97X-D3/6-311++G(3df,3pd)$ level of theory resulted in conformers that could be further stabilized by rotating one of the dihedral angles in the molecule. However, all such rotations (of the two identical rotors) resulted in β -scission of the central hydrogen atom, yielding $i-N_3H_4 + H$. Since $N_3H_5(T)$ rapidly dissociates, intersystem crossing (ISC) behavior in the N_3H_5 PES is expected to be negligible. Additional ISC effects might play a role in the exit channels of this PES, and were not determined within the present framework.

1
2
3 Reactions R1 and R2 (Table 2) describe hydrogen abstractions between N_2H_3 and NH_2 , where
4
5 the abstracting radical is different in each reaction. Both transition states, TS1 and TS2 (Fig. 3)
6
7 have similar angles between the atoms participating in the reaction, $\angle NHN$, of about 160-165°.
8
9 The reactions are synchronous and resemble the reactants geometry in the exothermic direction:
10
11 TS1 has a 16.0% N–H bond stretch fraction relative to N_2H_4 , and a 31.5% stretch relative to NH_2 ,
12
13 while TS2 has 10.3% and 40.8% stretches relative to N_2H_3 and NH_3 , respectively. Bond stretch
14
15 fractions throughout the discussion are defined as $(r_{TS} - r_{stable}) / r_{stable}$, where r_{stable} and r_{TS} are the
16
17 relevant bond lengths in the stable species (either reactant or product, where this bond exists)
18
19 and the TS, respectively. In the exothermic direction, Reaction R2 has an exceptionally low energy
20
21 barrier of just 4.8 kJ mol⁻¹ (Fig. 1). It could be explained by the hydrogen bond formed between
22
23 the nitrogen atom in the abstracting NH_2 group and one of the hydrogen atoms in N_2H_3 , stabilizing
24
25 this saddle point (Fig. 4).
26
27
28
29
30
31

32 The transition state of Reaction R3, leading to $H_2NN(S) + NH_3$ from the n- N_3H_5 isomer via a 1,2-
33
34 NH_3 elimination route, is asynchronous, characterized by relatively large stretches in both N–N
35
36 (46.0%) and terminal N–H (36.6%) bonds. These relatively large stretches explain the high E0 of
37
38 TS3, 128.3 and 183.9 kJ mol⁻¹ above the $H_2NN(S) + NH_3$ and n- N_3H_5 wells, respectively. The N–H
39
40 bond stretch fraction in the intermediate nitrogen site, however, is significantly lower (6.8%). The
41
42 $\angle NNN$ backbone angle is smaller than in the n- N_3H_5 isomer (108.79° vs. 116.70°). Indeed, a
43
44 Mulliken electronic population analysis⁶⁴ showed that the reacting NH_2 group (which leaves as
45
46 NH_3) and the non-reacting NH_2 group have net formal charges of -0.33 and +0.24, respectively,
47
48 while each of these groups has a net formal charge of -0.03 in the n- N_3H_5 isomer. The resulting
49
50 electrostatic attraction forces cause the backbone angle to be smaller than in the isomer.
51
52
53
54
55
56
57

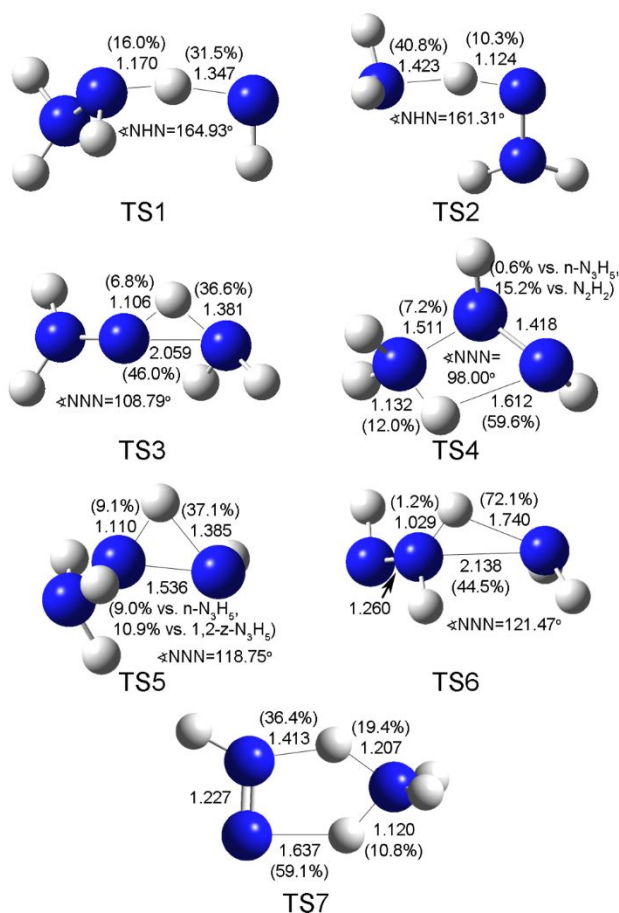
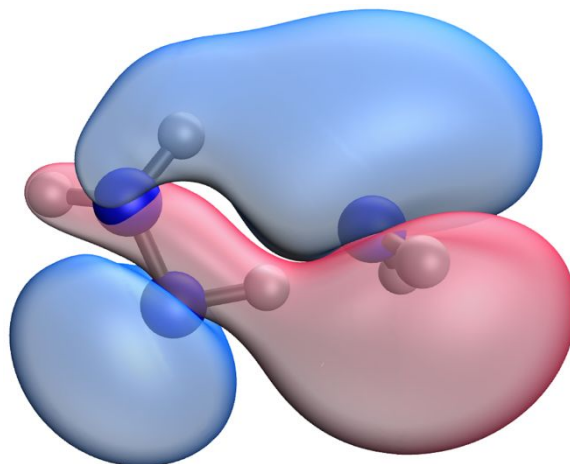


Figure 3. Geometric representation of transition states on the N_3H_5 PES optimized at the $\omega\text{B97x-D3/6-311++G(3df,3pd)}$ level of theory. Bond lengths are in Å and angles in degrees. Numbers in parentheses indicate the bond stretch fraction relative to the respective stable species. Quantitative geometric data was added where it benefits the discussion; geometric coordinates for all transition states are available in the Supporting Information.

TS4 is the saddle point of a 1,3- NH_3 elimination reaction of $n\text{-N}_3\text{H}_5$. While the cyclic group in TS3 (describing a 1,2- NH_3 elimination reaction) is -N-H-N-, the geometry of TS4 involves a very strained four-membered ring group, -N-H-N-N-, distorting the molecule backbone. The formed $\angle\text{NNN}$ angle in TS4 is significantly smaller than in $n\text{-N}_3\text{H}_5$, only 98.00° vs. 116.70° . The N-N bond not directly participating in the reaction (with a bond length of 1.418 Å, Fig. 3) is stretched relative to both reactant and product, in accordance with the high strain induced by the cyclic transition: slightly vs. $n\text{-N}_3\text{H}_5$ (0.6%), and more significantly vs. $\text{N}_2\text{H}_2(\text{S})$ (15.2%). As expected from the energetics of the reaction, the length of this bond is more similar to the respective value in

1
2
3 n-N₃H₅. This transition is asynchronous, since the hydrogen transfer has significantly progressed
4
5 (having a 12.0% stretch relative to ammonia and a 59.6% stretch relative to n-N₃H₅), while the N–
6
7 N scission has only started (7.2% stretch relative to n-N₃H₅).
8
9



10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25 **Figure 4.** Highest alpha-electron occupied molecular orbital (MO 12) in the triplet saddle point TS2,
26 computed at the ω B97x-D3/6-311++G(3df,3pd) level of theory.
27

28 The isomerization pathway via TS5 involves an internal hydrogen transfer between two
29 adjacent nitrogen atoms in n-N₃H₅; yet unlike TS3, here the intermediate nitrogen atom is a
30 hydrogen acceptor instead of a donor, resulting in a saddle point raised 82.3 kJ mol⁻¹ above TS3.
31
32 In contrast to TS3, the N–N bond is stretched significantly less (9.0% vs. n-N₃H₅ and 10.9% vs. 1,2-
33 z-N₃H₅ compared to 46.0% in TS3) and does not result in scission. The \angle NNN backbone angle is
34 also intermediate relative to the reacting isomers, and slightly closer to the angle in the higher
35 energy nitrene isomer. The distances of the migrating hydrogen with respect to both nitrogen
36 atoms are markedly uneven (9.1% vs. 1,2-z-N₃H₅ and 37.1% vs. n-N₃H₅); this criterion too suggests
37 a greater resemblance of the saddle point geometry to the nitrene isomer, in accordance with
38 the reaction energetics.
39
40
41
42
43
44
45
46
47
48
49
50
51

52 An additional 1,2-NH₃ elimination reaction in this system passes through TS6. Similarly to TS3
53 which belongs to the same reaction family, TS6 is also asynchronous with significant bond stretch
54
55
56
57

fractions with regard to 1,2-z-N₃H₅ (44.5% N–N stretch) as well as NH₃ (a 72.1% N–H stretch). The large N–H bond stretch fraction is particularly peculiar when compared to the minor N–H bond stretch fraction of the intermediate nitrogen site (only 1.2%), as well as to the respective stretch in TS3 (only 36.6%). Moreover, the N–N bond not directly participating in the reaction is closer in length to the N₂H₂(S) product (1.260 Å in TS6 vs. 1.231 Å in N₂H₂(S) and 1.385 Å in 1,2-z-N₃H₅). Finally, the formed \angle NNN backbone angle is slightly larger than in the reacting isomer (121.47° vs. 119.58°), unlike the TS3 case. A Mulliken electronic population analysis of TS6 shows that the reacting NH₂ group and the non-reacting NH group have net formal charges of -0.45 and -0.19, respectively. The resulting electrostatic repulsion forces cause the backbone angle to be wider than in the isomer. It is noted that these groups have net formal charges of +0.12 and -0.43, respectively, in 1,2-z-N₃H₅. Calculated high-pressure-limit rates for the above reactions (R1–R6), as well as estimated rates for barrierless reactions on the N₃H₅ diagram are given in Table 2.

Reaction R7 catalyzes the H₂NN(S) to N₂H₂(S) transformation using ammonia via a five member ring TS. This simultaneous hydrogen transfer TS is asynchronous. The bond lengths of the reacting hydrogens and their neighboring nitrogen atoms suggests an early TS, resembling H₂NN(S) + NH₃. Nevertheless, the N–N bond length (1.227 Å) is closer to the respective bond in N₂H₃(S) (1.231 Å) rather than to the bond in H₂NN(S) (1.210 Å).

Table 2. High-Pressure-Limit Rates of Elementary Reactions on the N₃H₅ PES^a

no. ^b	reaction	A ^c	n	Ea (kJ mol ⁻¹)	source ^d
R1	N ₂ H ₄ + NH(T) ↔ N ₂ H ₃ + NH ₂	6.09E+01	3.61	24.3	pw
R2	N ₂ H ₃ + NH ₂ ↔ H ₂ NN(T) + NH ₃	3.10E+00	3.43	-8.2	pw
R3	n-N ₃ H ₅ ↔ H ₂ NN(S) + NH ₃	1.04E+10	1.14	177.1	pw
R4	n-N ₃ H ₅ ↔ N ₂ H ₂ (S) + NH ₃	1.40E+09	0.92	213.3	pw
R5	n-N ₃ H ₅ ↔ 1,2-z-N ₃ H ₅	7.94E+09	0.85	103.9	pw
R6	1,2-z-N ₃ H ₅ ↔ N ₂ H ₂ (S) + NH ₃	6.57E+11	0.57	41.2	pw
R7	H ₂ NN(S) + NH ₃ ↔ N ₂ H ₂ (S) + NH ₃	2.07E-01	3.64	31.1	pw
B1	N ₂ H ₃ + NH ₂ ↔ n-N ₃ H ₅	5.02E+14	-0.43	0.2	ref 61

B2	$\text{N}_2\text{H}_3 + \text{NH}_2 \leftrightarrow \text{H}_2\text{NN}(\text{S}) + \text{NH}_3$	3.00E+10	0.50	0	est., pw
B3	$\text{N}_2\text{H}_3 + \text{NH}_2 \leftrightarrow \text{N}_2\text{H}_2(\text{S}) + \text{NH}_3$	9.20E+05	1.94	4.8	ref 65

^a Parameters are for the modified Arrhenius expression, $k = A T^n \exp(-E_a/[RT])$, in the 500–3000 K temperature range; the rate of Reaction B1 is valid in the 200–2500 K temperature range.

^b The R notations refer to reactions as discussed in the text, numbers match the transition states in Fig. 3. The B notations refer to barrierless reactions.

^c Units are s^{-1} , or $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ for first- or second-order reactions in the forward direction, respectively.

^d pw – calculated in the present work (see text); est. – estimated (see text).

It is noted that the N_2H_3 radical has strong coupling between large amplitude fluxional inversion of the amine group and a hindered rotor mode (Fig. S3). This behavior, characterized by discontinuities in the potential scan curve due to an abrupt geometry change in the nitrogen backbone, is known to occur in similar systems.¹⁶ A local maximum of $\sim 80 \text{ kJ mol}^{-1}$, reached before the inversion point, and a global maximum of $\sim 100 \text{ kJ mol}^{-1}$ suggest that this mode is significantly hindered. It was therefore not considered as a rotor in any of the calculations in the present work. Although thermodynamic properties of N_2H_3 are known,^{66,67} the authors are not aware of a literature discussion of its 1-D hindered rotor.

The rate of Reaction R1 (Table 2) was previously estimated by Konnov and De Ruyck⁹ based on experimental and theoretical values for other $\text{NH}(\text{T}) + \text{RH} \leftrightarrow \text{NH}_2 + \text{R}$ hydrogen abstraction reactions, implementing an activation energy correction based on the Evans-Polani correlation. The present calculation and the previous estimation were found to be similar at $\sim 1250 \text{ K}$, yet the Konnov and De Ruyck rate has a somewhat lower temperature dependence despite efforts to adjust its activation energy in that study (Fig. 5). Overall, the disagreement between these rates is acceptable, considering that one of the rates is an estimate.

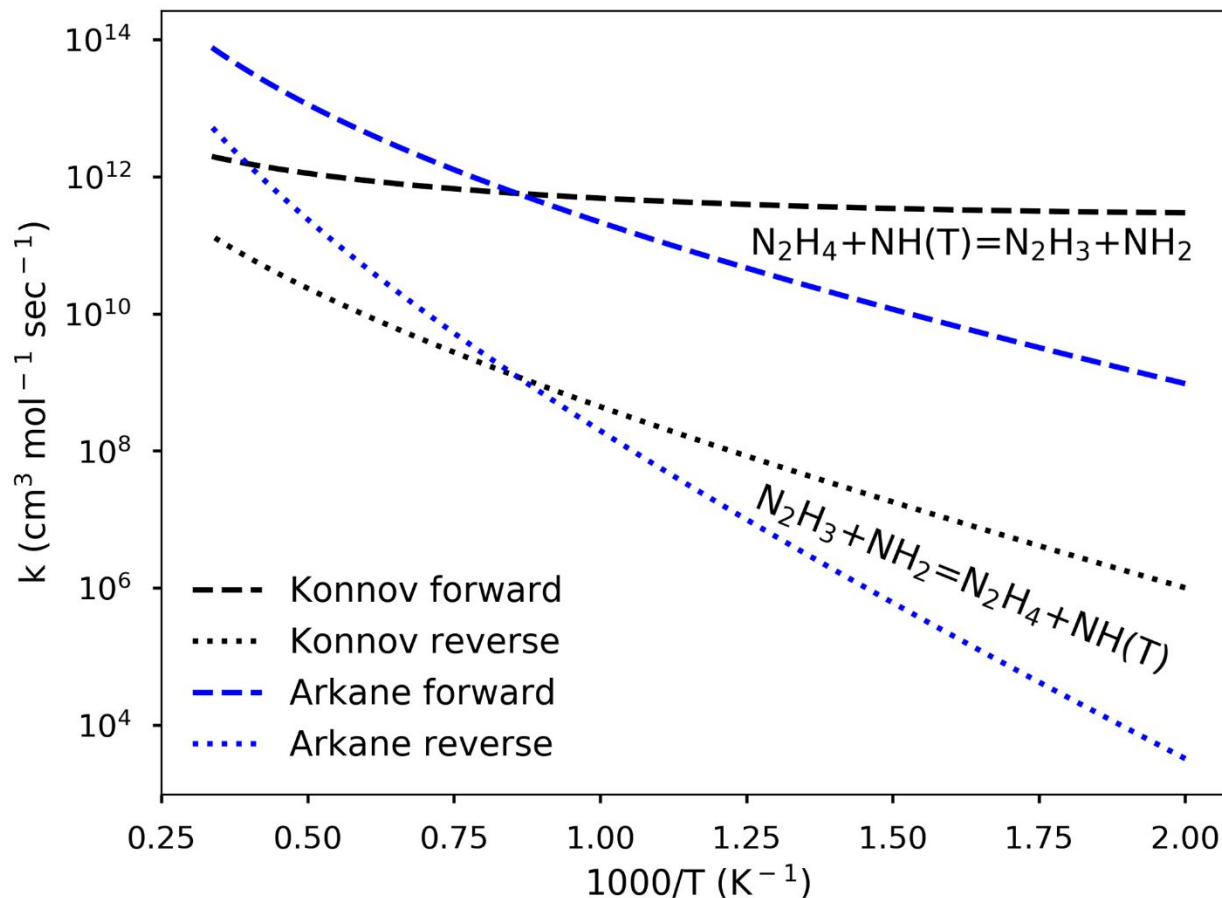


Figure 5. Rate comparisons of Reaction R1 (forward) and R-1 (reverse) between the present work calculation using Arkane and the rate estimated and reported by Konnov and De Ruyck.⁹ Thermodynamic data from Curran et al.⁶⁷ was used to compute reverse rates.

