A Consistent Reduced Network for HCN Chemistry in Early Earth and Titan Atmospheres: Quantum Calculations of Reaction Rate Coefficients

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Abstract: HCN is a key ingredient for synthesizing biomolecules such as nucleobases and amino acids. We calculate 42 reaction rate coefficients directly involved with or in competition with the production of HCN in the early Earth or Titan atmospheres. These reactions are driven by methane and nitrogen radicals produced via UV photodissociation or lightning. For every reaction in this network, we calculate rate coefficients at 298 K using canonical variational transition state theory (CVT) paired with computational quantum chemistry simulations at the BHandHLYP/aug-cc-pVDZ level of theory. We also calculate the temperature dependence of the rate coefficients for the reactions that have barriers from 50–400 K. We present 15 new reaction rate coefficients with no previous known value. 93% of our calculated coefficients are within an order of magnitude of the nearest experimental or recommended values. Above 320 K, the rate coefficient for the new reaction H2CN → HCN + H dominates. Contrary to experiments, we find the HCN reaction pathway, N + CH3 → HCN + H2, to be inefficient, and suggest the experimental rate coefficient actually corresponds to an indirect pathway, through the H2CN intermediate. We present CVT using energies computed with density functional theory as a feasible and accurate method for calculating a large network of rate coefficients of small-molecule reactions.

INTRODUCTION

HCN is a precursor to the building blocks of life. For example, HCN reacts to produce nucleobases, the building blocks of RNA/DNA, as well as amino acids, the building blocks of proteins, in aqueous environments.1–5 For adenine synthesis, HCN first condenses in water to form oligomers, which then forms adenine upon hydrolysis.6 HCN may have formed in the atmosphere of the prebiotic Earth through the reaction of photochemically driven and/or lightning-induced methane and nitrogen radicals.7–10 HCN is similarly produced in Titan’s present-day atmosphere.11

Given the significance HCN as a precursor to biomolecules, it is of interest to discern how much was produced in the early Earth atmosphere in order to understand whether it potentially played a role in the emergence of life in warm little ponds.11 Titan provides a good test environment for atmospheric HCN production, given that one can compare abundances from chemical simulations to the measured HCN profile from the Cassini mission.12

Chemical networks including a variety of species and reactions have been employed to simulate the atmospheric HCN composition of early Earth13–15 and Titan.12,16 The reaction rate coefficients in these networks are generally a combination of a) theoretical, b) experimental, and c) suggested values typically estimated using thermodynamics, similar reactions and/or experimental results at much higher temperatures. Each of these sources has errors associated with it, and there are often a range of experimental and theoretical values to choose from for a single reaction. As a result, atmospheric HCN compositions can vary by orders of magnitude from one simulation to the next. Therefore, it is perhaps unsurprising that, as of yet, no simulation has matched the HCN profile of Titan completely.

There are also several reactions without past experimental, theoretical, or suggested values that are missing in these networks that may play important roles in HCN formation (e.g. 1CH2 + 2N → H2CN and H2CN → HCN + H). The focus of this work is to create a theoretical reduced HCN chemical network, where all the rate coefficients are consistently calculated with the same theoretical and computational method. Using this strategy, all reactions can be theoretically validated before being employed in a chemical network, and key reaction pathways with previously unknown rate coefficients can be included. Furthermore, by constructing a model chemistry the errors for consistently calculated rate coefficients are expected to be similar, thus employing such a network has a chance to improve accuracy.

The limitation of calculating a consistent theoretical network is that one cannot feasibly include a large number of molecular species. For every additional species, there is a potential additional reaction with all the existing species in the network. Therefore in this work, we focus only on the small set of reactions involved in the production of HCN from methane and nitrogen dissociation radicals, as well as the direct competing reactions. This totals 42 reactions between 11 species. We are the first to calculate a completely consistent theoretical reac-

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tion network of this size for atmospheric chemistry simulations.

In the Background section of this paper, we motivate and describe the reactions in our chemical network. Then in the Methods section, we detail the theoretical and computational methods used to calculate the reaction rate coefficients in our network. In the Results section, we present the results of our calculations, including their conformance to experimental values, and the effects of spin configuration on these values. The reader who is just interested in the calculated rate coefficients can skip ahead to Tables 3 and 4, where we present the calculated rate coefficients in this network, and the Arrhenius coefficients for temperature dependences, respectively. Finally, in the Conclusions section we summarize the main results of the paper.

The supporting information (SI) contains a wealth of technical data and calculation details including: 1) a summary of the experimentally measured and previously theoretically calculated rate coefficients in this network, 2) an example rate coefficient calculation using the CVT method and a computational methods comparison, 3) a breakdown of the calculations of specific reactions, and 4) reaction path symmetry number calculations.

**BACKGROUND**

The abiotic production of biomolecules such as nucleobases and amino acids requires a reactive source of nitrogen, typically HCN or NH₃[24][25][26]. HCN can be produced in early Earth and Titan atmospheres through reactions involving N₂ and CH₄ dissociation products. Such dissociation products are produced when N₂ and CH₄ interact with UV photons[27], cosmic rays[28], or lightning[29]. N₂ and CH₄ photodissociation can be broken down into the following pathways:

\[ N₂ + hν \rightarrow N₂^+ + e^- \] (1)
\[ N₂^+ + e^- \rightarrow 4N + 2N \] (2)

\[ CH₄ + hν \rightarrow CH₃ + H \]
\[ \Phi_{118.2} = 0.26, \Phi_{121.6} = 0.42, \] (3)

\[ CH₄ + hν \rightarrow ^1CH₂ + H₂ \]
\[ \Phi_{118.2} = 0.17, \Phi_{121.6} = 0.48, \] (4)

\[ CH₄ + hν \rightarrow ^3CH₂ + 2H \]
\[ \Phi_{118.2} = 0.48, \Phi_{121.6} = 0.03, \] (5)

\[ CH₄ + hν \rightarrow CH + H₂ + H \]
\[ \Phi_{118.2} = 0.09, \Phi_{121.6} = 0.07, \] (6)

where the leading superscripts signify the singlet, doublet, and quartet spin states, hv signifies an ultraviolet photon and \( \Phi_{118.2} \) and \( \Phi_{121.6} \) signify the branching ratios measured from lab experiments at 118.2 and 121.6 nm, respectively[20][26].

Multiple possible pathways to produce HCN from the above radicals (at or near 298 K) have been reported from experiments or suggested in the literature. Note that molecular spin states are not included in this list and that each of these reactions represents 1–5 reaction spin configurations; each with a unique reaction rate coefficient.

\[ ^{1}CH₃ + N \rightarrow H₂CN + H \] (7)
\[ ^{1}CH₂ + N \rightarrow H₂CN \] (8)
\[ ^{1}H₂CN \leftrightarrow HCN + H \] (9)
\[ H₂CN + H \rightarrow HCN + H₂ \] (10)
\[ H₂CN + N \rightarrow HCN + NH \] (11)
\[ 2H₂CN \rightarrow HCN + H₂CNH \] (12)

Three experimentally reported or suggested reaction pathways have not been included in this list as our theoretical work shows they more likely proceed through two steps involving combinations of the above equations. These reactions are CH₃ + N \rightarrow HCN + H₂[25], CH₃ + N \rightarrow HCN + 2H[29] and CH₂ + N \rightarrow HCN + H[28] (see theoretical case studies in SI for complete analysis).