As mentioned above, while $\text{N}_2\text{H}_2(\text{S}) + \text{NH}_3$ is more stable, the formation route of $\text{H}_2\text{NN}(\text{S}) + \text{NH}_3$ has a lower barrier (TS3, Fig. 1). Indeed, the rate of the well-skipping reaction $\text{N}_2\text{H}_3 + \text{NH}_2 \leftrightarrow \text{H}_2\text{NN}(\text{S}) + \text{NH}_3$ is orders of magnitude faster than the respective rate of the competing reaction forming $\text{N}_2\text{H}_2(\text{S})$ throughout the entire temperature and pressure ranges considered here (Fig. 6 a, b). The RRK (Rice-Ramsperger-Kassel) estimation by Dean and Bozzelli⁶³ for $\text{N}_2\text{H}_3 + \text{NH}_2 \leftrightarrow \text{H}_2\text{NN}(\text{S}) +$ by a well-skipping reaction via $n\text{-N}_3\text{H}_5$ is shown here to over-estimate the respective calculated rates by about two orders of magnitude (Fig. 6 a), because Dean and Bozzelli assumed TS3 had a lower barrier. Due to higher collisional stabilization of $n\text{-N}_3\text{H}_5$, the $k(\text{T},\text{P})$ for $\text{N}_2\text{H}_3 + \text{NH}_2 \leftrightarrow \text{H}_2\text{NN}(\text{S}) + \text{NH}_3$ decreases at high pressures. Interestingly, this rate coefficient is not monotonic

1
2
3 with temperature at low pressures (Fig. 6 a) because this reaction over TS3 is competing with
4
5 dissociation back to the reactants.
6
7

8 Each of the product channels on this PES could also be formed via bimolecular non-pressure-
9
10 dependent routes from $\text{N}_2\text{H}_3 + \text{NH}_2$. While the direct route forming $\text{N}_2\text{H}_2(\text{S})$ is faster than the
11
12 respective well skipping reaction, the major formation route of $\text{H}_2\text{NN}(\text{S})$ is the well skipping
13
14 reaction at low pressures and temperatures and it is not negligible at the other studied conditions
15
16 (Fig 6 a, b). Accounting for both unimolecular and bimolecular pathways, $\text{H}_2\text{NN}(\text{S})$ formation is
17
18 favorable over $\text{H}_2\text{N}_2(\text{S})$ in this PES, contrary to a past kinetic stability estimation.¹⁷ Since rates for
19
20 both direct routes were estimated (in the present work and by Dean and Bozzelli), further work
21
22 to determine these values with lower uncertainties is desired.
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

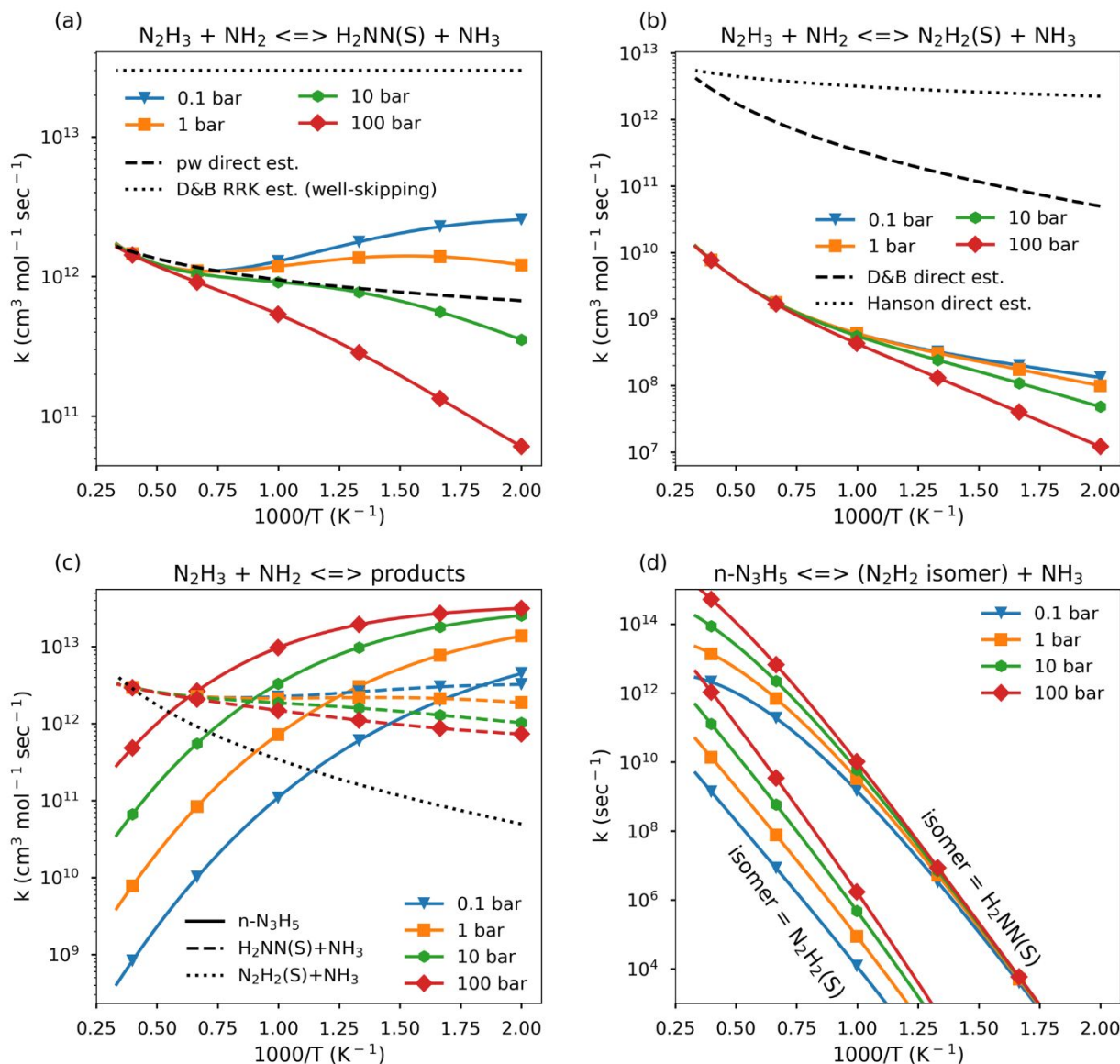


Figure 6. Rate comparisons of selected reactions on the N_3H_5 PES. 'D&B' in the legend refers to the book chapter by Dean and Bozzelli from 2000,⁶³ and 'Hanson' refers to a N/H/O rate constants review by Hanson and Salimian from 1984.⁶⁸ Present work is denoted as 'pw'. In (c), line types refer to the product/s, while the color refers to the pressure; the pressure-dependence of the $\text{N}_2\text{H}_2(\text{S}) + \text{NH}_3$ formation rate is negligible, while formation rates of $\text{H}_2\text{NN}(\text{S}) + \text{NH}_3$ include both pressure-dependent and direct routes; the updated Dean and Bozzelli rate for $\text{N}_2\text{H}_2(\text{S}) + \text{NH}_3$ is shown.

While 1,2-z- N_3H_5 formation in this network is negligible (rates not shown), n- N_3H_5 formation is significant due to the relatively high barriers surrounding this isomer (Fig. 1). As expected, n- N_3H_5 formation becomes more significant at high pressures due to collisional stabilization (Fig. 6

c). It is also the major product in the network below a pressure-dependent temperature threshold: at 0.1, 1, 10, 25, and 100 bar this threshold is about 550, 800, 1150, 1250, and 1600 K, respectively. The n-N₃H₅ isomer decomposes either while still excited at relatively low pressures if the temperature is high enough, forming preferably H₂NN(S) and NH₃ (Fig. 6 d), or after stabilization via hydrogen abstraction reactions mediated by the radical pool (mostly H, NH₂, and N₂H₃ in hydrazine decomposition systems). All relevant pressure-dependent rate coefficients for this PES are available in the Supporting Information.

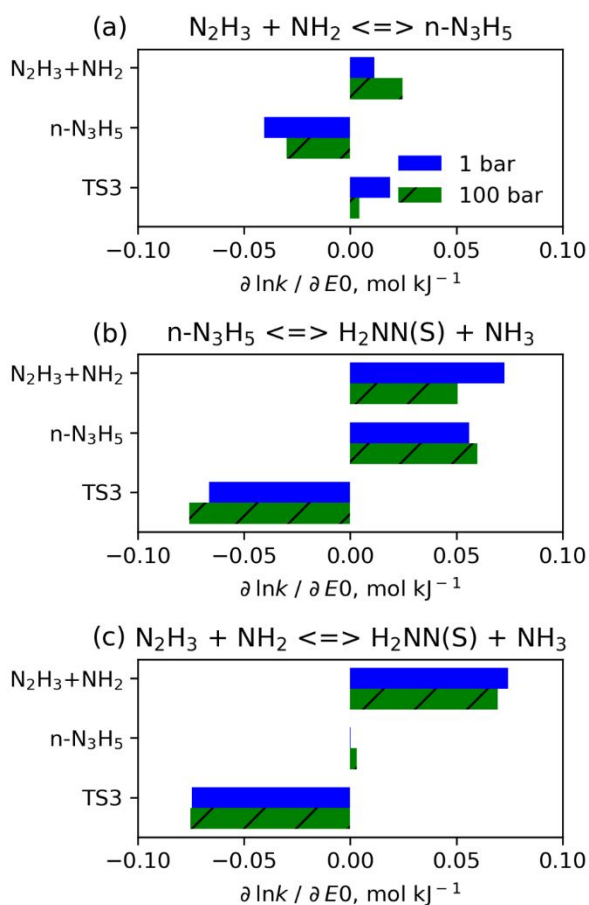


Figure 7. Normalized sensitivity coefficients to ZPE-corrected energies of N₂H₃ + NH₂, n-N₃H₅, and TS3 for selected pressure-dependent rates on the N₃H₅ potential at 1 and 100 bar and at 1500 K.

A sensitivity analysis of pressure-dependent rates on the N₃H₅ PES was conducted, implementing the chemically-significant eigenstate approach.^{69,70} This approach is more accurate

1
2
3 than the MSC approximation, yet less robust, i.e., often fails to converge for relatively large
4
5 systems. Therefore, only the $\text{N}_2\text{H}_3 + \text{NH}_2$, $n\text{-N}_3\text{H}_5$, and $\text{H}_2\text{NN}(\text{S}) + \text{NH}_3$ species on the N_3H_5 PES
6
7 were considered for the sensitivity analysis. Results for three selected pressure-dependent
8
9 reactions, describing $\text{H}_2\text{NN}(\text{S}) + \text{NH}_3$ formation either via formation of the $n\text{-N}_3\text{H}_5$ intermediate
10
11 or skipping the isomer well are shown (Fig. 7).
12
13
14

15 The sensitivity coefficients for the $\text{N}_2\text{H}_3 + \text{NH}_2 \leftrightarrow n\text{-N}_3\text{H}_5$ reaction (Fig. 7 a) suggest that this
16
17 reaction is in the pressure-dependent “fall-off” region at 1 bar and 1500 K. Increasing E0 of either
18
19 the $\text{N}_2\text{H}_3 + \text{NH}_2$ or the $n\text{-N}_3\text{H}_5$ wells changes the density of states around the entry well, increasing
20
21 or decreasing the rate, respectively. The sensitivity coefficients for $n\text{-N}_3\text{H}_5$ are lower at the higher
22
23 pressure, since at higher pressures the excited complex lifetime is much shorter, leading to less
24
25 significant competition from the route via TS3. The $\text{N}_2\text{H}_3 + \text{NH}_2$ well has a higher sensitivity
26
27 coefficient at the higher pressure, since the leak rate through the submerged barrier TS3 forming
28
29 $\text{H}_2\text{NN}(\text{S}) + \text{NH}_3$ is much lower at this condition, and a change in the entrance well E0 has a larger
30
31 relative impact.
32
33
34
35
36

37 The $n\text{-N}_3\text{H}_5 \leftrightarrow \text{H}_2\text{NN}(\text{S}) + \text{NH}_3$ reaction rate has a complex dependency on E0 of the adduct,
38
39 the $\text{N}_2\text{H}_3 + \text{NH}_2$ asymptote, and TS3 (Fig. 7 b). Perturbing the $n\text{-N}_3\text{H}_5$ well or the TS3 saddle point
40
41 results in the expected behavior of the system: increasing E0 of $n\text{-N}_3\text{H}_5$ or TS3 increases or
42
43 decreases the rate, respectively. The system is slightly more sensitive to these parameters at the
44
45 higher pressure (unlike the previous case) since this is a thermally activated reaction. Increasing
46
47 E0 of the $\text{N}_2\text{H}_3 + \text{NH}_2$ channel results in a slower reverse rate ($n\text{-N}_3\text{H}_5 \leftrightarrow \text{N}_2\text{H}_3 + \text{NH}_2$), changing
48
49 the branching ratio more in favor of the $\text{H}_2\text{NN}(\text{S}) + \text{NH}_3$ products. As the pressure increases, the
50
51
52
53
54
55
56
57

1
2
3 reverse reaction becomes even less favorable, as reflected in the respective sensitivity
4
5 coefficients at the different pressures.
6
7

8 The rate coefficient of the well-skipping reaction $\text{N}_2\text{H}_3 + \text{NH}_2 \leftrightarrow \text{H}_2\text{NN}(\text{S}) + \text{NH}_3$ (Fig 7 c) is
9
10 sensitive to the energies of the entry channel and transition state, as expected. Increasing E_0 of
11
12 the entry channel broadens the energy gap between this well and TS3, resulting in a higher rate,
13
14 while increasing E_0 of TS3 has the opposite effect. This rate coefficient is relatively insensitive to
15
16 the energy of $n\text{-N}_3\text{H}_5$.
17
18

19
20 The pressure-dependent rate sensitivity analysis allows one to assess the effects of
21
22 uncertainties in this system. All sensitivity coefficients had values below 0.1 mol kJ^{-1} . The
23
24 sensitivity coefficients of the important $\text{N}_2\text{H}_3 + \text{NH}_2 \leftrightarrow n\text{-N}_3\text{H}_5$ reaction, which has a significant
25
26 flux in this system (Fig. 6 c), were below 0.05 mol kJ^{-1} . Therefore, if we can determine the E_0 's to
27
28 within about 10 kJ mol^{-1} , the rate coefficient uncertainty due to uncertainties in energies will be
29
30 less than a factor of 2.
31
32
33

34
35 To assess the uncertainties due to estimations of barrierless reaction rates, we conducted a
36
37 sensitivity analysis for the pressure-dependent rate coefficient of $\text{N}_2\text{H}_3 + \text{NH}_2 \leftrightarrow \text{H}_2\text{NN}(\text{S}) + \text{NH}_3$
38
39 by perturbing the PES entry channel, $\text{N}_2\text{H}_3 + \text{NH}_2 \leftrightarrow n\text{-N}_3\text{H}_5$. At 1, 15, and 80 bar these normalized
40
41 (dimensionless) sensitivity coefficients were 0.06, 0.10, and 0.14, respectively. At 15 bar, for
42
43 example, perturbing the rate coefficient of the barrierless entry channel by factors of 1.05 and
44
45 1.50 resulted in 0.5% or 3.4% change, respectively, in the $k(\text{T,P})$ of $\text{N}_2\text{H}_3 + \text{NH}_2 \leftrightarrow \text{H}_2\text{NN}(\text{S}) + \text{NH}_3$.
46
47
48
49

50 We note that at high temperatures well merging could add additional uncertainties to the
51
52 calculated rates. For example, at high enough temperatures the $1,2\text{-z-N}_3\text{H}_5$ isomer could merge
53
54 with the $\text{N}_2\text{H}_2(\text{S}) + \text{NH}_3$ product well. Calculating the pressure-dependent rate of the well-skipping
55
56
57

1
2
3 reaction $\text{N}_2\text{H}_2 + \text{NH}_2 \leftrightarrow \text{N}_2\text{H}_2(\text{S}) + \text{NH}_3$ after forcing the above wells to merge has no significant
4
5 effect at 1000 K, yet reduces the rate by a factor of 1.25 at 3000 K.
6
7

8 **3.2. The N_4H_6 system**

9

10 High N_2H_3 concentration may lead to high fluxes on the N_4H_6 potential. The N_3H_5 and N_4H_6
11 systems are related since $\text{H}_2\text{NN}(\text{S})$, a major product of the N_3H_5 PES, could react with hydrazine
12 which has a high concentration at early times in the system. The $\text{N}_2\text{H}_4 + \text{H}_2\text{NN}(\text{S})$ well, in turn, is
13 one of the entry channels on the potential. Nevertheless, it is noted that $\text{H}_2\text{NN}(\text{S})$ may have more
14 important formation routes such as N_2H_3 disproportionation reactions. An additional entry
15 channel on this potential is $\text{N}_2\text{H}_3 + \text{N}_2\text{H}_3$. These two channels are inter-convertible bimolecularly
16 (Fig. 8).
17
18
19
20
21
22
23
24
25
26

27 Various non-P-dependent dissociation products could be formed from the two reacting N_2H_3
28 radicals on both the singlet and triplet surfaces, of which the $\text{N}_2\text{H}_4 + \text{N}_2\text{H}_2(\text{S})$ well is particularly
29 stable. For simplicity, the highly energetic wells $\text{NH}_3\text{NH} + \text{H}_2\text{NN}(\text{S})$, $\text{NH}_3\text{NH} + \text{H}_2\text{NN}(\text{T})$, and NH_3NH
30 + $\text{N}_2\text{H}_2(\text{T})$ with energies (on the scale selected for Fig. 8) of 183.1, 247.5, and 259.6 kJ mol^{-1} ,
31 respectively, are not shown. Two additional highly energetic product wells of the barrierless
32 reactions $1,2\text{-z-}\text{N}_4\text{H}_6 \leftrightarrow \text{NHNH}_2\text{NH} + \text{NH}_2$ and $2,3\text{-z-}\text{N}_4\text{H}_6 \leftrightarrow \text{NH}_2\text{NH}_2\text{N} + \text{NH}_2$ with energies of 682.7
33 and 706.4 kJ mol^{-1} , respectively, were excluded. Geometric representations of relevant species
34 and saddle points are given in Figs. 9, 10, respectively. Table S2 lists point groups, rotational
35 constants, and unscaled vibrational frequencies for all relevant species and transition states.
36
37
38
39
40
41
42
43
44
45
46
47
48
49

50 The high pressure limit rate for the entry channel $\text{N}_2\text{H}_3 + \text{N}_2\text{H}_3 \leftrightarrow \text{n-}\text{N}_4\text{H}_6$ (Reaction B4, Table
51 3) was estimated using RMG³⁰ based on its radical recombination reaction family
52 (“R_Recombination”). This rate was estimated to be slower by a factor of 2 with respect to the
53
54
55
56
57

1
2
3 estimate of Zhang et al. for the similar recombination Reaction B1 (Table 2).⁶¹ The high pressure
4
5 limit rates for the exit channels $n\text{-N}_4\text{H}_6 \leftrightarrow n\text{-N}_3\text{H}_4 + \text{NH}_2$, $1,2\text{-z-N}_4\text{H}_6 \leftrightarrow \text{NHNH}_2\text{NH} + \text{NH}_2$, and $2,3\text{-z-}$
6
7 $\text{N}_4\text{H}_6 \leftrightarrow i\text{N}_3\text{H}_4 + \text{NH}_2$ (Reactions B5–B7) were estimated similarly using the radical recombination
8
9 family in RMG. All high-pressure-limit rates are given in Table 3. The respective microcanonical
10
11 rates were calculated by Arkane using an inverse Laplace transform.
12
13
14

15
16 The pressure-dependent network on the singlet surface potential has three stable isomers, $n\text{-}$
17
18 N_4H_6 (tetrazane), $1,2\text{-z-N}_4\text{H}_6$, and $2,3\text{-z-N}_4\text{H}_6$ (Figs. 8, 9). Similar to the N_3H_5 case, additional
19
20 zwitterionic isomers could theoretically be thought of, yet only the two isomers listed above and
21
22 illustrated in Fig. 9 were found to be connected to the network by isomerizations. Most of the
23
24 saddle points on the N_4H_6 potential are located within a relatively narrow energy range of 56.4–
25
26 73.3 kJ mol^{-1} above $\text{N}_2\text{H}_4 + \text{H}_2\text{NN(S)}$ (Fig. 8), making the various transitions quite competitive. The
27
28 two exceptions are TS12 and TS15 with relatively high energies, which are expected to
29
30 significantly inhibit the flux through the respective channels.
31
32
33

34
35 Consequently, an interesting phenomenon emerges where a different entry channel would
36
37 favor a different final product. A chemically-activated complex formed by a $\text{N}_2\text{H}_4 + \text{H}_2\text{NN(S)}$
38
39 collision could form $n\text{-N}_4\text{H}_6$ via TS9, or $2,3\text{-z-N}_4\text{H}_6$ via TS10. The energized $n\text{-N}_4\text{H}_6$ is likely to either
40
41 be collisionally stabilized, or rapidly dissociate to form two N_2H_3 radicals, depending on the
42
43 pressure and temperature. If $2,3\text{-z-N}_4\text{H}_6$ is formed via TS10, it will rapidly dissociate to form either
44
45 $i\text{-N}_3\text{H}_4 + \text{NH}_2$ or $\text{NH}_2\text{NNH} + \text{NH}_3$.
46
47
48

49
50 On the other hand, an excited complex formed by a $\text{N}_2\text{H}_3 + \text{N}_2\text{H}_3$ collision will most likely be
51
52 collisionally stabilized, forming $n\text{-N}_4\text{H}_6$, or dissociate back to $\text{N}_2\text{H}_3 + \text{N}_2\text{H}_3$. The alternative
53
54 pathways for continued reaction via TS9 or TS11, or the barrierless dissociation to $n\text{-N}_3\text{H}_4 + \text{NH}_2$
55
56
57

are all significantly uphill compared to the $\text{N}_2\text{H}_3 + \text{N}_2\text{H}_3$ entry channel. Note that the $\text{N}_2\text{H}_3 + \text{N}_2\text{H}_3$ and $\text{N}_2\text{H}_4 + \text{H}_2\text{NN}(\text{S})$ entry channels are interconvertible bimolecularly via a relatively low energy saddle point, TS8, but $\text{N}_2\text{H}_3 + \text{N}_2\text{H}_3$ is more likely to undergo barrierless disproportionation to $\text{N}_2\text{H}_3 + \text{N}_2\text{H}_2(\text{S})$.

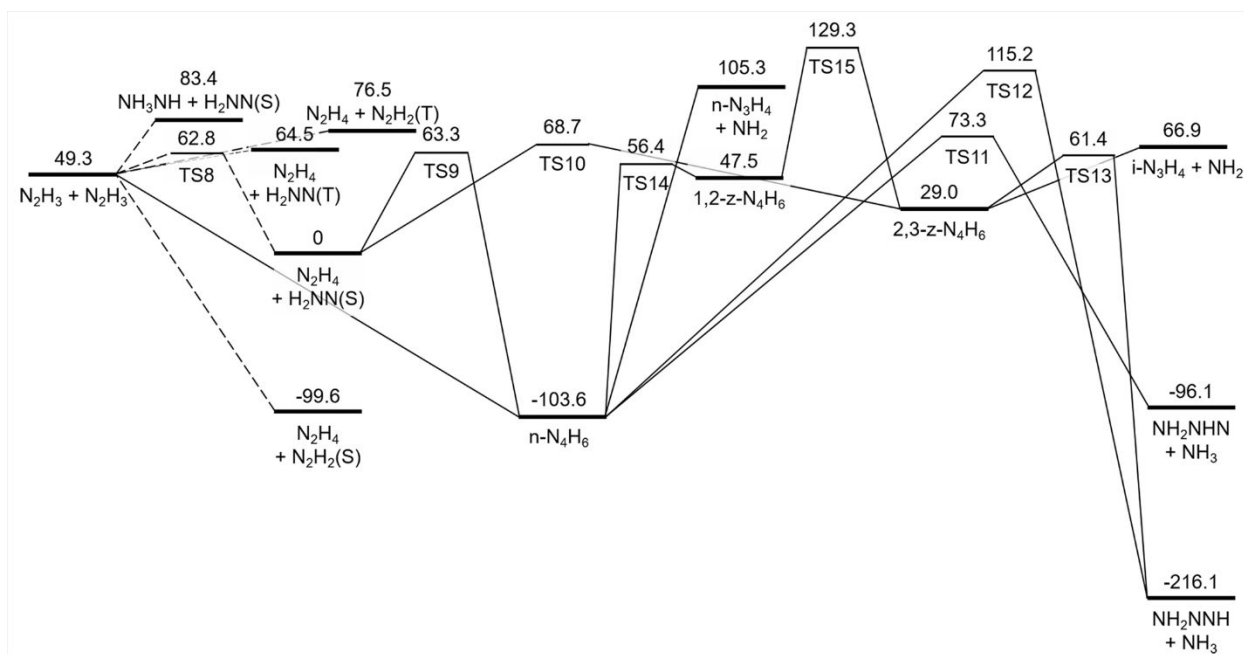


Figure 8. Reaction path diagram for the N_4H_6 potential. Dashed lines represent non-pressure-dependent pathways. (S) and (T) represent singlet or triplet multiplicities, respectively. Energies are in kJ mol^{-1} , and scaled relative to the $\text{N}_2\text{H}_4 + \text{H}_2\text{NN}(\text{S})$ entry channel, which was set at zero.

TS8 is the saddle point of the $\text{N}_2\text{H}_3 + \text{N}_2\text{H}_3$ disproportionation reaction forming $\text{N}_2\text{H}_4 + \text{H}_2\text{NN}(\text{S})$. It is an early and synchronous transition state, as expected from the reactants and products energetics. It is noted that this reaction was found to be intrinsically different from a similar reaction on the N_3H_5 potential, $\text{N}_2\text{H}_3 + \text{NH}_2 \leftrightarrow \text{H}_2\text{NN}(\text{S}) + \text{NH}_3$ (Reaction B2, Table 2), where the latter was determined to be barrierless.

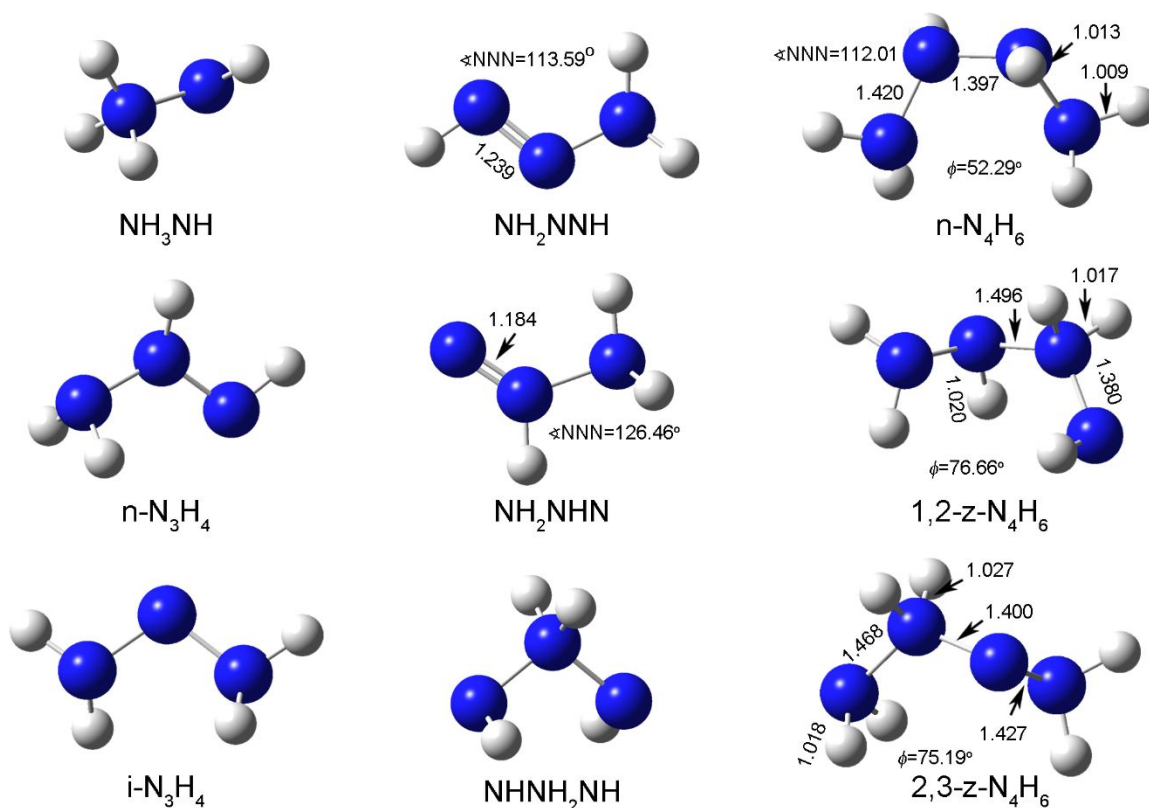


Figure 9. Geometric representation of species on the N_4H_6 PES optimized at the ω B97x-D3/6-311++G(3df,3pd) level of theory. Species already given in Fig. 2 were not reproduced here. Bond orders shown for illustration purpose only. Bond lengths are in Å and angles in degrees. ϕ is the dihedral angle between the four nitrogen backbone atoms. Quantitative geometric data was added where it benefits the discussion; geometric coordinates for all species are available in the Supporting Information.

TS9, a saddle point of a nitrene insertion into an N–N bond, is asynchronous. Most interestingly, the N–N bond length in the substructure originated from N_2H_4 is shorter than the respective bond lengths in both the reactant N_2H_4 and the product $n-N_4H_6$ (1.379 vs. 1.420 and 1.397 Å, respectively). TS8 and TS9 are geometrically and energetically similar (Figs. 8, 10). The major difference between these geometries is the orientation of the terminal hydrogens not directly participating in the reaction, which causes the complex to either recombine or fall apart due to electrostatic forces.