There are also multiple competing reaction pathways to the above reactions at or near 298 K. In this network, we only include competing pathways involving the radicals produced from N₂ and CH₄ dissociation in the atmosphere. One exception is that we also include the reactions of NH with H and N as recombination pathways to H₂ and N₂. See Table 1 for list of primary molecular species.

\[ CH₄ + H \leftrightarrow CH₃ + H₂ \] (13)
\[ CH₄ + N \rightarrow H₂CNH + H \] (14)
\[ CH₃ + H \rightarrow CH₄ \] (15)
\[ 2CH₃ \rightarrow C₂H₆ \] (16)

† Reactions without experimental or suggested values for at least one spin configuration in this network.
TABLE 1. List of primary molecular species involved in this study and their spin states.

| Species | Spin state | Ground/Excited state |
|---------|------------|----------------------|
| HCN     | singlet    | ground               |
| H$_2$CN | doublet    | ground               |
| N$_2$   | singlet    | ground               |
| $^2$N   | doublet    | excited              |
| $^4$N   | quartet    | ground               |
| CH$_4$  | singlet    | ground               |
| CH$_3$  | doublet    | ground               |
| $^1$CH$_2$ | singlet    | excited              |
| $^3$CH$_2$ | triplet    | ground               |
| CH      | doublet    | ground               |
| H$_2$   | singlet    | ground               |
| H       | doublet    | ground               |
| $^3$NH  | triplet    | ground               |

$^2$CH$_2$ + H $\longrightarrow$ CH$_3$ (17)  
$^1$CH$_2$ + H$_2$ $\longrightarrow$ CH$_4$ (18)  
$^1$CH$_2$ + H$_2$ $\longleftrightarrow$ CH$_3$ + H (19)  
$^1$CH$_2$ + CH$_4$ $\longrightarrow$ C$_2$H$_6$ (20)  
$^1$CH$_2$ + CH$_4$ $\longleftrightarrow$ 2 CH$_3$ (21)  
$^1$CH + H $\longrightarrow$ CH$_2$ (22)  
$^1$CH + H$_2$ $\longrightarrow$ CH$_3$ (23)  
$^1$CH + N $\longrightarrow$ CN + H (24)  
2 CH $\longrightarrow$ C$_2$H$_2$ (25)  
CH + CH$_4$ $\longrightarrow$ C$_2$H$_4$ + H (26)  
NH + H $\longleftrightarrow$ H$_2$ + N (27)  
$^1$NH + N $\longrightarrow$ N$_2$ + H (28)

Four experimentally reported two-step reaction pathways have been reduced to their first steps in this list. These reactions are

CH$_2$ + H $\longrightarrow$ CH$_3$  
CH$_2$ + H$_2$ $\longrightarrow$ CH$_4$  
$^1$CH$_2$ + H$_2$ $\longleftrightarrow$ CH$_3$ + H  
$^1$CH$_2$ + CH$_4$ $\longrightarrow$ C$_2$H$_4$  
$^1$CH$_2$ + CH$_4$ $\longleftrightarrow$ 2 CH$_3$.

Our theoretical work shows the first steps are the rate-limiting steps, and the intermediates are reactants with other available reaction pathways in our chemical network (see theoretical case studies in SI for complete details).

One other experimentally reported reaction has not been included in this list. This reaction is

CH$_4$ + $^2$N $\longrightarrow$ $^1$H$_3$CNH $\longrightarrow$ CH$_3$ + $^3$NH.

Experiments suggest that $^1$H$_3$CNH decays into CH$_3$ + $^3$NH with a branching ratio of 0.3 ± 0.1, and that the majority of $^1$H$_3$CNH decays into $^1$H$_2$CNH + H ($\Phi$ = 0.8 ± 0.2). Our theoretical work also suggests $^1$H$_3$CNH preferentially decays into $^1$H$_2$CNH + H, however we alternatively find the decay into CH$_3$ + $^3$NH to be very inefficient ($k \sim 10^{-29}$ cm$^3$ s$^{-1}$); therefore we do not consider this decay pathway in this network.

The focus of this work is to calculate the rate coefficients for an atmospheric HCN reaction network which can be applied to both Titan and early Earth atmospheres. For each reaction, a detailed analysis of spin state configurations and an series of computational quantum chemistry simulations are performed at temperatures between 50–400 K.

In Table 2, we summarize the molecules and spin states involved in this reaction network. We define reactions with rate coefficients greater than $10^{-21}$ s$^{-1}$ for unimolecular reactions or greater than $10^{-21}$ cm$^3$ s$^{-1}$ for bimolecular reactions as “fast,” and exclude the “slow” reactions with smaller rate coefficients from this network.
TABLE 2. Detailed list of reactions considered in this study, including the accessible potential energy surfaces, and spin-state configurations. The focus of this network is reactions involved in the production of HCN from nitrogen and methane dissociation radicals. Direct competing reactions are also included. We define a fast reaction rate coefficient to be $>10^{-21}$ s$^{-1}$ for unimolecular reactions and $>10^{-21}$ cm$^3$ s$^{-1}$ for bimolecular reactions.

| Reaction equation | PES | Spin Configuration | Fast $k_f$(298)? | Fast $k_r$(298)? |
|-------------------|-----|--------------------|------------------|------------------|
| $\text{H}_2\text{CN} \leftrightarrow \text{HCN} + \text{H}$ | doublet | $\text{H}_2\text{CN} \leftrightarrow \text{HCN} + \text{H}$ | Y | Y |
| $\text{H}_2\text{CN} + \text{H} \leftrightarrow \text{HCN} + \text{H}_2$ | singlet | $\text{H}_2\text{CN} + \text{H} \leftrightarrow \text{HCN} + \text{H}_2$ | Y | N |
| $\text{H}_2\text{CN} + \text{N} \leftrightarrow \text{HCN} + \text{NH}$ | singlet | $\text{H}_2\text{CN} + 2\text{N} \leftrightarrow \text{HCN} + 1\text{NH}$ | N | N |
| | | triplet | $\text{H}_2\text{CN} + 4\text{N} \leftrightarrow \text{HCN} + 3\text{NH}$ | Y | N |
| | | & | $\text{H}_2\text{CN} + 2\text{N} \leftrightarrow \text{HCN} + 3\text{NH}$ | N | N |
| 2$\text{H}_2\text{CN} \leftrightarrow \text{HCN} + \text{H}_2\text{CN}$ | singlet | 2$\text{H}_2\text{CN} \leftrightarrow \text{HCN} + \text{H}_2\text{CN}$ | Y | N |
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atoms), from the reactant geometry, to the product geometry. In some cases, the minimum energy path (MEP) from reactants to products requires proceeding through a geometry of higher potential energy than the reactant and product geometries. This increase in potential energy along a reaction coordinate is known as the energy barrier. The peak of the energy barrier describes the conventional transition state.

In reality, reactions have more than one dimension (e.g. bond distances, angles between bonds, dihedral angles), thus the energy barrier is more appropriately described as a saddle point, and the MEP is the path of steepest descent from saddle point to the reactant and product minima. The rate of a reaction can be described as how frequently molecules travel the entire MEP, and is quantified by the reaction rate coefficient, \( k \).

We calculate gas phase chemical reaction rate coefficients using canonical variational transition state theory (CVT). The basis for this method is to vary the reaction coordinate (e.g. the carbon-hydrogen bond distance) along the MEP in order to find the minimum rate constant. Unlike conventional transition state theory, CVT allows us to calculate reaction rate coefficients for both barrierless and non-barrierless reactions, while minimizing the error due to trajectories that recross the transition state rather than descend into product. This can be visualized as finding a location past the saddle point of the MEP, that recrossing reactants tend not to reach (see Figure 1). This location is determined as the location where the generalized transition state (GT) rate coefficient is at its smallest value, therefore providing best dynamical bottleneck.