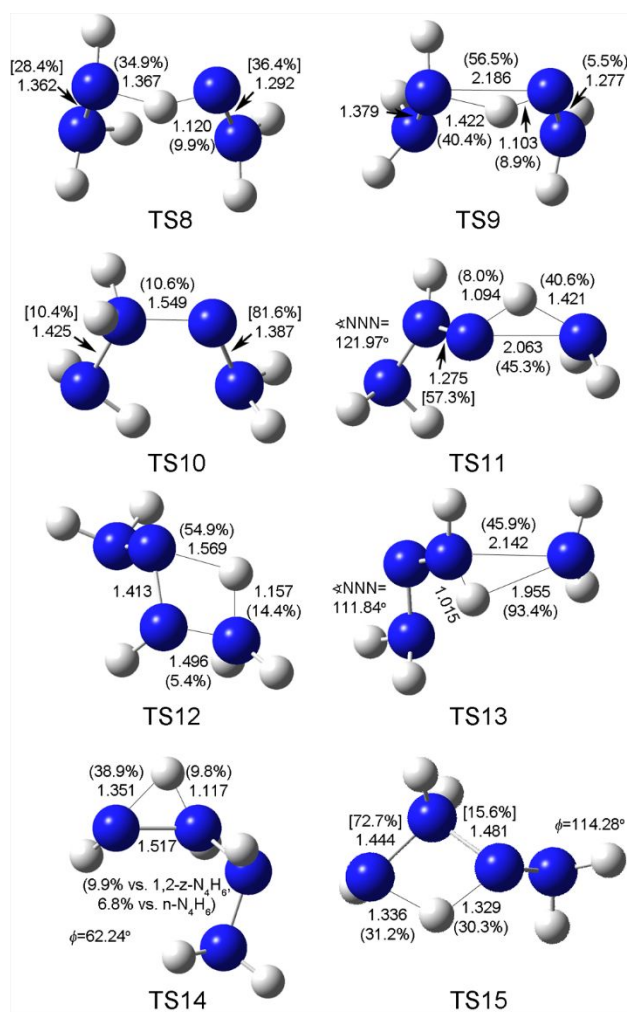


Figure 10. Geometric representation of transition states on the N_4H_6 PES optimized at the $\omega\text{B97x-D3/6-311++G(3df,3pd)}$ level of theory. Bond lengths are in Å and angles in degrees. Numbers in parentheses indicate the bond stretch fraction relative to the respective stable species. Numbers in brackets indicate the relative bond stretch fraction out of the total change between the respective reactant and product in the direction specified in Table 3. ϕ is the dihedral angle between the four nitrogen backbone atoms. Quantitative geometric data was added where it benefits the discussion; geometric coordinates for all transition states are available in the Supporting Information.

The addition reaction $\text{N}_2\text{H}_4 + \text{H}_2\text{NN}(\text{S}) \leftrightarrow 2,3\text{-z-N}_4\text{H}_6$ passes through TS10. This TS has a similar geometry to the product except the central N–N bond has stretched significantly. It is an asynchronous transition in which the N–N bond length of the $\text{H}_2\text{NN}(\text{S})$ reactant stretches considerably (81.6% stretch fraction) before reaching the saddle point while the N–N bond length of the N_2H_4 reactant hardly stretches (10.4% stretch fraction). Relative bond stretch fractions

throughout the discussion are defined as $(r_{\text{TS}} - r_{\text{reactant}}) / (r_{\text{product}} - r_{\text{reactant}})$, where r_{reactant} , r_{product} , and r_{TS} are the relevant bond lengths in the reactant, product, and the TS, respectively.

Two reactions of the 1,2-NH₃ elimination family on this potential pass through transition states TS11 and TS13. In both cases, the \angle NNN backbone angles of the forming products in the TS are close to the values of the stable NH₂NHN and NH₂NNH products, respectively. Both are asynchronous, primarily characterized by a highly stretched N–N bond of the leaving NH₂ group (45.3% and 93.4%, respectively), and a low stretch of the N–H bond to be ruptured. In fact, the respective N–H bond in TS13 is shorter than in the reactant and overall the geometry and energies indicate that NH₂ was nearly dissociated but grabbed an H atom as it departed. Methods developed for roaming reactions⁷¹ may be helpful for better evaluating this rate.

A 1,3-NH₃ elimination reaction on this surface, $n\text{-N}_4\text{H}_6 \leftrightarrow \text{NH}_2\text{NNH} + \text{NH}_3$, has a strained four-membered ring transition geometry, TS12. This transition state is also asynchronous with the central N–N bond stretched relative to both reactants and products, and a small \angle NNN ring angle of 98.78°, all of which are similar characteristics to TS4 (Fig. 3).

TS14 and TS15 are saddle points of isomerization reactions on this surface: $n\text{-N}_4\text{H}_6 \leftrightarrow 1,2\text{-z-N}_4\text{H}_6$ and $1,2\text{-z-N}_4\text{H}_6 \leftrightarrow 2,3\text{-z-N}_4\text{H}_6$. Note that no direct reaction was identified between $n\text{-N}_4\text{H}_6$ and $2,3\text{-z-N}_4\text{H}_6$. Exhaustive searches for such saddle point always lead to dissociation of the complex into N₂H₄ and H₂NN(S), as this pathway resembles the geometry of TS9 (Fig. 10). The transition geometry of TS14 is synchronous and late as expected from the reaction energetics. Facilitating the internal hydrogen transfer in this reaction causes the N–N bond over which this transfer occurs to stretch relative to both relevant isomers. The geometry of TS15, on the other hand, is asynchronous; although the hydrogen stretches nearly evenly on both sides (30.3% and

31.2%), the outer N–N bond stretches considerably (72.7% relative bond stretch fraction) while the internal N–N bond stretches slightly (15.6% relative bond stretch fraction).

Table 3. High-Pressure-Limit Rates of Elementary Reactions on the N_4H_6 PES^a

no. ^b	reaction	A ^c	n	Ea (kJ mol ⁻¹)	source ^d
R8	$N_2H_3 + N_2H_3 \leftrightarrow N_2H_4 + H_2NN(S)$	1.11E-01	3.21	-1.5	pw
R9	$N_2H_4 + H_2NN(S) \leftrightarrow n-N_4H_6$	4.73E-01	3.55	50.6	pw
R10	$N_2H_4 + H_2NN(S) \leftrightarrow 2,3-z-N_4H_6$	2.29E+00	2.96	55.4	pw
R11	$n-N_4H_6 \leftrightarrow NH_2NHN + NH_3$	3.00E+12	0.83	178.7	pw
R12	$n-N_4H_6 \leftrightarrow NH_2NNH + NH_3$	7.70E+10	0.84	214.1	pw
R13	$2,3-z-N_4H_6 \leftrightarrow NH_2NNH + NH_3$	4.03E+13	0.26	38.7	pw
R14	$n-N_4H_6 \leftrightarrow 1,2-z-N_4H_6$	7.90E+11	0.59	158.6	pw
R15	$1,2-z-N_4H_6 \leftrightarrow 2,3-z-N_4H_6$	1.74E+10	0.91	74.4	pw
B4	$N_2H_3 + N_2H_3 \leftrightarrow n-N_4H_6$	2.51E+14	-0.43	0.2	est., pw
B5	$n-N_3H_4 + NH_2 \leftrightarrow n-N_4H_6$	5.02E+14	-0.43	0.2	est., pw
B6	$NHNH_2NH + NH_2 \leftrightarrow 1,2-z-N_4H_6$	5.02E+14	-0.43	0.2	est., pw
B7	$i-N_3H_4 + NH_2 \leftrightarrow 2,3-z-N_4H_6$	1.17E+16	-1.26	2.8	est., pw
B8	$N_2H_3 + N_2H_3 \leftrightarrow N_2H_4 + N_2H_2(S)$	1.20E+13	0	0	ref [9]

^a Parameters are for the Modified Arrhenius Expression, $k = A T^n \exp(-E_a/[RT])$, in the 500–3000 K Temperature Range.

^b The R notations refer to reactions as discussed in the text, numbers match the transition states in Fig. 10. The B notations refer to barrierless reactions.

^c Units are s⁻¹, or cm³ mol⁻¹ s⁻¹ for first- or second-order reactions in the forward direction, respectively.

^d pw – calculated in the present work (see text); est. – estimated (see text).

The $n-N_4H_6$ formation rate is higher when entering from the $N_2H_3 + N_2H_3$ channel, compared to $N_2H_4 + H_2NN(S)$ (Fig. 11), due to the relatively high energy barrier in the later (Fig. 8). As expected, more $n-N_4H_6$ is formed with respect to both entry channels as the pressure increases. The rate coefficient of the estimated Reaction B4 (Table 3) is within a factor of 2 from the rate of the calculated and comparable Reaction B1 (Table 2) forming $n-N_3H_5$ for all studied conditions (Fig. 6 c, Fig. 11).

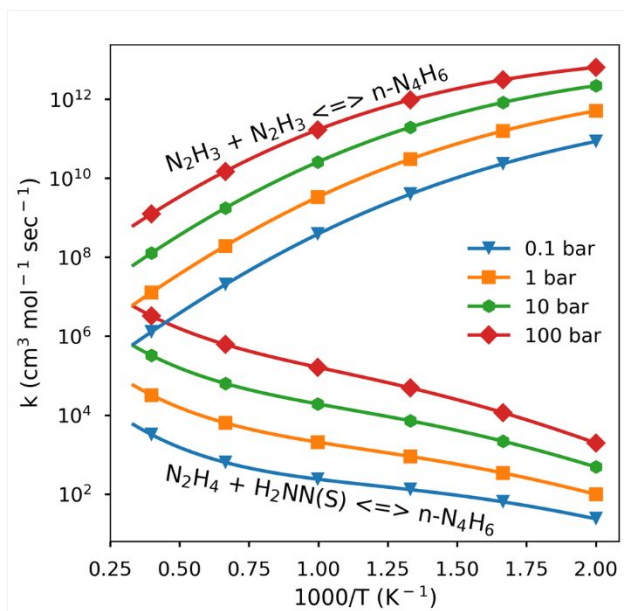


Figure 11. Rate coefficient comparison of $n\text{-N}_4\text{H}_6$ formation from each of the entry channels as a function of temperature and pressure.

Rate coefficient comparison starting from each of the entry channels on the N_4H_6 potential suggests a single dominant product channel, $\text{N}_2\text{H}_4 + \text{N}_2\text{H}_2(\text{S})$, though at high pressures $n\text{-N}_4\text{H}_6$ formation is comparable; $\text{N}_2\text{H}_4 + \text{H}_2\text{NN}(\text{S})$ would preferably form $\text{N}_2\text{H}_3 + \text{N}_2\text{H}_3$ (Fig. 12 a), which in turn mostly yield $\text{N}_2\text{H}_4 + \text{N}_2\text{H}_2(\text{S})$ (Fig. 12 b). The tendency of N_2H_3 radicals to react via a disproportionation route rather than recombine to form $n\text{-N}_4\text{H}_6$ was previously observed experimentally at 298 K and 1 bar, and a branching ratio of four was determined.¹⁹ Our calculated rate for the recombination Reaction R9 at these conditions ($3.0\text{E}+12 \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$) is a factor of 3.3 lower than the disproportionation rate (Reaction R8) estimated by Konnov and De Ruyck,⁹ in accordance with the experimental observation. Consequently, the experimental observation along with the present calculations suggest that the rate of Reaction B8 could not be much lower than the value suggested by Konnov and De Ruyck⁹ at these conditions. The gap between the rates of the two routes is shown here to increase with temperature and decrease with pressure. At relatively high pressures and low temperatures, $n\text{-N}_4\text{H}_6$ formation becomes significant, yet at the conditions relevant to hydrazine decomposition (1500 K and 25 bar), the formation rate of tetrazane from

N_2H_3 recombination is two orders of magnitude lower than the formation rate of the disproportionation products, $\text{N}_2\text{H}_4 + \text{N}_2\text{H}_2(\text{S})$. Also of importance are reactions yielding $n\text{-N}_3\text{H}_4 + \text{NH}_2$, $\text{NH}_2\text{NHN} + \text{NH}_3$, while formation rates of $\text{NH}_2\text{NNH} + \text{NH}_3$ and $i\text{-N}_3\text{H}_4 + \text{NH}_2$ from the $\text{N}_2\text{H}_3 + \text{N}_2\text{H}_3$ entry channel are negligible (Fig. S11), in accordance with the discussion above.

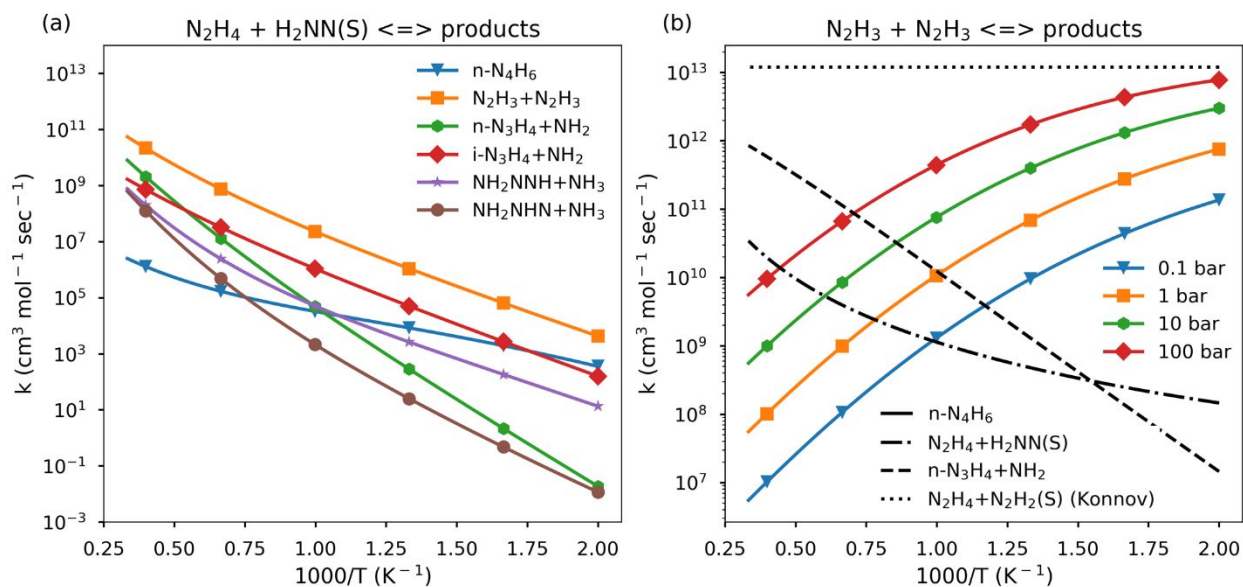


Figure 12. Rate comparisons of $\text{N}_2\text{H}_4 + \text{H}_2\text{NN}(\text{S})$ and $\text{N}_2\text{H}_3 + \text{N}_2\text{H}_3$ reactions. Rates in (a) are given at a representative pressure of 10 bar. In (b), line types refer to the product/s, while the color refers to the pressure; the pressure-dependence rate for $n\text{-N}_3\text{H}_4 + \text{NH}_2$ formation via a well-skipping reaction is negligible; the rate for $\text{N}_2\text{H}_4 + \text{H}_2\text{NN}(\text{S})$ formation includes both a direct route (via TS8) and the well-skipping route; the dotted line is an estimated rate by Konnov and De Ruyck.⁹

3.3. Thermodynamic properties

The present work emphasizes the importance of accounting for triazane ($n\text{-N}_3\text{H}_5$) when kinetically studying hydrazine decomposition systems (Fig. 6 c). Tetrazane ($n\text{-N}_4\text{H}_6$) formation in this system only becomes important at high pressures and relatively low temperatures (Fig. 12) due to fall-off into $\text{N}_2\text{H}_3 + \text{N}_2\text{H}_3$. The main decomposition pathways of triazane are formation of $\text{H}_2\text{NN}(\text{S}) + \text{NH}_3$ at high temperatures (Fig. 6 d), as well as hydrogen abstraction reactions due to interactions with the radical pool (mainly H, NH, and N_2H_3). The latter results in the formation of primary or secondary radicals, $n\text{-N}_3\text{H}_4$ or $i\text{-N}_3\text{H}_4$, respectively (Fig. 9). Preliminary RMG predictions

suggest that the $n\text{-N}_3\text{H}_4$ radical primarily decomposes into $\text{NH}_2 + \text{N}_2\text{H}_2(\text{S})$ via a beta-scission reaction, while the $i\text{-N}_3\text{H}_4$ radical primarily abstracts a hydrogen atom from $\text{N}_2\text{H}_2(\text{S})$, forming $n\text{-N}_3\text{H}_5 + \text{NNH}$. Consequently, $n\text{-N}_3\text{H}_5$, $n\text{-N}_3\text{H}_4$, and $i\text{-N}_3\text{H}_4$ should all be considered in future kinetic models of similar systems.