The CVT reaction rate coefficient is expressed as \( k_{CVT}(T, s) = \min_s \{ k_{GT}(T, s) \} \). (31)

Neglecting the tunneling effect, the generalized transition state theory (GT) reaction rate coefficient can be approximated via the Eyring Equation. The Eyring equation uses a statistical mechanics approach to calculate the rate coefficient by dividing the density of forward-crossing states per unit time by the density of reactant states.

\[
k_{GT}(T, s) = \frac{\sigma k_B T}{h} \frac{Q^i(T, s) e^{-E_0(s)/RT}}{\prod_{i=1}^{N} Q^i_{ni}(T)}
\] (32)

where \( \sigma \) is the reaction path symmetry number or reaction path multiplicity (i.e. the number of equivalent reaction paths from reactants to products), \( k_B \) is the Boltzmann constant \( (1.38 \times 10^{-23} \text{ J K}^{-1}) \), \( T \) is temperature (K), \( h \) is the Planck constant \( (6.63 \times 10^{-34} \text{ J s}) \), \( Q^i \) is the partition function of the transition state per unit volume \( (\text{cm}^{-3}) \), with its zero of energy at the saddle point, \( Q_i \) is the partition function of species \( i \) per unit volume, with its zero of energy at the equilibrium position of species \( i \) (i.e. as if it is infinitely separated from any other reactant), \( n_i \) is the stoichiometric coefficient of species \( i \), \( N \) is the number of reactant species, \( E_0 \) is the energy barrier (the difference in zero-point energies between the generalized transition state and the reactants) \( (\text{kJ mol}^{-1}) \), and \( R \) is the gas constant \( (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \).

Because classical partition functions involve integrating over the Boltzmann factor \( e^{-\frac{E}{RT}} \), an additional exponential factor appears naturally in the Eyring equation due to the difference in zeros of energy between the transition state and reactant states.

To find the location along the MEP where the GT rate coefficient is at its smallest value, we use the maximum Gibbs free energy criterion, which gives a compromise of energetic and entropic effects. To obtain a similar accuracy for all calculations, we use a reaction coordinate precision of 0.01 \( \AA \). Looking at the quasithermodynamic representation of transition-state theory, we see that the maximum value for \( \Delta G_{GT}(T, s) \) corresponds to a minimum value for \( k_{GT}(T, s) \)

\[
k_{GT}(T, s) = \frac{k_B T}{h} K^0 e^{-\Delta G_{GT}(T, s)/RT},
\] (33)

where \( K^0 \) is the reaction quotient under standard state conditions (i.e. 1 for unimolecular reactions, and 1 cm\(^3\) for bimolecular reactions), and \( \Delta G_{GT}(T, s) \) is the difference in the Gibbs free energy between transition state and reactants \( (\text{kJ mol}^{-1}) \).

The conventional transition state, energy barrier, and variational transition state are illustrated with a potential energy diagram in Figure 1.

The zero-point energies and partition functions for the reactants and transition states are calculated using the Gaussian 09 software package. A brief summary of the theory behind these calculations is detailed below. We refer the reader to Ochterski for further details.

The partition functions per unit volume are expanded into their 4 components

\[
Q = \frac{q_t}{V} q_e q_v q_r.
\] (34)

where \( q_t \) is the translational component, \( V \) is the volume \( (\text{cm}^{-3}) \), \( q_e \) is the electronic component, \( q_v \) is the vibrational component, \( q_r \) is the rotational component not including the rotational symmetry number (this is included in the reaction path multiplicity).

From classical statistical mechanics, the translational partition function per unit volume is \( \frac{q_t}{V} \)

\[
\frac{q_t}{V} = \left( \frac{2 \pi m k_B T}{h^2} \right)^{3/2},
\] (35)

where \( m \) is the mass of the species \( (\text{kg}) \).

The electronic partition function is estimated as the degeneracy of the first energy level, i.e. the spin multiplicity.
FIG. 1. A schematic representation of a reaction: proceeding from the reactants, over the potential energy barrier, $E_0$, through the transition state (red circle), and onto the products. The variational transition state (gold circle) is a location beyond the conventional transition state, where reactants that recross the barrier tend not to reach. The variational transition state is located where the reaction rate coefficient is at a minimum, thus providing the best dynamical bottleneck.

\[ q_e = 2S + 1, \]  

(36)

where $S$ is the total spin due to unpaired electrons. For example, a hydrogen atom has 1 unpaired electron of spin $1/2$, and thus its $q_e = 2(1/2) + 1 = 2$.

Gaussian calculates the vibrational partition function as a quantum harmonic oscillator. We note that for the zero-point energies of molecules, Gaussian places the zero of energy at the bottom of the internuclear potential. Thus, with this same location for the zero of energy, the vibrational partition function equates to

\[ q_v = \prod_{n=1}^{N} \frac{e^{-\Theta_n/2T}}{1 - e^{-\Theta_n/T}}, \]  

(37)

where $N$ is the number of vibrational modes, $\Theta_n$ is the vibrational temperature of the $n^{th}$ mode ($\Theta_n = \frac{\hbar \omega_n}{k_B}$), and $T$ is temperature.

By default, Gaussian calculates the rotational partition function as a rigid rotor. For linear molecules excluding rotational symmetry,

\[ q_r = \left( \frac{T}{\Theta_r} \right)^{3/2}, \]  

(38)

and for polyatomic molecules excluding rotational symmetry,

\[ q_r = \left( \frac{T^{3/2}}{\Theta_{r_x}\Theta_{r_y}\Theta_{r_z}} \right)^{3/2}, \]  

(39)

where $\Theta_r$ is the rotational temperature ($\Theta_r = \frac{\hbar^2}{8\pi^2 I_k}$), and $I$ is the moment of inertia (in the case of a polyatomic molecule, $I_x$, $I_y$, and $I_z$ are the principal moments of inertia).

Gaussian displays an output for the rotational symmetry number ($\sigma_r$) of each molecule, however for all the reactants, transition states and products in our study, Gaussian displayed $\sigma_r = 1$. For this reason we calculate the rotational symmetry in Equation 32 manually (the calculated symmetry numbers are listed in Table S10 in SI).

Quantum Computational Simulations

We perform quantum computational simulations with the Gaussian software package using the Becke-Half-and-Half-Lee-Yang-Parr (BHandHLYP) density functional. We chose BHandHLYP for two reasons. Firstly, it is a relatively inexpensive method that can be used for an extended transition state study such as this. Secondly, in a computational methods comparison of the well-studied reaction $\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2$, BHandHLYP provided the most accurate rate coefficient compared to calculations using HF, CCSD, B3LYP, and M06-2x (see computational methods comparison in SI for more details). CAM-B3LYP also provided an accurate rate coefficient for this reaction, however the value from BHandHLYP offers a better compromise between experimental and suggested values.

Hartree-Fock (HF) methods tend to overestimate the energy barrier, whereas Density Functional Theory (DFT) methods (e.g. B3LYP) tend to underestimate the energy barrier. BHandHLYP is a hybrid functional that improves performance by using 50% HF and 50% DFT for the exchange energy calculation. All simulations are performed with the augmented correlation consistent polarized valence double zeta (aug-cc-pVDZ) basis set in order to achieve reasonable computation times.

Typically, when there is only one reaction spin configuration for a given PES, we do not specify the local spins in Gaussian when calculating the MEP. However in some cases not specifying the local spin, regardless of the number of possible spin configurations, leads to convergence issues. In these cases we specify the local spins to allow the calculation to converge. When there is more than one reaction spin configuration for a given PES, e.g., $\text{CH}_3 + 4\text{N} \rightarrow ^3\text{H}_3\text{CN} \cdot \rightarrow \text{H}_2\text{CN} + \text{H}$ and $\text{CH}_3 + 2\text{N} \rightarrow ^3\text{H}_3\text{CN} \cdot \rightarrow \text{H}_2\text{CN} + \text{H}$ on the triplet surface, we specify the local spins of the reactants in Gaussian to find the MEP’s for each individual spin configuration.
Temperatures in the early Earth and Titan atmospheres fit comfortably within the range of 50–400 K. The CVT rate coefficient equation for reactions with barriers includes a temperature-dependent exponential term (see Equation 32). This exponential temperature dependence typically leads to reaction rate coefficients which vary by multiple orders of magnitude over 50–400 K. The exponential term is omitted for barrierless reactions, and thus the temperature dependence for barrierless reaction rate coefficients is much smaller. Typically rate coefficients for barrierless reactions have either no temperature dependence, or a weak temperature dependence, varying by less than a factor of two or three from 50–400 K.