Table 4 Comparison of Relative EO + ZPE (kJ mol^{-1}) of $n\text{-N}_3\text{H}_5$, $n\text{-N}_3\text{H}_4$, $i\text{-N}_3\text{H}_4$, and $n\text{-N}_4\text{H}_6$ at the CBS-QB3, CCSD(T)-F12a/aug-cc-pVTZ// $\omega\text{B97x-D3/6-311++G(3df,3pd)}$, and CCSD(T)-F12a-cc-pVTZ-F12// $\omega\text{B97x-D3/6-311++G(3df,3pd)}$ + BAC Levels of Theory.

species	CBS-QB3	CCSD(T)-F12a/aug-cc-pVTZ	CCSD(T)-F12a/cc-pVTZ-F12 + BAC ^a	T1 ^b
$n\text{-N}_3\text{H}_5$	0	0	0	0.0104
$n\text{-N}_3\text{H}_4$	125.3	127.5	126.8	0.0234
$i\text{-N}_3\text{H}_4$	86.1	89.1	88.2	0.0211
$n\text{-N}_4\text{H}_6$	92.3	95.9	96.2	0.0109

^a Using bond additivity corrections (BAC)

^b The T1 diagnostic parameter,²⁸ calculated using the CCSD(T)-F12a/aug-cc-pVTZ level of theory

Energies at zero K of $n\text{-N}_3\text{H}_5$, $n\text{-N}_3\text{H}_4$, $i\text{-N}_3\text{H}_4$, and $n\text{-N}_4\text{H}_6$ were compared using methods described above, and are given in Table 4. The CCSD(T)-F12a methods consistently predicted energy differences a few kJ mol^{-1} higher than the CBS-QB3 computation, yet well within the reported CBS-QB3 2σ error bar. Thermodynamic properties were computed using Arkane at the CCSD(T)-F12a/cc-pVTZ-F12// $\omega\text{B97x-D3/6-311++G(3df,3pd)}$ level of theory, implementing rotor scans performed at the B3LYP/6-311++G(3df,3pd) level of theory (Table 5). The $n\text{-N}_3\text{H}_4$ and $i\text{-N}_3\text{H}_4$ radicals have strong coupling between large amplitude fluxional inversion and a hindered rotor modes (Figs. S6, S7), which makes it challenging to compute their heat capacities. Therefore, only RRHO enthalpies and entropies at 298 K are reported for these radicals.

Table 5 Thermodynamic Properties of $n\text{-N}_3\text{H}_5$, $n\text{-N}_3\text{H}_4$, $i\text{-N}_3\text{H}_4$, and $n\text{-N}_4\text{H}_6$ at the CCSD(T)-F12a/cc-pVTZ-F12// $\omega\text{B97x-D3/6-311++G(3df,3pd)}$ Level of Theory.^a

species	ΔH_f°	ΔS_f°	$C_p(T)^b$								
			300 K	400 K	500 K	600 K	800 K	1000 K	1500 K	2000 K	2400 K
$n\text{-N}_3\text{H}_5$	203.3	276.9	75.1	86.3	95.5	103.7	117.3	128.0	145.7	155.9	161.3
$n\text{-N}_3\text{H}_4$	322.5	274.1	–	–	–	–	–	–	–	–	–

i-N ₃ H ₄	289.6	262.7	–	–	–	–	–	–	–	–	–
n-N ₄ H ₆	299.7	289.8	80.6	99.4	115.2	128.6	150.4	166.6	191.5	205.4	213.3

^a Enthalpies are given in kJ mol⁻¹, entropies and constant pressure heat capacities are given in J mol⁻¹ K⁻¹.

^b No *C_p* values are reported for the N₃H₄ radicals, see text.

The calculated standard heat of formation and entropy of formation of n-N₃H₅ (Table 5) are comparable with respective past values calculated using the G2 method,⁷² 198.7 kJ mol⁻¹ and 261.5 J mol⁻¹ K⁻¹, respectively.¹⁷ The NASA polynomials for the thermodynamic properties of triazane and tetrazane are given in the Supporting Information.

4. Conclusions

A detailed kinetic analysis of the N₃H₅ and N₄H₆ potentials was presented. On the N₄H₆ potential, the N₂H₄ + H₂NN(S) entry channel mostly yields N₂H₃ + N₂H₃, while the N₂H₃ + N₂H₃ channel, in turn, would primarily result in the formation of N₂H₄ + N₂H₂(S) by direct disproportionation. Overall, hydrazine on this surface mainly catalyzes isomer transformation from H₂NN(S) to N₂H₂(S). At high pressures and low temperatures, tetrazane (n-N₄H₆) formation becomes significant.

Starting from the N₂H₃ + NH₂ entry channel, all bimolecular product wells on the N₃H₅ potential can be reached directly via a bimolecular reaction. In fact, the rate contribution of the well-skipping pathway forming N₂H₂(S) + NH₃ to the overall rate is negligible, while the well-skipping route forming H₂NN(S) + NH₃ has a significant contribution and dominates in the low pressure and low temperature regime. Starting from N₂H₃ + NH₂, H₂NN(S) formation is kinetically more favorable than N₂H₂(S) under 2500 K. However, triazane (n-N₃H₅) becomes the dominant product of N₂H₃ + NH₂ reaction below 550, 800, 1150, 1250, and 1600 K at 0.1, 1, 10, 25, and 100 bar,

1
2
3 respectively. Triazane is predicted to form either $\text{H}_2\text{NN}(\text{S}) + \text{NH}_3$ or primary/secondary N_3H_4
4
5 radicals, all of which should be taken into consideration in kinetic models of hydrazine.
6
7

8 Theoretical predictions of reaction rates have been derived from ab-initio transition state
9 theory coupled with master equation simulations as necessary. The determined pressure-
10 dependent rates should be of considerable utility to future efforts of kinetic modelling of
11 hydrazine decomposition and related systems.
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 **Supporting Information.** Transport properties (Table S1), stationary point properties (Table S2),
4 relaxed rotor scans (Figs. S1–S10), branching ratios of $\text{N}_2\text{H}_3 + \text{N}_2\text{H}_3$ (Fig. S11), NASA polynomials
5
6 for $n\text{-N}_3\text{H}_5$ and $n\text{-N}_4\text{H}_6$, geometric coordinates, and pressure-dependent rates
7
8
9

10 **Acknowledgments**

11
12
13
14
15 This overall project was funded primarily by the Gas Phase Chemical Physics Program of the US
16
17 Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences,
18
19 Geosciences, and Biosciences (under Award number DE-SC0014901). A.G.D. was supported by
20
21 The George J Elbaum Scholarship in Engineering, The Ed Satell Foundation, and The Zuckerman
22
23 STEM Leadership Program. K.B.M. was supported by the Army Research Office under award
24
25 number W911NF1710531. A.W.J. was supported by the US Department of Energy, Office of Basic
26
27 Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences through Argonne
28
29 National Laboratory. All financial support is gratefully acknowledged. We thank Dr. Hiroumi Tani
30
31 from Japan Aerospace Exploration Agency (JAXA) for helpful conversations.
32
33
34
35
36
37

38 **References**

- 39
40
41 (1) Rothgery, E. F. *Hydrazine and its Derivatives*; 2004; Vol. 13.
42
43 <https://doi.org/10.1002/0471238961.0825041819030809.a01.pub2>.
44
45
46 (2) Gray, P.; Lee, J. C.; Spencer, M. Combustion, Flame and Explosion of Hydrazine and
47
48 Ammonia I — The Spontaneous Ignition of Pure Gaseous Hydrazine. *Combust. Flame* **1963**,
49
50 *7*, 315–321. [https://doi.org/10.1016/0010-2180\(63\)90206-2](https://doi.org/10.1016/0010-2180(63)90206-2).
51
52
53 (3) Auzanneau, M.; Roux, M. Self-Detonation Range in Inert Atmosphere of Ternary Systems
54
55
56
57

- Using Hydrogen Peroxide and Hydrazine or Hydrazine Derivatives. *Combust. Sci. Technol.* **1990**, *73*, 505–520. <https://doi.org/10.1080/00102209008951667>.
- (4) *Dynamics of Detonations and Explosions: Detonations*; Leyer, J.-C., Borisov, A. A., Kuhl, A. L., Sirignano, W. A., Eds.; American Institute of Aeronautics and Astronautics: Washington DC, 1991. <https://doi.org/10.2514/4.866067>.
- (5) Rath, M.; Schmitz, H.; Steenborg, M. Development of a 400 N Hydrazine Thruster for ESA's Atmospheric Reentry Demonstrator. In *32nd Joint Propulsion Conference and Exhibit*; American Institute of Aeronautics and Astronautics: Reston, Virginia, 1996. <https://doi.org/10.2514/6.1996-2866>.
- (6) Yang, A.-S.; Kuo, T.-C. Design Analysis of a Satellite Hydrazine Propulsion System. *J. Propuls. Power* **2002**, *18*, 270–279. <https://doi.org/10.2514/2.5966>.
- (7) Anflo, K.; Mollerberg, R.; Neff, K.; King, P. High Performance Green Propellant for Satellite Applications. In *45th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit*; American Institute of Aeronautics and Astronautics: Reston, Virginia, 2009. <https://doi.org/10.2514/6.2009-4878>.
- (8) Halat-Augier, C.; Dupre, G.; Paillard, C. E. Thermal Decomposition of Gaseous Hydrazine behind a Reflected Shock Wave. *Proc. 20th Int. Symp. Shock waves* **1996**, *2*, 893–943.
- (9) Konnov, A. A.; De Ruyck, J. Kinetic Modeling of the Decomposition and Flames of Hydrazine. *Combust. Flame* **2001**, *124*, 106–126. [https://doi.org/10.1016/S0010-2180\(00\)00187-5](https://doi.org/10.1016/S0010-2180(00)00187-5).
- (10) Hwang, D. Y.; Mebel, A. M. Reaction Mechanism of N₂/H₂ conversion to NH₃: A Theoretical Study. *J. Phys. Chem. A* **2003**, *107*, 2865–2874. <https://doi.org/10.1021/jp0270349>.

- 1
2
3 (11) Klippenstein, S. J.; Harding, L. B.; Ruscic, B.; Sivaramakrishnan, R.; Srinivasan, N. K.; Su, M.;
4 Michael, J. V. Thermal Decomposition of NH_2OH and Subsequent Reactions: Ab Initio
5 Transition State Theory and Reflected Shock Tube Experiments. *Society* **2009**, 10241–
6 10259. <https://doi.org/10.1021/jp905454k>.
7
8
9
10
11
12 (12) Asatryan, R.; Bozzelli, J. W.; Da Silva, G.; Swinnen, S.; Tho Nguyen, M. Formation and
13 Decomposition of Chemically Activated and Stabilized Hydrazine. *J. Phys. Chem. A* **2010**,
14 *114*, 6235–6249. <https://doi.org/10.1021/jp101640p>.
15
16
17
18
19 (13) Wiberg, N.; Bayer, H.; Bachhuber, H. Isolation of Tetrazene, N_4H_4 . *Angew. Chemie Int. Ed.*
20 **1975**, *14*, 177–178. <https://doi.org/10.1002/anie.197501771>.
21
22
23
24 (14) Zhao, M.; Gimarc, B. M. Strain Energies of $(\text{NH})_n$ Rings, $n = 3-8$. *J. Phys. Chem.* **1994**, *98*,
25 7497–7503. <https://doi.org/10.1021/j100082a019>.
26
27
28
29 (15) Inagaki, S.; Ishitani, Y.; Kakefu, T. Geminal Delocalization of σ -Electrons and Ring
30 Strains. *J. Am. Chem. Soc.* **1994**, *116*, 5954–5958. <https://doi.org/10.1021/ja00092a052>.
31
32
33
34 (16) Ball, D. W. High-Level Ab Initio Calculations on Hydrogen-Nitrogen Compounds.
35 Thermochemistry of Tetrazetidine, N_4H_4 . *J. Mol. Struct. THEOCHEM* **2002**, *619*, 37–43.
36
37
38
39 [https://doi.org/10.1016/S0166-1280\(02\)00397-4](https://doi.org/10.1016/S0166-1280(02)00397-4).
40
41
42 (17) Schlegel, H. B.; Skancke, A. Thermochemistry, Energy Comparisons, and Conformational
43 Analysis of Hydrazine, Triazane, and Triaminoammonia. *J. Am. Chem. Soc.* **1993**, *115*,
44 7465–7471. <https://doi.org/10.1021/ja00069a053>.
45
46
47
48 (18) Ball, D. W. Tetrazane: Hartree–Fock, Gaussian-2 and -3, and Complete Basis Set
49 Predictions of Some Thermochemical Properties of N_4H_6 . *J. Phys. Chem. A* **2001**, *105*, 465–
50 470. <https://doi.org/10.1021/jp002675u>.
51
52
53
54
55
56
57

- 1
2
3 (19) Stief, L. J. Ratio of Disproportionation to Combination of N_2H_3 Radicals. *J. Chem. Phys.*
4
5 **1970**, *52*, 4841–4845. <https://doi.org/10.1063/1.1673721>.
6
7
8 (20) Lin, Y.-S.; Li, G.-D.; Mao, S.-P.; Chai, J.-D. Long-Range Corrected Hybrid Density Functionals
9
10 with Improved Dispersion Corrections. *J. Chem. Theory Comput.* **2013**, *9*, 263–272.
11
12 <https://doi.org/10.1021/ct300715s>.
13
14
15 (21) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-consistent Molecular Orbital
16
17 Methods. XX. A Basis Set for Correlated Wave Functions. *J. Chem. Phys.* **1980**, *72*, 650–654.
18
19 <https://doi.org/10.1063/1.438955>.
20
21
22 (22) Zimmerman, P. M. Growing String Method with Interpolation and Optimization in Internal
23
24 Coordinates: Method and Examples. *J. Chem. Phys.* **2013**, *138*, 184102.
25
26 <https://doi.org/10.1063/1.4804162>.
27
28
29 (23) Gonzalez, C.; Schlegel, H. B. An Improved Algorithm for Reaction Path Following. *J. Chem.*
30
31 *Phys.* **1989**, *90*, 2154–2161. <https://doi.org/10.1063/1.456010>.
32
33
34 (24) Adler, T. B.; Knizia, G.; Werner, H.-J. A Simple and Efficient CCSD(T)-F12 Approximation. *J.*
35
36 *Chem. Phys.* **2007**, *127*, 221106. <https://doi.org/10.1063/1.2817618>.
37
38
39 (25) Knizia, G.; Adler, T. B.; Werner, H.-J. Simplified CCSD(T)-F12 Methods: Theory and
40
41 Benchmarks. *J. Chem. Phys.* **2009**, *130*, 054104. <https://doi.org/10.1063/1.3054300>.
42
43
44 (26) Dunning, T. H. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The
45
46 Atoms Boron through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
47
48 <https://doi.org/10.1063/1.456153>.
49
50
51 (27) Computational Chemistry Comparison and Benchmark Database, National Institute of
52
53 Standards and Technology (NIST), U.S. Department of Commerce, available online:
54
55
56
57
58
59
60