Temperature dependence for rate coefficients can be expressed using the Arrhenius equation:

\[ k(T) = \alpha \left( \frac{T}{300} \right)^\beta e^{-\gamma/T} \]

where \( \alpha \), \( \beta \), and \( \gamma \) are fitting parameters, which we will refer to as the Arrhenius coefficients. Units for \( k(T) \) are \( s^{-1} \) for unimolecular reactions and \( cm^3s^{-1} \) for bimolecular reactions.

We calculate the rate coefficients for the reactions with barriers at 50, 100, 200, 298, and 400 K and fit the results to the expression above to obtain the Arrhenius coefficients. For the sake of feasibility, we assume the rate coefficient for barrierless reactions is constant within this temperature range, as is typical.

### RESULTS

For detailed results, see theoretical case studies for 35 of the reactions in SI.

In Table 3, we display the reaction rate coefficients calculated using the CVT method described above at 298 K, and the comparative ranges of experimental values.

#### Conformance to Experiments

Of the 42 total reactions in this network, ~54% have been studied experimentally at or near 298 K (see the “k(298) experimental” column in Table 3 for experimental values). Another ~10% have been estimated based on the rate coefficients of similar bond additions and decompositions, and/or thermodynamics. 36% of the reactions have no experimental rate coefficients (those with no “k(298) experimental” value in Table 3), and in most cases, we are the first to calculate them theoretically.

| Reaction equation | Forward or Reverse? | Barrier? | k(298) calculated | k(298) experimental | Error factor |
|-------------------|---------------------|---------|-------------------|---------------------|-------------|
| H2CN ←→ HCN + H   | F                   | Y       | 1.6 × 10⁻¹¹       |                     |             |
|                   | R                   | Y       | 2.7 × 10⁻¹⁴       |                     |             |
| H2CN + H ←→ HCN + H2 | F             | N       | 1.8 × 10⁻¹¹       | 8.3 × 10⁻¹¹         | 5           |
| H2CN + 3N ←→ HCN + 3NH | F        | Y       | 9.4 × 10⁻¹³       | 4.4 × 10⁻¹⁸         | 47          |
| 2H2CN ←→ HCN + H2CN | F                   | N       | 3.7 × 10⁻¹⁴       | 3.3 × 8.3 × 10⁻¹²   | 89          |
| CH4 + H ←→ CH3 + H2 | F                   | Y       | 8.1 × 10⁻¹⁸       | 8.2 × 10⁻¹⁹ - 3.5 × 10⁻¹⁷ | 1           |
|                   | R                   | Y       | 3.2 × 10⁻²¹       | 9.6 × 10⁻²¹ - 1.3 × 10⁻²⁰ | 3           |
| CH4 + 2N ←→ H2CNH ←→ H2CNH + H | F | Y | 4.7 × 10⁻¹¹ | 2.4 × 4.5 × 10⁻¹² | 10 |
| CH4 + H ←→ CH4   | F                   | N       | 7.9 × 10⁻¹¹       | 1.5 - 4.7 × 10⁻¹⁰  | 2           |
| CH3 + 4N ←→ 3H3CN · ←→ H2CN + H | F | N | 3.3 × 10⁻¹¹ | 5.0 - 7.7 × 10⁻¹¹ | 1.5 |
| CH3 + 2N ←→ 3H3CN · ←→ H2CN + H | F | N | 1.0 × 10⁻¹⁰ |                     |             |
| CH3 + 2N ←→ 1H3CN · ←→ H2CN + H | F | N | 3.1 × 10⁻¹¹ |                     |             |
| 2CH3 ←→ C2H6     | F                   | N       | 7.3 × 10⁻¹³       | 3.5 - 6.5 × 10⁻¹⁷  | 48          |
| 1CH2 + H ←→ CH3   | F                   | N       | 8.4 × 10⁻¹¹       | 5.0 × 10⁻¹¹         | 2           |
| 1CH2 + H2 ←→ CH4  | F                   | N       | 1.0 × 10⁻¹¹       | 7.0 × 10⁻¹² - 1.3 × 10⁻¹⁰ | 1 |
| 1CH2 + 4N ←→ 4H2CN | F         | N       | 1.1 × 10⁻¹⁰       |                     |             |
| 1CH2 + 3N ←→ 4H2CN | F         | N       | 1.5 × 10⁻¹⁰       |                     |             |
| 1CH2 + 1CH2 ←→ C2H4 | F        | N       | 9.9 × 10⁻¹²       | 5.0 × 10⁻¹¹         | 5           |
| 1CH2 + 3CH2 ←→ C2H4 | F         | N       | 3.5 × 10⁻¹¹       | 3.0 × 10⁻¹¹         | 1           |
| 1CH2 + CH3 ←→ C2H5 · ←→ C2H4 + H | F | N | 2.3 × 10⁻¹¹ | 3.0 × 10⁻¹¹ | 1 |
It is often assumed that experiments provide the closest values to the true reaction rate coefficients. However, for a single reaction, separate experiments can measure coefficients that differ by over 2 orders of magnitude (e.g. for CH + CH₄ → C₂H₄ + H, k = 2.0 × 10⁻¹² to 3.0 × 10⁻¹⁰ cm³s⁻¹). This variation can be due to differing experimental methods, instrumentation, and analytical techniques. Furthermore, the reactions reported in experiments may not correspond to direct pathways. Instead there may be intermediates embedded in multiple reaction steps that correspond to the overall measured reaction rate coefficient. Theoretical analysis and mechanistic modeling can be used to sort out the most likely steps in a multiple-step reaction in order to avoid the inclusion of redundant reaction pathways in chemical networks.

In this work, we calculate the reaction rate coefficients for the reactions involved in HCN production from atmospheric nitrogen and methane radicals, as well as the most direct competing reactions. This network includes 15 reactions that have no experimental or suggested value in the literature, and six of these are directly involved in atmospheric HCN synthesis. All our calculations are performed at the same level of theory, i.e. BH/HandHLYP/aug-cc-pVDZ, therefore we expect the error in the rate coefficients to be similar for all reactions.

The largest discrepancy between experiments and theory is for the reaction of CH₃ + N → products. Stief et al. measured the rate coefficient of CH₃ + N → products to be 8.6 × 10⁻¹¹ cm³s⁻¹, and Marston et al. reported the experimental branching ratios to be

\[ \text{CH₃ + N \rightarrow H₂CN + H} \quad \Phi \sim 0.9, \]

and

\[ \text{CH₃ + N \rightarrow HCN + H₂} \quad \Phi \sim 0.1. \]

However, we find only the first of these reactions has an efficient rate coefficient (k = 3.3 × 10⁻¹¹ cm³s⁻¹), and that the second reaction is very inefficient (k ∼ 10⁻²⁸ cm³s⁻¹). This result agrees with past theoretical work, which suggests the measurement of the second reaction likely corresponds to a series of reactions passing through the H₂CN intermediate. For more details of our analysis, see theoretical case study 4 in SI.
Our theoretical reaction rate coefficients are within an order of magnitude of the closest experimental or suggested value from the literature 93% of the time. The theoretical reaction rate coefficients for H$_2$CN + 4N $\rightarrow$ HCN + 3NH, 2CH$_3$ $\rightarrow$ C$_2$H$_6$, and 2H$_2$CN $\rightarrow$ HCN + H$_2$CNH, on the other hand, differ by factors of 47, 48, and 89 from the closest experimental values, respectively. In the case of 2H$_2$CN $\rightarrow$ HCN + H$_2$CNH, we are unable to converge the calculations beyond a H-N bond distance of 1.95 Å, and in this case, the rate coefficients increase towards the experimental values with increasing H-N bond distance. Therefore we expect the major source of discrepancy between theory and experiment for this reaction is due to computational convergence. With regards to the other two reactions, we find the discrepancies to be due to our chosen computational method. Calculations at the CCSD/aug-cc-pVDZ level of theory bring the rate coefficient for 2CH$_3$ $\rightarrow$ C$_2$H$_6$ to within its experimental range. CCSD calculations, however, do not universally increase accuracy. The rate coefficient for H$_2$CN + 4N $\rightarrow$ HCN + 3NH when calculated using CCSD/aug-cc-pVDZ is over 3 orders of magnitude smaller than the experimental value. On the other hand, this reaction rate coefficient comes to within ~80% of the experimental value when using CAM-B3LYP/aug-cc-pVDZ. Because CAM-B3LYP has less short-range HF exchange than BHandHLYP, this method is expected to predict a smaller barrier height than BHandHLYP. Thus in this case, where BHandHLYP overestimates the barrier height (underestimates the rate coefficient) with respect to the experimental value, CAM-B3LYP brings the calculated rate coefficient closer to the experimental value. Of future interest would be to test the accuracy of all the rate coefficients in our network when calculated with CAM-B3LYP/aug-cc-pVDZ.