- 1
2
3 <https://cccbdb.nist.gov/vibscalejust.asp>; last accessed: April 2019.
4
5
6 (28) Lee, T. J.; Rice, J. E.; Scuseria, G. E.; Schaefer, H. F. Theoretical Investigations of Molecules
7
8 Composed Only of Fluorine, Oxygen and Nitrogen: Determination of the Equilibrium
9
10 Structures of FOOF, (NO)₂ and FNNF and the Transition State Structure for FNNF Cis-Trans
11
12 Isomerization. *Theor. Chim. Acta* **1989**, *75*, 81–98. <https://doi.org/10.1007/BF00527711>.
13
14
15 (29) Becke, A. D. Density-functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem.*
16
17 *Phys.* **1993**, *98*, 5648–5652. <https://doi.org/10.1063/1.464913>.
18
19
20 (30) Gao, C. W.; Allen, J. W.; Green, W. H.; West, R. H. Reaction Mechanism Generator:
21
22 Automatic Construction of Chemical Kinetic Mechanisms. *Comput. Phys. Commun.* **2016**,
23
24 *203*, 212–225. <https://doi.org/10.1016/j.cpc.2016.02.013>.
25
26
27 (31) 2019, Reaction Mechanism Generator, RMG-Py v2.3.0,
28
29 <https://github.com/ReactionMechanismGenerator/RMG-Py>.
30
31
32 (32) Shao, Y.; Gan, Z.; Epifanovsky, E.; Gilbert, A. T. B.; Wormit, M.; Kussmann, J.; Lange, A. W.;
33
34 Behn, A.; Deng, J.; Feng, X.; et al. Advances in Molecular Quantum Chemistry Contained in
35
36 the Q-Chem 4 Program Package. *Mol. Phys.* **2015**, *113*, 184–215.
37
38 <https://doi.org/10.1080/00268976.2014.952696>.
39
40
41
42 (33) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M. Molpro: A General-
43
44 Purpose Quantum Chemistry Program Package. *Wiley Interdiscip. Rev. Comput. Mol. Sci.*
45
46 **2012**, *2*, 242–253. <https://doi.org/10.1002/wcms.82>.
47
48
49 (34) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M.; Celani, P.; Györffy, W.;
50
51 Kats, D.; Korona, T.; Lindh, R.; et al. Molpro, Version 2015.1, a Package of Ab Initio
52
53 Programs. Cardiff, UK 2015.
54
55
56
57
58
59
60

- 1
2
3 (35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.;
4
5 Montgomery, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C., et al. Gaussian 03, Revision D.01,
6
7 Gaussian, Inc.: Wallingford, Ct, 2009.
8
9
10 (36) Gilbert, A. IQmol. version 2.11, <http://iqmol.org/> 2018.
11
12
13 (37) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales,
14
15 C. M.; Landis, C. R.; Weinhold, F. NBO 6.0. Theoretical Chemistry Institute, University of
16
17 Wisconsin, Madison (2013).
18
19
20 (38) Montgomery, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. A Complete Basis Set
21
22 Model Chemistry. VII. Use of the Minimum Population Localization Method. *J. Chem. Phys.*
23
24 **2000**, *112*, 6532–6542. <https://doi.org/10.1063/1.481224>.
25
26
27 (39) Simmie, J. M.; Somers, K. P. Benchmarking Compound Methods (CBS-QB3, CBS-APNO, G3,
28
29 G4, W1BD) against the Active Thermochemical Tables: A Litmus Test for Cost-Effective
30
31 Molecular Formation Enthalpies. *J. Phys. Chem. A* **2015**, *119*, 7235–7246.
32
33 <https://doi.org/10.1021/jp511403a>.
34
35
36 (40) Montgomery, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. A Complete Basis Set
37
38 Model Chemistry. VI. Use of Density Functional Geometries and Frequencies. *J. Chem.*
39
40 *Phys.* **1999**, *110*, 2822–2827. <https://doi.org/10.1063/1.477924>.
41
42
43 (41) Bao, J. L.; Zheng, J.; Alecu, I. M.; Lynch, B. J.; Zhao, Y.; D.G., T. Database of Frequency Scale
44
45 Factors for Electronic Model Chemistries
46
47 <https://comp.chem.umn.edu/freqscale/version3b2.htm>.
48
49
50 (42) Alecu, I. M.; Zheng, J.; Zhao, Y.; Truhlar, D. G. Computational Thermochemistry: Scale
51
52 Factor Databases and Scale Factors for Vibrational Frequencies Obtained from Electronic
53
54
55
56
57
58
59
60

- 1
2
3 Model Chemistries. *J. Chem. Theory Comput.* **2010**, *6*, 2872–2887.
4
5 <https://doi.org/10.1021/ct100326h>.
6
7
8 (43) Truhlar, D. G.; Garrett, B. C.; Klippenstein, S. J. Current Status of Transition-State Theory.
9
10 *J. Phys. Chem.* **1996**, *100*, 12771–12800. <https://doi.org/10.1021/jp953748q>.
11
12
13 (44) Wong, B. M.; Green, W. H. Effects of Large-Amplitude Torsions on Partition Functions:
14
15 Beyond the Conventional Separability Assumption. *Mol. Phys.* **2005**, *103*, 1027–1034.
16
17 <https://doi.org/10.1080/00268970412331333627>.
18
19
20 (45) Eckart, C. The Penetration of a Potential Barrier by Electrons. *Phys. Rev.* **1930**, *35*, 1303–
21
22 1309. <https://doi.org/10.1103/PhysRev.35.1303>.
23
24
25 (46) Kislov, V. V.; Mebel, A. M.; Aguilera-Iparraguirre, J.; Green, W. H. Reaction of Phenyl
26
27 Radical with Propylene as a Possible Source of Indene and Other Polycyclic Aromatic
28
29 Hydrocarbons: An Ab Initio/RRKM-ME Study. *J. Phys. Chem. A* **2012**, *116*, 4176–4191.
30
31 <https://doi.org/10.1021/jp212338g>.
32
33
34
35 (47) Allen, J. W.; Goldsmith, C. F.; Green, W. H. Automatic Estimation of Pressure-Dependent
36
37 Rate Coefficients. *Phys. Chem. Chem. Phys.* **2012**, *14*, 1131–1155.
38
39 <https://doi.org/10.1039/C1CP22765C>.
40
41
42 (48) Goodwin, D. G.; Moffat, H. K.; Speth, R. L. Cantera: An Object-Oriented Software Toolkit
43
44 for Chemical Kinetics, Thermodynamics, and Transport Processes, 2018.
45
46 <https://doi.org/10.5281/zenodo.170284>.
47
48
49 (49) CHEMKIN-PRO 15131, Reaction Design: San Diego, 2013
50
51
52 (50) Jasper, A. W.; Miller, J. A. Collisional Energy Transfer in Unimolecular Reactions: Direct
53
54 Classical Trajectories for $\text{CH}_4 \rightleftharpoons \text{CH}_3 + \text{H}$ in Helium. *J. Phys. Chem. A* **2009**, *113*, 5612–5619.
55
56
57

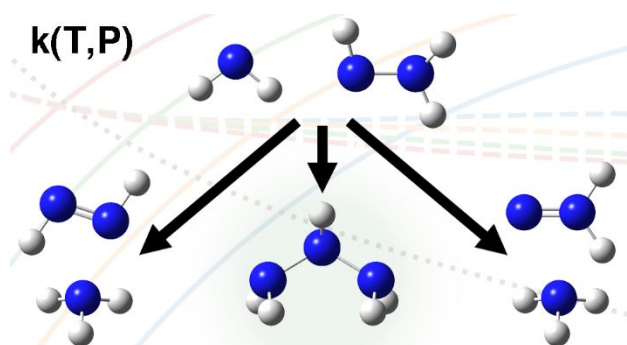
- 1
2
3 <https://doi.org/10.1021/jp900802f>.
- 4
5
6 (51) Jasper, A. W.; Miller, J. A.; Klippenstein, S. J. Collision Efficiency of Water in the
7
8 Unimolecular Reaction $\text{CH}_4 (+\text{H}_2\text{O}) \rightleftharpoons \text{CH}_3 + \text{H} (+\text{H}_2\text{O})$: One-Dimensional and Two-
9
10 Dimensional Solutions of the Low-Pressure-Limit Master Equation. *J. Phys. Chem. A* **2013**,
11
12 *117*, 12243–12255. <https://doi.org/10.1021/jp409086w>.
- 13
14
15 (52) Jasper, A. W.; Pelzer, K. M.; Miller, J. A.; Kamarchik, E.; Harding, L. B.; Klippenstein, S. J.
16
17 Predictive a Priori Pressure-Dependent Kinetics. *Science (80-.)*. **2014**, *346*, 1212–1215.
18
19 <https://doi.org/10.1126/science.1260856>.
- 20
21
22 (53) A.W., J.; M.J., D. Parameterization Strategies for Intermolecular Potentials for Predicting
23
24 Trajectory-Based Collision Parameters. *J. Chem. Theory Comput.* **2019**, No. submitted.
- 25
26
27 (54) Jasper, A. W.; Oana, C. M.; Miller, J. A. “Third-Body” Collision Efficiencies for Combustion
28
29 Modeling: Hydrocarbons in Atomic and Diatomic Baths. *Proc. Combust. Inst.* **2015**, *35*,
30
31 197–204. <https://doi.org/10.1016/j.proci.2014.05.105>.
- 32
33
34 (55) Greenwald, E. E.; North, S. W.; Georgievskii, Y.; Klippenstein, S. J. A Two Transition State
35
36 Model for Radical–Molecule Reactions: A Case Study of the Addition of OH to C_2H_4 . *J. Phys.*
37
38 *Chem. A* **2005**, *109*, 6031–6044. <https://doi.org/10.1021/jp058041a>.
- 39
40
41 (56) Jasper, A. W.; Miller, J. A. Theoretical Unimolecular Kinetics for $\text{CH}_4 + \text{M} \rightleftharpoons \text{CH}_3 + \text{H} + \text{M}$ in
42
43 Eight Baths, $\text{M} = \text{He}, \text{Ne}, \text{Ar}, \text{Kr}, \text{H}_2, \text{N}_2, \text{CO},$ and CH_4 . *J. Phys. Chem. A* **2011**, *115*, 6438–
44
45 6455. <https://doi.org/10.1021/jp200048n>.
- 46
47
48 (57) Klippenstein, S. J.; Miller, J. A.; Jasper, A. W. Kinetics of Propargyl Radical Dissociation. *J.*
49
50 *Phys. Chem. A* **2015**, *119*, 7780–7791. <https://doi.org/10.1021/acs.jpca.5b01127>.
- 51
52
53 (58) Tranter, R. S.; Jasper, A. W.; Randazzo, J. B.; Lockhart, J. P. A.; Porterfield, J. P.
- 54
55
56
57
58
59
60

- 1
2
3 Recombination and Dissociation of 2-Methyl Allyl Radicals: Experiment and Theory. *Proc.*
4
5
6 *Combust. Inst.* **2017**, *36*, 211–218. <https://doi.org/10.1016/j.proci.2016.06.040>.
7
- 8 (59) Jasper, A. W.; Miller, J. A. Lennard–Jones Parameters for Combustion and Chemical
9
10 Kinetics Modeling from Full-Dimensional Intermolecular Potentials. *Combust. Flame* **2014**,
11
12 *161*, 101–110. <https://doi.org/10.1016/j.combustflame.2013.08.004>.
13
14
- 15 (60) Jasper, A. W.; Kamarchik, E.; Miller, J. A.; Klippenstein, S. J. First-Principles Binary Diffusion
16
17 Coefficients for H, H₂, and Four Normal Alkanes + N₂. *J. Chem. Phys.* **2014**, *141*, 124313.
18
19 <https://doi.org/10.1063/1.4896368>.
20
21
- 22 (61) Zhang, P.; Klippenstein, S. J.; Sun, H.; Law, C. K. Ab Initio Kinetics for the Decomposition of
23
24 Monomethylhydrazine (CH₃NHNH₂). *Proc. Combust. Inst.* **2011**, *33*, 425–432.
25
26 <https://doi.org/10.1016/j.proci.2010.05.010>.
27
28
- 29 (62) Förstel, M.; Tsegaw, Y. A.; Maksyutenko, P.; Mebel, A. M.; Sander, W.; Kaiser, R. I. On the
30
31 Formation of N₃H₃ Isomers in Irradiated Ammonia Bearing Ices: Triazene (H₂NNNH) or
32
33 Triimide (HNHNNH). *ChemPhysChem* **2016**, *17*, 2726–2735.
34
35 <https://doi.org/10.1002/cphc.201600414>.
36
37
- 38 (63) Dean, A. M.; Bozzelli, J. W. Combustion Chemistry of Nitrogen. In *Gas-Phase Combustion*
39
40 *Chemistry*; Springer New York: New York, NY, 2000; pp 125–341.
41
42 https://doi.org/10.1007/978-1-4612-1310-9_2.
43
44
- 45 (64) Mulliken, R. S. Electronic Population Analysis on LCAO–MO Molecular Wave Functions. I.
46
47 *J. Chem. Phys.* **1955**, *23*, 1833–1840. <https://doi.org/10.1063/1.1740588>.
48
49
- 50 (65) Chang, A. Y.; Bozzelli, J. W.; Dean, A. M. Kinetic Analysis of Complex Chemical Activation
51
52 and Unimolecular Dissociation Reactions Using QRRK Theory and the Modified Strong
53
54
55
56
57

- 1
2
3 Collision Approximation. *Zeitschrift für Phys. Chemie* **2000**, *214*, 1533.
4
5 <https://doi.org/10.1524/zpch.2000.214.11.1533>.
6
7
8 (66) Simmie, J. M. A Database of Formation Enthalpies of Nitrogen Species by Compound
9
10 Methods (CBS-QB3, CBS-APNO, G3, G4). *J. Phys. Chem. A* **2015**, *119*, 10511–10526.
11
12 <https://doi.org/10.1021/acs.jpca.5b06054>.
13
14
15 (67) Bugler, J.; Somers, K. P.; Simmie, J. M.; Güthe, F.; Curran, H. J. Modeling Nitrogen Species
16
17 as Pollutants: Thermochemical Influences. *J. Phys. Chem. A* **2016**, *120*, 7192–7197.
18
19 <https://doi.org/10.1021/acs.jpca.6b05723>.
20
21
22 (68) Hanson, R. K.; Salimian, S. Survey of Rate Constants in the N/H/O System. In *Combustion*
23
24 *Chemistry*; Springer New York: New York, NY, 1984; pp 361–421.
25
26 https://doi.org/10.1007/978-1-4684-0186-8_6.
27
28
29 (69) Klippenstein, S. J.; Miller, J. A. From the Time-Dependent, Multiple-Well Master Equation
30
31 to Phenomenological Rate Coefficients. *J. Phys. Chem. A* **2002**, *106*, 9267–9277.
32
33 <https://doi.org/10.1021/jp021175t>.
34
35
36 (70) Miller, J. A.; Klippenstein, S. J. Master Equation Methods in Gas Phase Chemical Kinetics. *J.*
37
38 *Phys. Chem. A* **2006**, *110*, 10528–10544. <https://doi.org/10.1021/jp062693x>.
39
40
41 (71) Prozument, K.; Suleimanov, Y. V.; Buesser, B.; Oldham, J. M.; Green, W. H.; Suits, A. G.;
42
43 Field, R. W. A Signature of Roaming Dynamics in the Thermal Decomposition of Ethyl
44
45 Nitrite: Chirped-Pulse Rotational Spectroscopy and Kinetic Modeling. *J. Phys. Chem. Lett.*
46
47 **2014**, *5*, 3641–3648. <https://doi.org/10.1021/jz501758p>.
48
49
50 (72) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. Gaussian-2 Theory for Molecular
51
52 Energies of First- and Second-row Compounds. *J. Chem. Phys.* **1991**, *94*, 7221–7230.
53
54
55
56
57
58
59
60

1
2
3 <https://doi.org/10.1063/1.460205>.
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Table of Contents Graphic



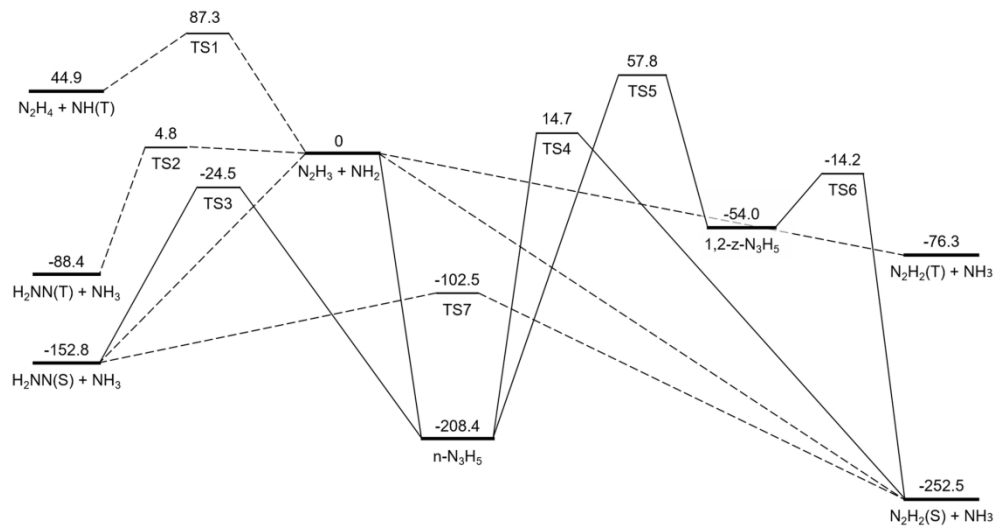


Figure 1. Reaction path diagram for the N_3H_5 PES. Dashed lines represent non-pressure-dependent pathways. (S) and (T) represent singlet or triplet multiplicities, respectively. Energies are in kJ mol^{-1} , and scaled relative to the $N_2H_3 + NH_2$ entry channel, which was set at zero.