### Temperature Dependencies

In Table 4 we display the Arrhenius coefficients for the reactions in this network for temperatures between 50 and 400 K. We also display the temperature-dependent rate coefficients for the 10 reactions that have barriers in Figure 2.

| Reaction equation | Forward or Reverse? | Temperature range (K) | α   | β   | γ   |
|-------------------|---------------------|-----------------------|-----|-----|-----|
| H$_2$CN $\leftrightarrow$ HCN + H | F | 50–400 | 7.9×10$^{14}$ | 0 | 16952 |
| H$_2$CN + H $\rightarrow$ HCN + H$_2$ | R | 50–400 | 6.5×10$^{-11}$ | 0.7 | 2318 |
| H$_2$CN + 4N $\leftrightarrow$ HCN + 3NH | F | 50–400 | 1.8×10$^{-11}$ | 0 | 0 |
| 2H$_2$CN $\leftrightarrow$ HCN + H$_2$CNH | R | 50–400 | 7.8×10$^{-12}$ | 1.63 | 938 |
| CH$_4$ + H $\leftrightarrow$ CH$_3$ + H$_2$ | F | 279–400 | 1.2×10$^{-11}$ | 0 | 758 |
| CH$_4$ + 2N $\leftrightarrow$ H$_2$CNH + H | F | 50–400 | 3.7×10$^{-14}$ | 0 | 0 |
| CH$_3$ + H $\leftrightarrow$ CH$_4$ | F | 50–400 | 5.5×10$^{-11}$ | 0.6 | 4689 |
| CH$_3$ + 4N $\leftrightarrow$ H$_3$CN$^-$ $\leftrightarrow$ H$_2$CN + H | F | 50–400 | 1.5×10$^{-11}$ | -0.32 | 6632 |
| CH$_3$ + 2N $\leftrightarrow$ H$_3$CN$^-$ $\leftrightarrow$ H$_2$CN + H | R | 50–400 | 4.7×10$^{-10}$ | 0 | 700 |
| CH$_3$ + 2N $\leftrightarrow$ H$_3$CN$^-$ $\leftrightarrow$ H$_2$CN + H | F | 50–400 | 7.9×10$^{-11}$ | 0 | 0 |
| CH$_3$ + 2N $\leftrightarrow$ H$_3$CN$^-$ $\leftrightarrow$ H$_2$CN + H | F | 50–400 | 3.3×10$^{-11}$ | 0 | 0 |
| CH$_3$ + 2N $\leftrightarrow$ H$_3$CN$^-$ $\leftrightarrow$ H$_2$CN + H | F | 50–400 | 1.0×10$^{-10}$ | 0 | 0 |
| CH$_3$ + 2N $\leftrightarrow$ H$_3$CN$^-$ $\leftrightarrow$ H$_2$CN + H | F | 50–400 | 3.1×10$^{-11}$ | 0 | 0 |
| CH$_3$ + 2N $\leftrightarrow$ H$_3$CN$^-$ $\leftrightarrow$ H$_2$CN + H | F | 50–400 | 7.3×10$^{-13}$ | 0 | 0 |
| 2CH$_3$ $\leftrightarrow$ C$_2$H$_6$ | F | 50–400 | 8.4×10$^{-11}$ | 0 | 0 |
| 1CH$_2$ + H $\leftrightarrow$ CH$_3$ | F | 50–400 | 1.0×10$^{-10}$ | 0 | 0 |
| 1CH$_2$ + 2N $\leftrightarrow$ H$_2$CN | F | 50–400 | 1.1×10$^{-10}$ | 0 | 0 |
| 1CH$_2$ + 2N $\leftrightarrow$ H$_2$CN | F | 50–400 | 1.5×10$^{-10}$ | 0 | 0 |
| 1CH$_2$ + 1CH$_2$ $\leftrightarrow$ C$_2$H$_4$ | F | 50–400 | 9.9×10$^{-12}$ | 0 | 0 |
| 1CH$_2$ + 3CH$_2$ $\leftrightarrow$ C$_2$H$_4$ | F | 50–400 | 3.5×10$^{-11}$ | 0 | 0 |
| 1CH$_2$ + 3CH$_2$ $\leftrightarrow$ C$_2$H$_4$ + H | F | 50–400 | 2.3×10$^{-11}$ | 0 | 0 |
| 1CH$_2$ + CH$_4$ $\leftrightarrow$ C$_2$H$_6$ | F | 50–400 | 6.1×10$^{-13}$ | 0 | 0 |
| 3CH$_2$ + H $\leftrightarrow$ CH$_3$ | F | 50–400 | 5.6×10$^{-10}$ | 0 | 0 |
| 3CH$_2$ + H $\leftrightarrow$ CH$_3$ + H | R | 50–400 | 5.4×10$^{-11}$ | 0 | 3661 |
| 3CH$_2$ + 4N $\leftrightarrow$ 2H$_2$CN | F | 50–400 | 4.2×10$^{-11}$ | 0.82 | 6504 |
The majority of the reactions with barriers fit to one Arrhenius expression for the 50–400 K temperature range, however there were two special cases that had discontinuities: H$_2$CN + 3N $\rightarrow$ HCN + 3NH at 279 K, and H$_2$ + 2N $\rightarrow$ 3NH + H at 304 K. First-order rate coefficients have units s$^{-1}$. Second-order rate coefficients have units cm$^3$s$^{-1}$.

The characteristic temperature creates a discontinuity in the temperature dependent rate coefficient, that is better fit to two separate sets of Arrhenius coefficients.

The rate coefficients of four of the reactions with barriers do not decrease rapidly with decreasing temperatures, and remain “fast” (k $> 10^{-21}$ cm$^3$s$^{-1}$) in the entire 50–400 K temperature range:

\[
\text{CH}_4 + 2\text{N} \longrightarrow \text{H}_3\text{C}_\text{N}_2 \longrightarrow \text{I}_2\text{H}_2\text{C}_\text{N}_2 + \text{H},
\]

\[
\text{3NH} + \text{H} \longrightarrow \text{H}_2 + 4\text{N},
\]

\[
\text{H}_2 + 2\text{N} \longrightarrow \text{NH}_2 \cdot \longrightarrow 3\text{NH} + \text{H},
\]

\[
\text{H}_2\text{CN} + 4\text{N} \longrightarrow \text{HCN} + 3\text{NH}.
\]
$\text{CH}_3 + \text{N} \longrightarrow \text{H}_2\text{CN} + \text{H}$

has three spin configurations. If the nitrogen is in the ground state, the reaction passes through the excited state $^3\text{H}_2\text{CN}$ intermediate before decaying into $\text{H}_2\text{CN} + \text{H}$ directly, or after passing through the $^3\text{H}_2\text{CNH}$ intermediate. If the nitrogen is in the excited state, the reaction can either pass through the excited state $^3\text{H}_2\text{CN}$ intermediate, or the ground state $^1\text{H}_2\text{CN}$ intermediate, before decaying into $\text{H}_2\text{CN} + \text{H}$ directly, or after passing through the $^3\text{H}_2\text{CNH}$ or $^1\text{H}_2\text{CNH}$ intermediates. In other words, on the triplet PES there are two possible reactions: $\text{CH}_3 + ^4\text{N} \longrightarrow ^3\text{H}_3\text{CN} \longrightarrow \text{H}_2\text{CN} + \text{H}$ and $\text{CH}_3 + ^2\text{N} \longrightarrow ^3\text{H}_3\text{CN} \longrightarrow \text{H}_2\text{CN} + \text{H}$, and on the singlet PES there is one reaction: $\text{CH}_3 + ^2\text{N} \longrightarrow ^1\text{H}_3\text{CN} \longrightarrow \text{H}_2\text{CN} + \text{H}$. The first steps of these reactions are the rate-limiting steps, and these steps are barrierless. All reactions have the same products, a ground state H$_2$CN molecule and H atom. However, the rate coefficient for $\text{CH}_3 + ^2\text{N} \longrightarrow ^3\text{H}_3\text{CN} \longrightarrow \text{H}_2\text{CN} + \text{H}$ is larger than the other two reactions by a factor of 3 (see Table 3 for calculated values).