177x94mm (300 x 300 DPI)

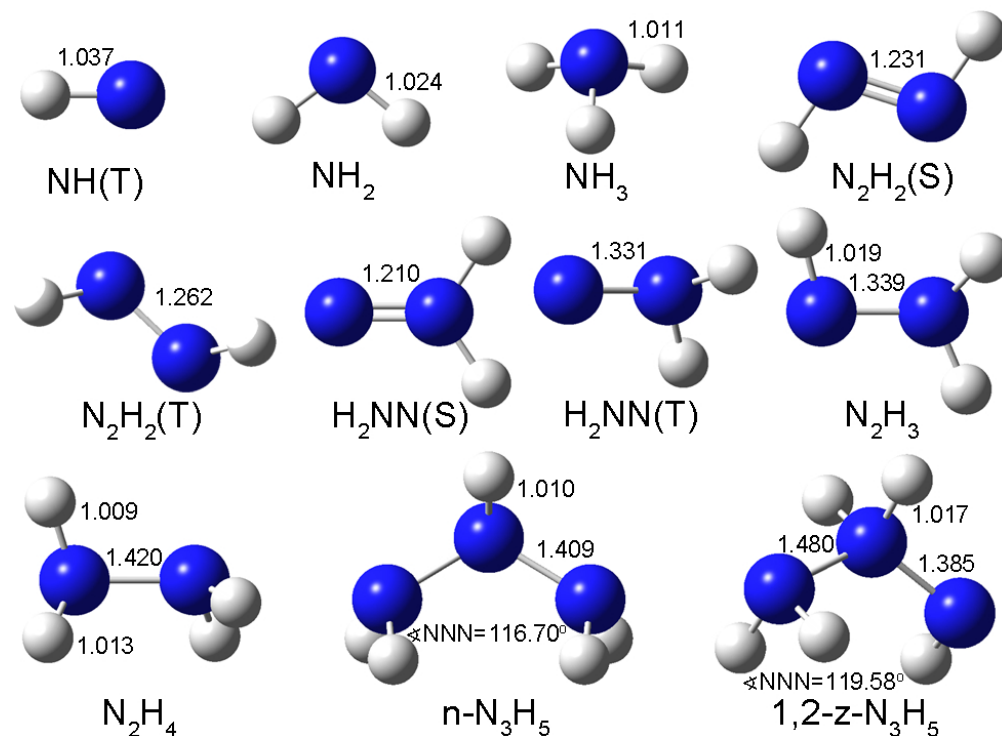


Figure 2. Geometric representation of species on the N_3H_5 PES optimized at the $\omega B97x-D3/6-311++G(3df,3pd)$ level of theory. Bond orders shown for illustration purpose only. Bond lengths are in Å and angles in degrees. Quantitative geometric data was added where it benefits the discussion; geometric coordinates for all species are available in the Supporting Information.

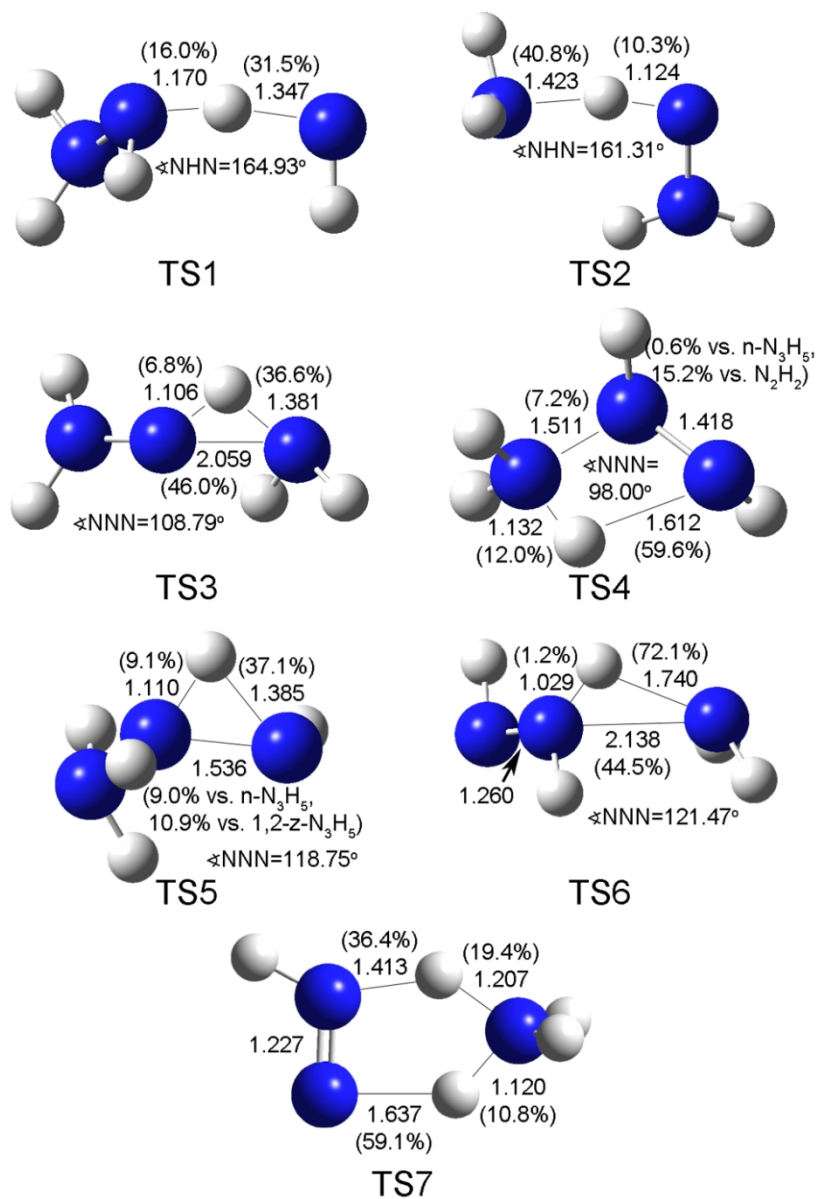


Figure 3. Geometric representation of transition states on the N_3H_5 PES optimized at the $\omega\text{B97x-D3/6-311++G(3df,3pd)}$ level of theory. Bond lengths are in Å and angles in degrees. Numbers in parentheses indicate the bond stretch fraction relative to the respective stable species. Quantitative geometric data was added where it benefits the discussion; geometric coordinates for all transition states are available in the Supporting Information.

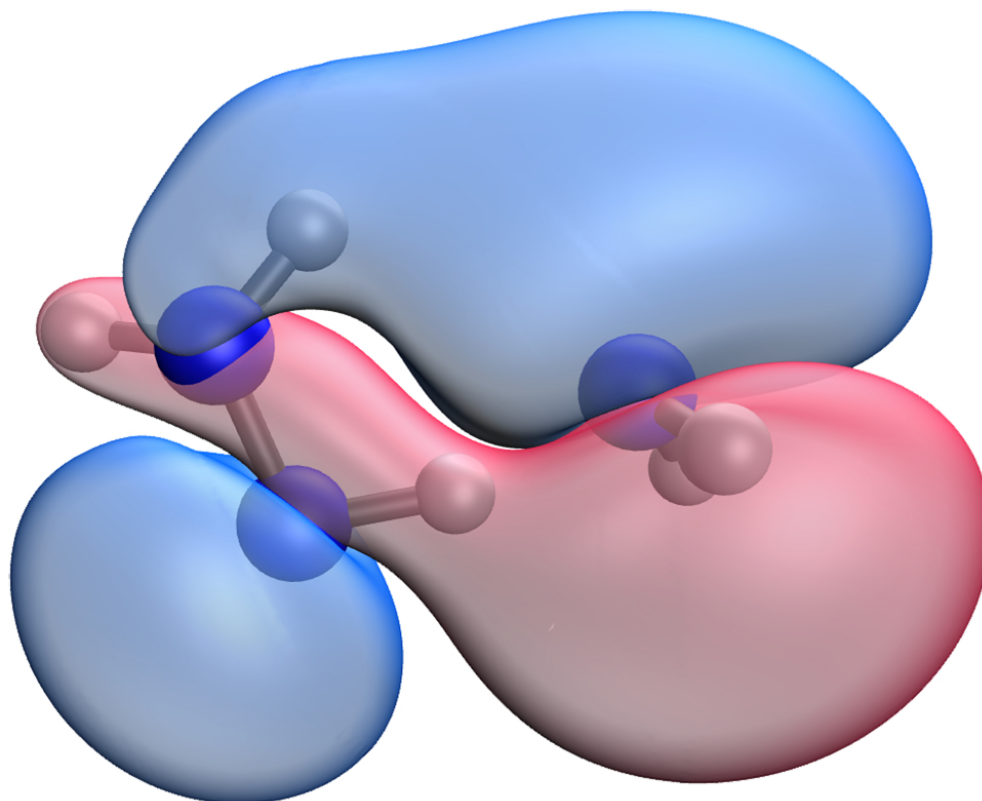


Figure 4. Highest alpha-electron occupied molecular orbital (MO 12) in the triplet saddle point TS2, computed at the ω B97x-D3/6-311++G(3df,3pd) level of theory.

82x67mm (300 x 300 DPI)

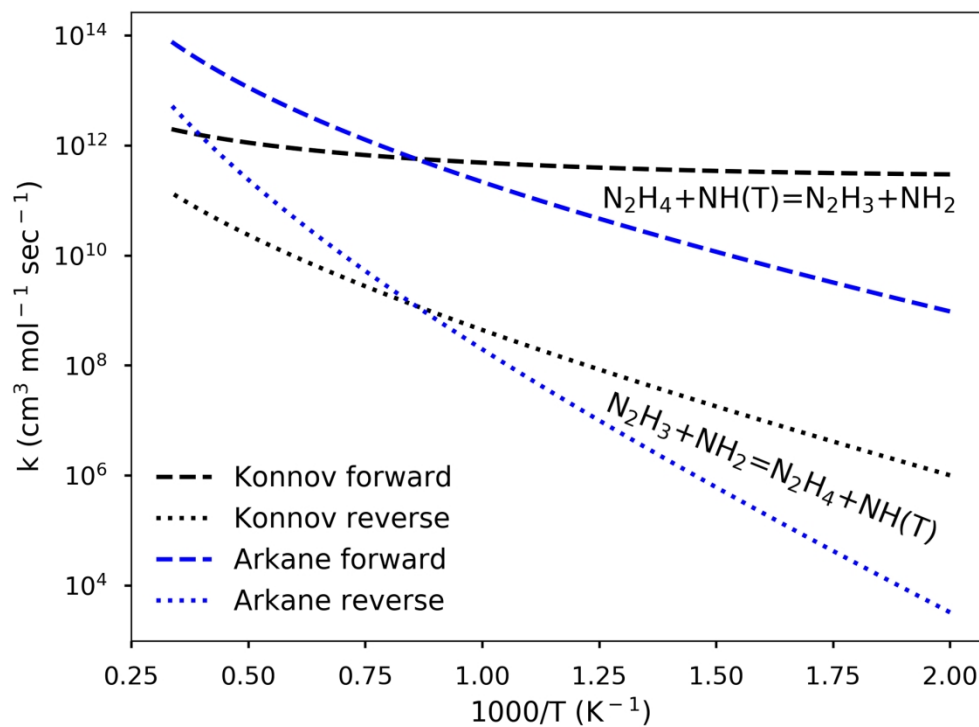


Figure 5. Rate comparisons of Reaction R1 (forward) and R-1 (reverse) between the present work calculation using Arkane and the rate estimated and reported by Konnov and De Ruyck.⁹ Thermodynamic data from Curran et al.⁶⁵ was used to compute reverse rates.

177x129mm (300 x 300 DPI)

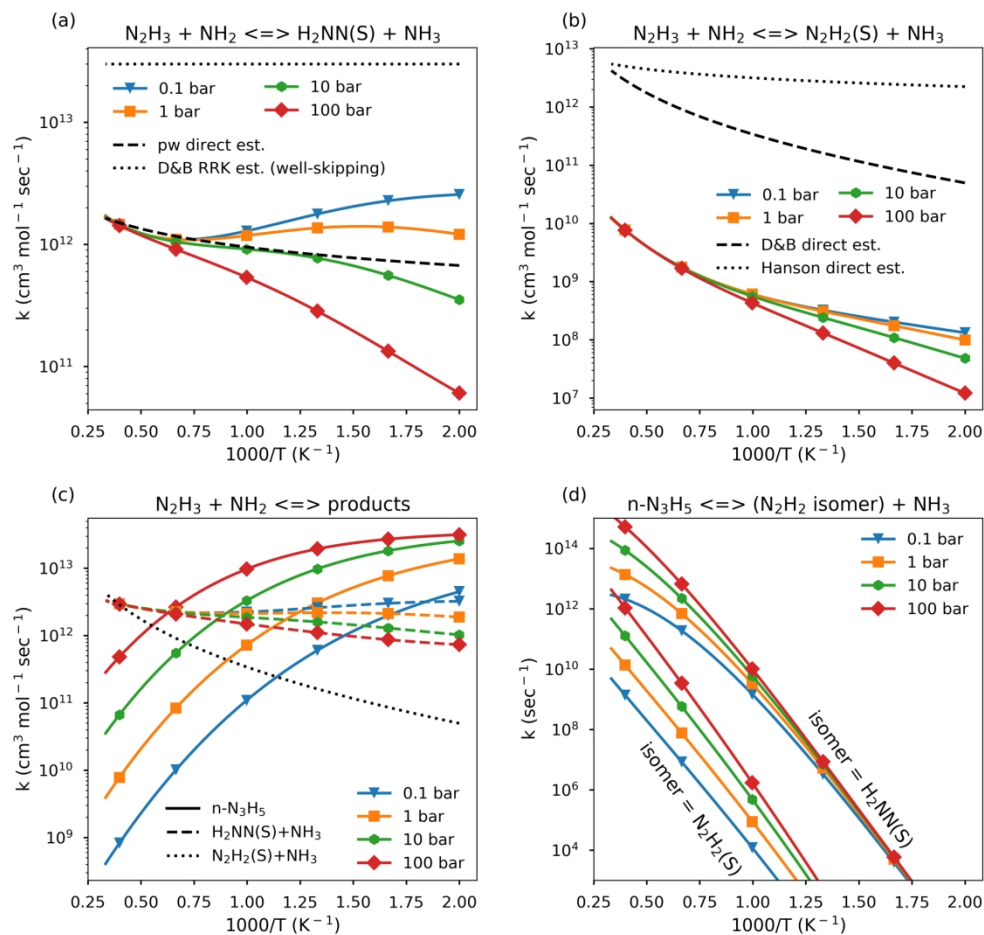


Figure 6. Rate comparisons of selected reactions on the N_3H_5 PES. 'D&B' in the legend refers to the book chapter by Dean and Bozzelli from 2000,⁶¹ and 'Hanson' refers to a N/H/O rate constants review by Hanson and Salimian from 1984.⁶⁶ Present work is denoted as 'pw'. In (c), line types refer to the product/s, while the color refers to the pressure; the pressure-dependence of the $\text{N}_2\text{H}_2(\text{S}) + \text{NH}_3$ formation rate is negligible, while formation rates of $\text{H}_2\text{NN}(\text{S}) + \text{NH}_3$ include both pressure-dependent and direct routes; the updated Dean and Bozzelli rate for $\text{N}_2\text{H}_2(\text{S}) + \text{NH}_3$ is shown.