Rate coefficients for different reaction spin configurations can also vary by several orders of magnitude, especially if a reaction barrier exists. The reaction $\text{H}_2\text{CN} + \text{N} \longrightarrow \text{HCN} + \text{NH}$ has three spin configurations that produce ground state HCN. On the singlet surface, there is $\text{H}_2\text{CN} + ^2\text{N} \longrightarrow \text{HCN} + ^1\text{NH}$, and on the triplet surface, there is $\text{H}_2\text{CN} + ^4\text{N} \longrightarrow \text{HCN} + ^3\text{NH}$ and $\text{H}_2\text{CN} + ^2\text{N} \longrightarrow \text{HCN} + ^3\text{NH}$. All these reactions have an energy barrier, but only the spin configuration involving the $^4\text{N}$ atom is efficient. We calculate the rate coefficient for $\text{H}_2\text{CN} + ^4\text{N} \longrightarrow \text{HCN} + ^3\text{NH}$ to be $9.4 \times 10^{-13}$ cm$^3$s$^{-1}$, which is 16 and 18 orders of magnitude larger than our calculated rate coefficients for $\text{H}_2\text{CN} + ^2\text{N} \longrightarrow \text{HCN} + ^3\text{NH}$ and $\text{H}_2\text{CN} + ^2\text{N} \longrightarrow \text{HCN} + ^1\text{NH}$, respectively.

Different spin configurations for two reactants can also lead to different products. For example, when $^1\text{CH}_2$ and $\text{CH}_4$ react on the singlet surface, they come together to form $\text{C}_2\text{H}_6$. When the hydrogen from $\text{CH}_4$ bonds with the carbon of $^1\text{CH}_2$, the resultant $\text{CH}_3$ molecules each have an unpaired electron of opposite spin, allowing these molecules to rapidly bond to form $\text{C}_2\text{H}_6$. However, when $^3\text{CH}_2$ and $\text{CH}_4$ react on the triplet surface, they react directly to form two $\text{CH}_3$ molecules, each with an unpaired electron of the same spin. The rate coefficient of $^1\text{CH}_2 + \text{CH}_4 \longrightarrow \text{C}_2\text{H}_6$ is also 5 orders of magnitude larger than $^3\text{CH}_2 + \text{CH}_4 \longrightarrow 2\text{CH}_3$. This is largely due to the fact that $^1\text{CH}_2 + \text{CH}_4 \longrightarrow \text{C}_2\text{H}_6$ is barrierless, whereas $^3\text{CH}_2 + \text{CH}_4 \longrightarrow 2\text{CH}_3$ has an energy barrier.

In this work, we use canonical variational transition state theory (CVT) to calculate 42 rate coefficients that are directly involved with or are in competition with HCN production in early Earth or Titan atmospheres. Approximately 36% of these reactions have no previously reported experimental or suggested value. To make such a large network of calculations feasible, we make use of computational quantum chemistry simulations at an accurate yet inexpensive level of theory: BHHandHLYP/aug-cc-pVDZ. Moreover, we only calculate the temperature dependence of the rate coefficients for the reactions that have barriers. By using one level of theory for all reaction rate coefficient calculations, we expect the computational errors to be similar.

In this network, we focus on HCN production from methane and nitrogen radicals, which are produced in the atmosphere via UV photodissociation or lightning. Dissociation of $\text{CH}_4$ and $\text{N}_2$ produces both excited and ground state species, therefore we calculate the rate coefficients for multiple spin configurations involving these species. The reactions in our network have 1–5 spin configurations.

We list our five most important results below.

- We provide consistently calculated rate coefficients for 15 reactions that have no previously suggested values. In this sense, we fill a substantial gap in the data. These previously unknown rate coefficients include those of several key reactions in the pathway to produce atmospheric HCN (e.g. $\text{CH}_2 + \text{N} \longrightarrow \text{H}_2\text{CN}$ and $\text{H}_2\text{CN} \longrightarrow \text{HCN} + \text{H}_2$).

- Of the reactions in our network with past experimental or suggested values, 93% are within an order of magnitude of these values. The remaining 7% differ by less than 2 orders of magnitude from experimental values. These discrepancies are either due to convergence issues or our chosen computation method. When convergence isn’t an issue, re-running rate coefficient calculations at the similarly expensive CAM-B3LYP/aug-cc-pVDZ level of theory or the more expensive CCSD/aug-cc-pVDZ level of theory decreases the discrepancy between theory and experimental values.

- We find the reaction of $\text{CH}_3 + \text{N} \longrightarrow \text{HCN} + \text{H}_2$ on the singlet surface to be inefficient, with a rate coefficient near $10^{-28}$ cm$^3$s$^{-1}$ (confirming the results of Cinac and Largé). This is in contrast to experimental results which suggest a rate coefficient to have a value near $10^{-11}$ cm$^3$s$^{-1}$. The experimental result may be due to the measurement of multi-step reaction, e.g., $\text{CH}_3 + \text{N} \longrightarrow \text{H}_2\text{CN} + \text{H}$ and $\text{H}_2\text{CN} + \text{H} \longrightarrow \text{HCN} + \text{H}_2$. However, we cannot exclude the possibility of a spin-forbidden process accounting for this experimental value.
• The effects of reaction spin configuration on the rate coefficient can be both subtle and substantial. For a given reaction, differences in rate coefficients between spin configurations can range from factors of order unity, up to 18 orders of magnitude. If there is a barrier involved with one or more of the reaction spin configurations, the difference between their reaction rate coefficients tends to be much greater than if all the reaction spin configurations are barrierless.

• Seven reaction rate coefficients in our network decrease rapidly with decreasing temperature, and become “slow” ($k < 10^{-21}$) at temperatures below $\sim 100-300$ K. One reaction, H$_2$CN $\rightarrow$ HCN + H, increases rapidly for increasing temperatures; above 320 K, this reaction has the highest rate coefficient in the network.

Overall, we find CVT and computational quantum chemistry simulations at the BHandHLYP/aug-cc-pVDZ level of theory to be a feasible and accurate method for calculating a large set of small-molecule, multiple-spin configuration reaction rate coefficients for a range of terrestrial atmospheric temperatures. We also note that although calculations at the CCSD/aug-cc-pVDZ level of theory often lead to improvements in the rate coefficients’ conformance to experimental values, computational cost and convergence issues made calculating all the rate coefficients at this level of theory impossible. Based on a limited number of calculations, we also find CAM-B3LYP to be an accurate alternative functional for performing CVT rate coefficient calculations and recommend it for a wider study.

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SUPPORTING INFORMATION

Experimental Data

Experiments and reviews have measured and suggested reaction rate coefficients for several of the reactions in this network at or near ~298 K. These values are listed in Table S1.
TABLE S1: All available experimental or recommended reaction rate coefficients for the reactions in this study. For brevity, only the 13 most recent experimental rate coefficients are listed for \( \text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6 \); for a complete listing, we refer the reader to the NIST Chemical Kinetics Database \(^{66}\). First-order rate coefficients have units \( \text{s}^{-1} \). Second-order rate coefficients have units \( \text{cm}^3\text{s}^{-1} \).

| Reaction | \( k(298\text{K}) \) | Technique | Temp. (K) | Pressure (Torr) | Reference(s) |
|----------|-----------------|-----------|----------|----------------|---------------|
| \( \text{H}_2\text{CN} + \text{H} \rightarrow \text{HCN} + \text{H}_2 \) | \( 8.3 \times 10^{-11} \) | Z | independent | | Tomeczek and Gradon\(^{67}\) |
| \( \text{H}_2\text{CN} + ^4\text{N} \rightarrow \text{HCN} + ^3\text{NH} \) | \( 4.4 \times 10^{-11} \) | M | 298 | 1 | Nesbitt et al.\(^{68}\) |
| \( 2\text{H}_2\text{CN} \rightarrow \text{HCN} + \text{H}_2\text{CNH} \) | \( 3.3 - 8.3 \times 10^{-12} \) | M | 300 | 120–480 | Horne and Norrish\(^{69}\) |
| \( \text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2 \) | \( 3.5 \times 10^{-17} \) | M | 298 | | Lawrence and Firestone\(^{70}\) |
| \( \text{CH}_4 + 4\text{N} \rightarrow \text{HCN} + 3\text{NH} \) | \( 4.4 \times 10^{-11} \) | M | 298 | 0.55 | Jones and M.\(^{71}\) |
| \( 2\text{H}_2\text{CN} \rightarrow \text{HCN} + \text{H}_2\text{CNH} \) | \( 3.3 - 8.3 \times 10^{-12} \) | S | 300 | | Umemoto et al.\(^{72}\) |
| \( \text{CH}_4 + ^2\text{N} \rightarrow \text{H}_2\text{CNH} + \text{H} \) | \( ^a4.5 \times 10^{-12} \) | M | 298 | 700 | Takayanagi et al.\(^{72}\) |
| \( ^a3.7 \times 10^{-12} \) | M | 300 | 6 | Umemoto et al.\(^{72}\) |
| \( ^a2.7 \times 10^{-12} \) | M | 295 | 20 | Umemoto et al.\(^{72}\) |
| \( ^a2.4 \times 10^{-12} \) | M | 300 | 3–5 | Umemoto et al.\(^{72}\) |
| \( ^a3.2 \times 10^{-12} \) | S | 298 | | Umemoto et al.\(^{72}\) |
| \( \text{CH}_4 + ^2\text{N} \rightarrow \text{CH}_3 + ^3\text{NH} \) | \( ^b1.7 \times 10^{-12} \) | M | 298 | 700 | Takayanagi et al.\(^{72}\) |
| \( ^b1.4 \times 10^{-12} \) | M | 300 | 6 | Umemoto et al.\(^{72}\) |
| \( ^b1.0 \times 10^{-12} \) | M | 295 | 20 | Umemoto et al.\(^{72}\) |
| \( ^b9.0 \times 10^{-13} \) | M | 300 | 3–5 | Umemoto et al.\(^{72}\) |
| \( ^b1.2 \times 10^{-12} \) | S | 298 | | Umemoto et al.\(^{72}\) |
| \( \text{CH}_3 + \text{H} \rightarrow \text{CH}_4 \) | \( 4.7 \times 10^{-10} \) | M | 300 | high-pressure limit | Brouard et al.\(^{77}\) |
| \( 3.3 \times 10^{-10} \) | M | 308 | high-pressure limit | Cheng and Yeh\(^{78}\) |
| \( 2.5 \times 10^{-10} \) | M | 309 | high-pressure limit | Cheng et al.\(^{79}\) |
| \( 2.0 \times 10^{-10} \) | M | 296 | 735–755 | Sworski et al.\(^{80}\) |
| \( 1.5 \times 10^{-10} \) | M | 300 | high-pressure limit | Patrick et al.\(^{81}\) |
| \( 3.4 \times 10^{-10} \) | F | 298 | high-pressure limit | Michael et al.\(^{82}\) |
| \( 3.5 \times 10^{-10} \) | S | independent | high-pressure limit | Cobos and Troe\(^{83}\) |
| \( 3.5 \times 10^{-10} \) | S | independent | high-pressure limit | Baulch et al.\(^{83}\) |
| \( 2.0 \times 10^{-10} \) | S | 298 | high-pressure limit | Tsang\(^{84}\) |
| \( \text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H} \) | \( ^c1.3 \times 10^{-20} \) | M | 300 | | Kobrinsky and Pacey\(^{85}\) |
| \( ^c1.2 \times 10^{-20} \) | S | 300 | | Tsang and Hampson\(^{85}\) |
| \( ^c9.6 \times 10^{-21} \) | S | 300 | | Baulch et al.\(^{85}\) |
| \( \text{CH}_3 + ^4\text{N} \rightarrow \text{HCN} + \text{H}_2 \) | \( 8.6 \times 10^{-12} \) | M | 298 | 0.3–1.6 | Marston et al.\(^{88}\) |
| \( \text{CH}_3 + ^4\text{N} \rightarrow \text{H}_2\text{CN} + \text{H} \) | \( 7.7 \times 10^{-11} \) | M | 298 | 0.3–1.6 | Marston et al.\(^{88}\) |
| \( 5.0 \times 10^{-11} \) | S | independent | | Miller and Bowman\(^{87}\) |
| \( 2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6 \) | \( 6.5 \times 10^{-11} \) | M | 300 | high-pressure limit | Walter et al.\(^{88}\) |
| Reaction                                      | Rate Coefficient | Units | Temperature | Authors                     |
|-----------------------------------------------|------------------|-------|-------------|-----------------------------|
| $5.1 \times 10^{-11}$                         | M                | 300   | 750         | Fulle and Hippler           |
| $4.5 \times 10^{-11}$                         | M                | 298   | 591         | Becker et al                |
| $4.5 \times 10^{-11}$                         | M                | 279   | 600         | Berman and Lin              |
| $3.0 \times 10^{-11}$                         | M                | 294   | 750         | McIlroy and Tully           |
| $2.3 \times 10^{-11}$                         | M                | 298   | 100         | Butler et al                |
| $1.7 \times 10^{-11}$                         | M                | 298   | 1–9         | Bosnali and Perner          |
| $1.0 \times 10^{-12}$                         | M                | 298   |             | Braun et al                 |

**Previous Theoretical Data**

Previous theoretical studies have been performed on the reactions in this network. In Table S2, we list the theoretical rate coefficients and the methods that were employed to calculate them.
TABLE S2: Previous theoretical rate coefficients for the reactions in this study. For sources that performed multiple rate coefficient calculations with different theoretical and/or computational methods, we list the range of their results here. First-order rate coefficients have units s⁻¹. Second-order rate coefficients have units cm³s⁻¹.