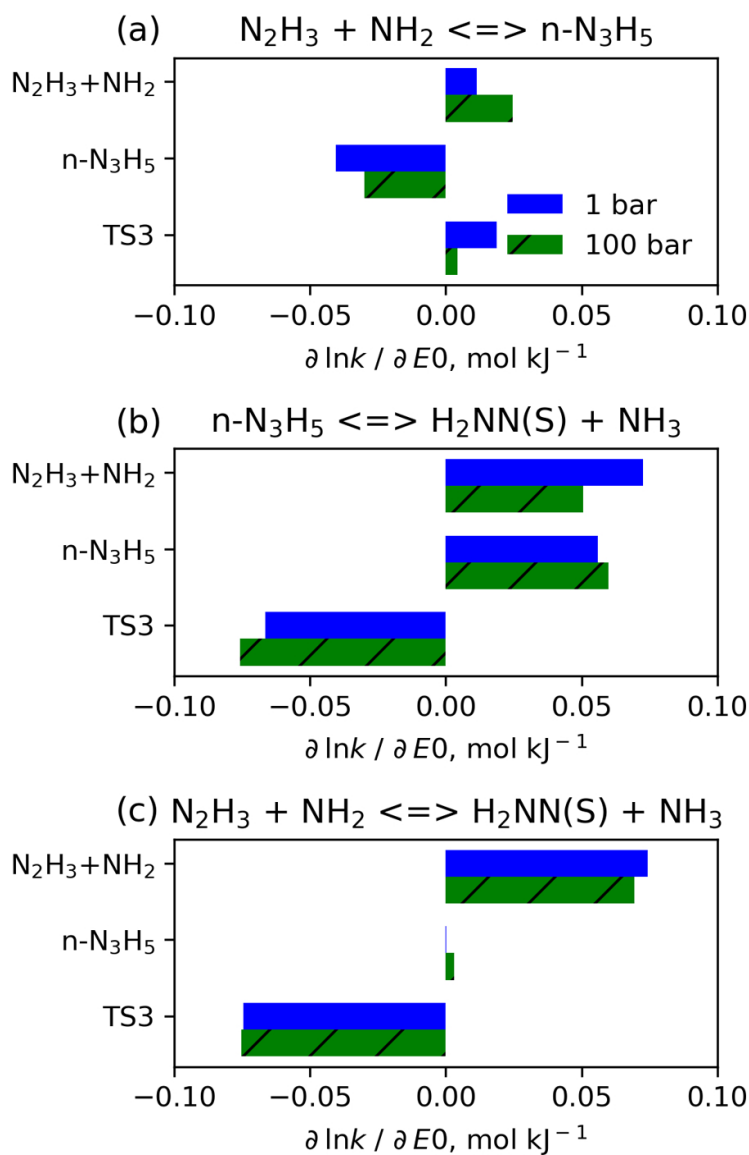


Figure 7. Normalized sensitivity coefficients to ZPE-corrected energies of $\text{N}_2\text{H}_3 + \text{NH}_2$, $\text{n-N}_3\text{H}_5$, and TS3 for selected pressure-dependent rates on the N_3H_5 potential at 1 and 100 bar and at 1500 K.

82x123mm (300 x 300 DPI)

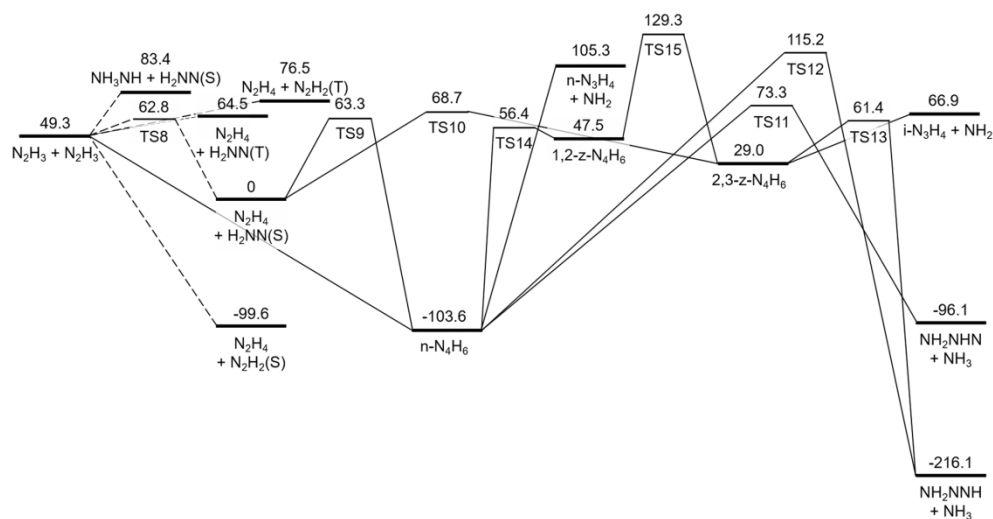


Figure 8. Reaction path diagram for the N_4H_6 potential. Dashed lines represent non-pressure-dependent pathways. (S) and (T) represent singlet or triplet multiplicities, respectively. Energies are in kJ mol^{-1} , and scaled relative to the $N_2H_4 + H_2NN(S)$ entry channel, which was set at zero.

177x93mm (300 x 300 DPI)

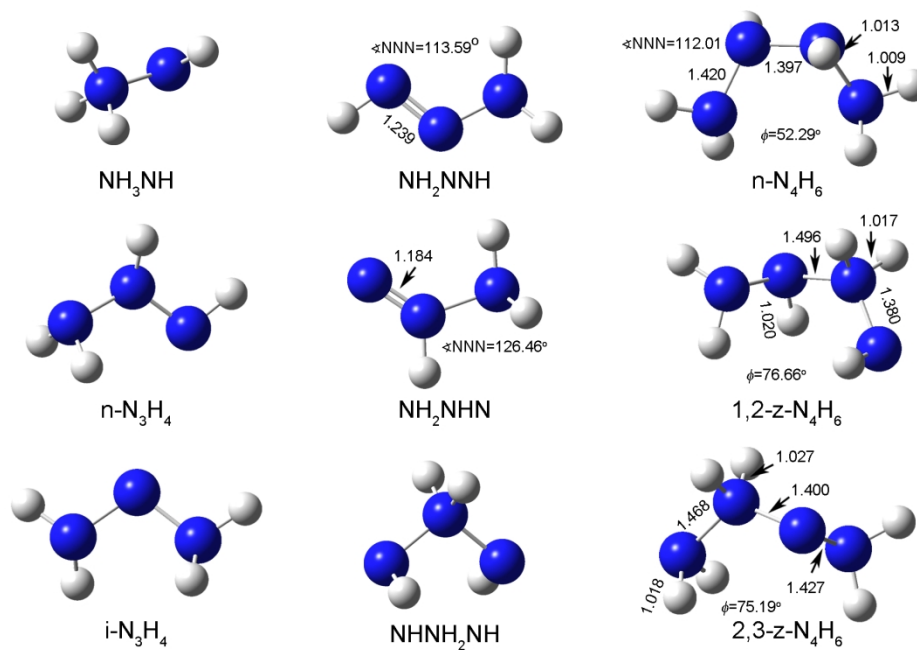


Figure 9. Geometric representation of species on the N_4H_6 PES optimized at the $\omega B97x-D3/6-311++G(3df,3pd)$ level of theory. Species already given in Fig. 2 were not reproduced here. Bond orders shown for illustration purpose only. Bond lengths are in Å and angles in degrees. ϕ is the dihedral angle between the four nitrogen backbone atoms. Quantitative geometric data was added where it benefits the discussion; geometric coordinates for all species are available in the Supporting Information.

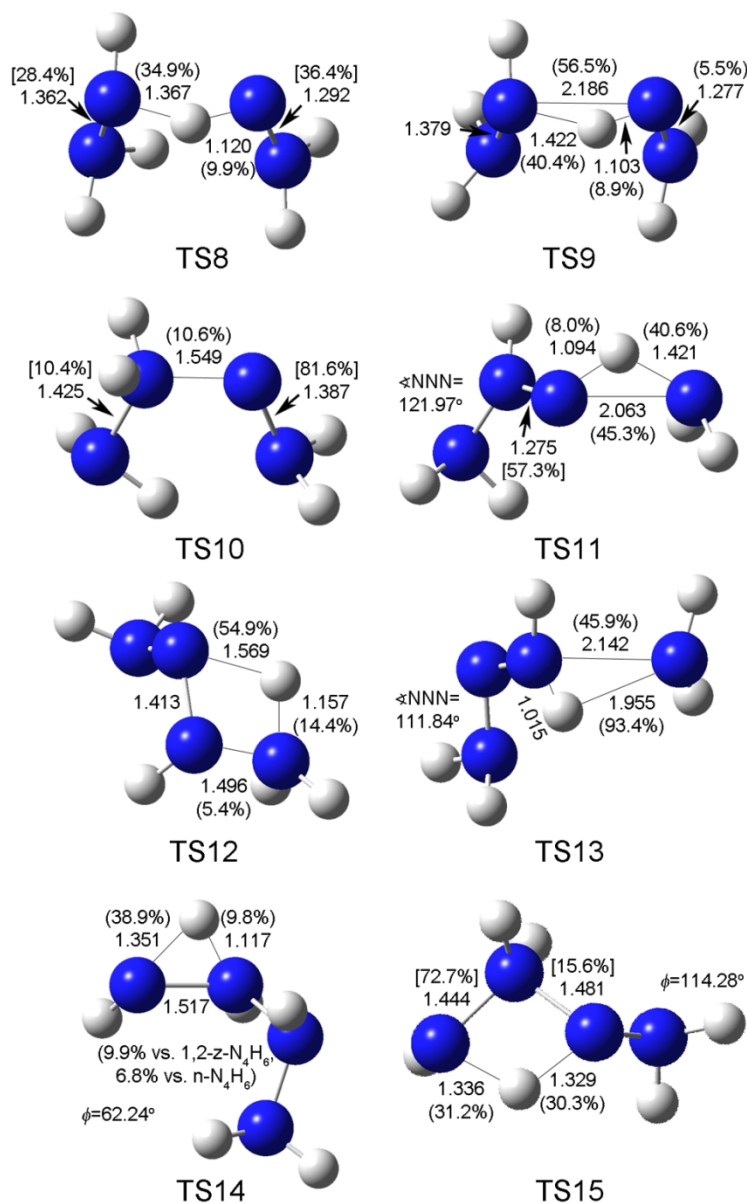


Figure 10. Geometric representation of transition states on the N_4H_6 PES optimized at the $\omega B97x-D3/6-311++G(3df,3pd)$ level of theory. Bond lengths are in Å and angles in degrees. Numbers in parentheses indicate the bond stretch fraction relative to the respective stable species. Numbers in brackets indicate the relative bond stretch fraction out of the total change between the respective reactant and product in the direction specified in Table 3. Φ is the dihedral angle between the four nitrogen backbone atoms. Quantitative geometric data was added where it benefits the discussion; geometric coordinates for all transition states are available in the Supporting Information.

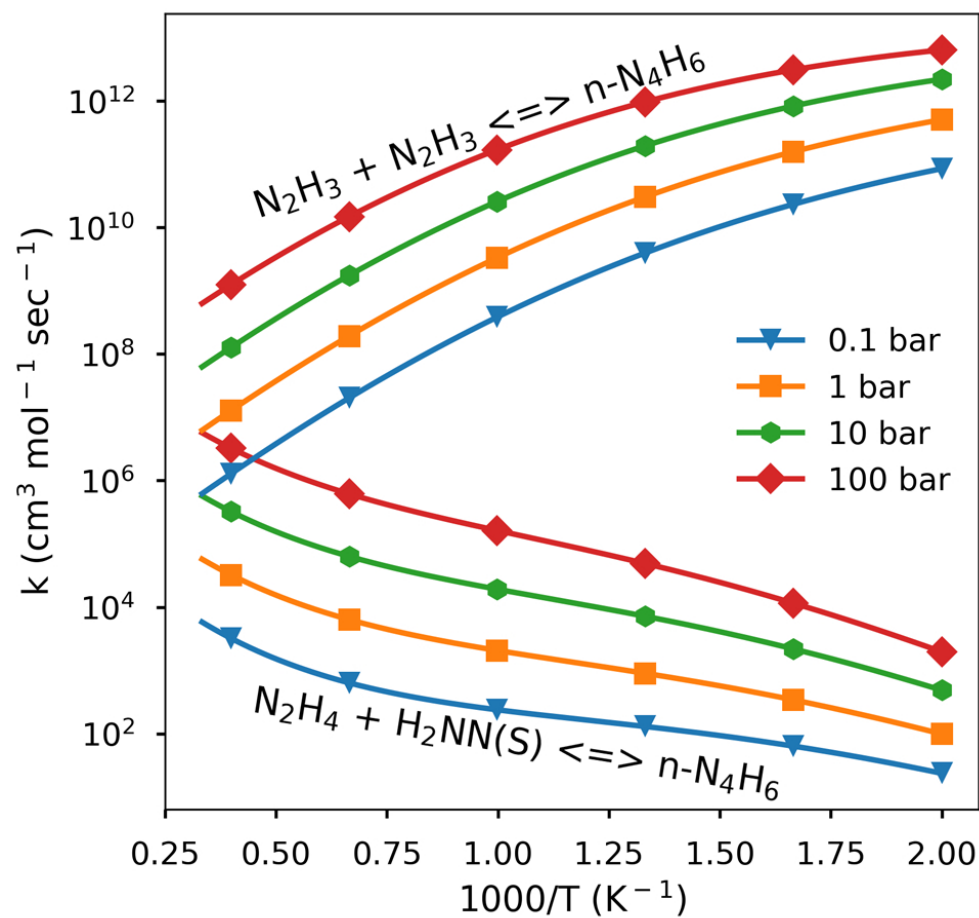


Figure 11. Rate coefficient comparison of $n\text{-N}_4\text{H}_6$ formation from each of the entry channels as a function of temperature and pressure.

82x80mm (300 x 300 DPI)

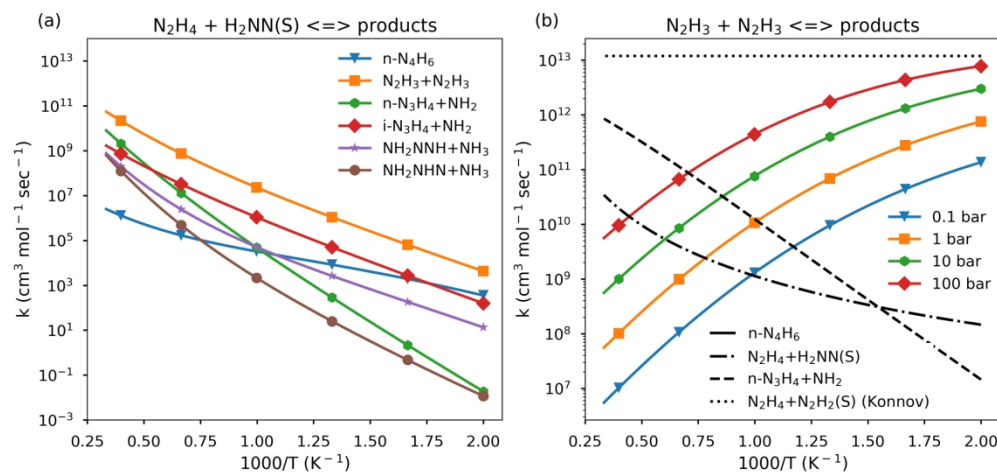


Figure 12. Rate comparisons of $\text{N}_2\text{H}_4 + \text{H}_2\text{NN(S)}$ and $\text{N}_2\text{H}_3 + \text{N}_2\text{H}_3$ reactions. Rates in (a) are given at a representative pressure of 10 bar. In (b), line types refer to the product/s, while the color refers to the pressure; the pressure-dependence rate for $n\text{-N}_3\text{H}_4 + \text{NH}_2$ formation via a well-skipping reaction is negligible; the rate for $\text{N}_2\text{H}_4 + \text{H}_2\text{NN(S)}$ formation includes both a direct route (via TS8) and the well-skipping route; the dotted line is an estimated rate by Konnov and De Ruyck.⁹