| k(293K) | Theory | Computational Method | Reference(s) |
|---------|--------|----------------------|--------------|
| 4.1×10⁻²¹–2.2×10⁻¹⁸ | TST, quantum dynamics | CCSD(T)/cc-pVTZ<sup>a</sup> | Kerkeni and Clarity<sup>111</sup> |
| 8.4×10⁻¹⁹–2.1×10⁻¹⁸ | CVT + SCT<sup>b</sup> | BH&HLYP/6-311G(d,p), PMP4/6-311+G(2df,2pd)<sup>c</sup> | Truong and Duncan<sup>112</sup> |
| 1.6×10⁻¹⁸ | CVT + SCT | PMP4/cc-pVTZ<sup>d</sup> | Maity et al<sup>113</sup> |
| 1.3×10⁻¹⁸ | CVT + SCT<sup>e</sup> | QCISD/6-311G(d,p) | Truong<sup>113</sup> |
| 9.8×10⁻¹⁹ | CVT + µOMT | | Espinosa-García and Cortada<sup>114</sup> |
| 6.5×10⁻¹⁹ | CVT + µOMT | | Espinosa-García and Cortada<sup>114</sup> |
| 3.0×10⁻²¹–6.0×10⁻¹⁹ | TST, quantum dynamics | CCSD(T)/cc-pVTZ<sup>a</sup> | Kerkeni and Clarity<sup>111</sup> |
| 3.8×10⁻¹⁹ | BEBO | | Clark and Dovi<sup>115</sup> |
| 8.7×10⁻²¹–2.4×10⁻¹⁹ | TST, CVT, CVT + SCT | | Pu and Truhlar<sup>116</sup> |
| 1.8×10⁻²¹–1.6×10⁻¹⁹ | TST | G2(MP2)<sup>f</sup>, BAC-MP4<sup>g</sup> | Berry et al<sup>117</sup> |
| 8.1×10⁻²⁰ | TST + tunneling | UMP2/6-31G(d,p) | Bryukov et al<sup>118</sup> |
| 4.6×10⁻²⁰ | TST + WTC | PMP4SDTQ/6-311G**<sup>h</sup> | Gonzalez et al<sup>119</sup> |
| 1.2×10⁻¹⁹ | CVT + µOMT | | Espinosa-García and Cortada<sup>114</sup> |
| 1.1×10⁻¹⁹ | CVT + SCT | PMP4/cc-pVTZ<sup>d</sup> | Joseph et al<sup>120</sup> |
| 1.5–8.2×10⁻²⁰ | CVT + SCT<sup>b</sup> | BH&HLYP/6-311G(d,p), PMP4/6-311+G(2df,2pd)<sup>c</sup> | Truong and Duncan<sup>112</sup> |
| 8.0×10⁻²⁰ | CVT + µOMT | | Espinosa-García and Cortada<sup>114</sup> |
| 5.2×10⁻²⁰ | CVT + SCT<sup>e</sup> | QCISD/6-311G(d,p) | Espinosa-García and Cortada<sup>114</sup> |
| 1.7×10⁻²⁰ | TST + tunneling | UMP2/6-31G(d,p) | Espinosa-García and Cortada<sup>114</sup> |
| 1.9×10⁻¹⁰ | CVT + RRKM | CCSD(T)/CBS | Alves et al<sup>121</sup> |
| 9.1×10⁻¹² | µVT + RRKM | CCSD(T)/cc-pVTZ<sup>i</sup> | Cimas and Largo<sup>20</sup> |
| 1.8×10⁻¹⁰ | CVT + RRKM | | Takayanagi et al<sup>22</sup> |
| 6.7×10⁻¹⁰ | CVT | CASCF(5,5)/6-311G** | Hase and Duchovics<sup>123</sup> |
| 4.7×10⁻¹⁰ | CVT + RRKM | | Forst<sup>124</sup> |
| 4.3–4.7×10⁻¹⁰ | µVT + RRKM, CVT + RRKM | | Troe and Ushakov<sup>125</sup> |
| 3.3×10⁻¹⁰ | SACM/CT | CASPT2/cc-pVDZ<sup>k</sup> | Harding et al<sup>115</sup> |
| 3.2×10⁻¹⁰ | VRC-TST | CASPT2/cc-pVDZ<sup>k</sup> | Hase et al<sup>126</sup> |
| 2.0–2.7×10⁻¹⁰ | CVT | MP4/6-31G** | Takahashi et al<sup>127</sup> |
| 2.1×10⁻¹⁰ | CVT | MRD-CI/6-31G** | | |
| 2×10⁻¹⁰ | CVT | MCSCF-CI/DZP<sup>f</sup> | Li et al<sup>128</sup> |
| 1.8×10⁻¹⁰–4.6×10⁻¹⁰ | CVT | CASPT2/ANO-L<sup>m</sup> | Wardlaw and Marcus<sup>129</sup> |
| 6.9–8.4×10⁻¹¹ | LTS | MC | Darvesh et al<sup>130</sup> |
| 3.3×10⁻¹¹ | CVT | MRD-CI/DZ | Pesa et al<sup>131</sup> |
| 7.2×10⁻¹¹ | FTST | MC | Fors<sup>132</sup> |
| 5.8–6.7×10⁻¹¹ | µVT + RRKM | CAS+1+2/cc-pVDZ | Klippenstein and Harding<sup>133</sup> |
| 6.3×10⁻¹¹ | CVT | CASPT2/cc-pVDZ<sup>k</sup> | Klippenstein et al<sup>134</sup> |
| 5.8×10⁻¹¹ | VRC-TST | CASPT2/cc-pVDZ<sup>k</sup> | Wagner and Wardlaw<sup>135</sup> |
| 5.5×10⁻¹¹ | RRKM + FTST | MRCI+Q/aug-cc-pVTZ | Wang et al<sup>136</sup> |
| 5.6×10⁻¹¹ | CVT | B3LYP/6-311G** | Lorant et al<sup>137</sup> |
| 2.0×10⁻¹¹ | CVT | | |
| 3CH₂ + H₂ --> CH₃ + H | TST | G2M(RCC2)<sup>n</sup> | Lu et al<sup>115</sup> |
\[3\text{CH}_2 + 4\text{N} \rightarrow \text{H}_2\text{CN} \cdot \rightarrow \text{HCN} + \text{H}\]

7.9 \times 10^{-11} \quad \text{quantum dynamics} \quad \text{MP4SDTQ/6-311++G(3df,3pd)} \quad \text{Herbst et al.}^{159}

\[3\text{CH}_2 + 3\text{CH}_2 \rightarrow \text{C}_2\text{H}_2 + 2\text{H}\]

1.5 \times 10^{-10} \quad \text{VRC-TST} \quad \text{CASPT2/aug-cc-pVTZ} \quad \text{Jasper et al.}^{159}

\[3\text{CH}_2 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{H}\]

2.2 \times 10^{-10} \quad \text{VRC-TST} \quad \text{CASPT2/aug-cc-pVTZ} \quad \text{Jasper et al.}^{159}

\[\text{CH} + \text{H}_2 \rightarrow \text{CH}_3\]

7.8 \times 10^{-11} \quad \text{RRKM} \quad \text{McIlroy and Tully}^{159}

\[\text{CH} + \text{H}_2 \rightarrow \text{CH}_3 \cdot \rightarrow 3\text{CH}_2 + \text{H}\]

3.3 \times 10^{-11} \quad \text{QCT} \quad \text{MRCI/aug-cc-pVTZ} \quad \text{Mayneris et al.}^{159}

\[3\text{NH} + 4\text{N} \rightarrow \text{N}_2 + \text{H}\]

1.9 \times 10^{-11} \quad \text{quantum dynamics} \quad \text{MRCI+Q/AVTZ} \quad \text{Daranlot et al.}^{160}

\[3\text{NH} + \text{H} \rightarrow \text{H}_2 + 4\text{N}\]

1.5 \times 10^{-12} \quad \text{CT} \quad \text{MRCI/aug-cc-pVQZ} \quad \text{Adam et al.}^{160}

\[2\text{N} + \text{H}_2 \rightarrow \text{NH}_2 \cdot \rightarrow 3\text{NH} + \text{H}\]

2.5–3.3 \times 10^{-12} \quad \text{quantum dynamics, QCT} \quad \text{FOCI/TZP} \quad \text{Takayanagi et al.}^{164}

\[2.7–2.9 \times 10^{-12} \quad \text{QCT} \quad \text{FOCI/TZP} \quad \text{Kobayashi et al.}^{165}

\[1.8–2.7 \times 10^{-12} \quad \text{QCT, CVT} \quad \text{MCQDPT2/6-311++G**} \quad \text{Suzuki et al.}^{124}

\[8.9 \times 10^{-13} \quad \text{QCT} \quad \text{MRCI/aug-pVTZ} \quad \text{Pederson et al.}^{166}

\text{\textsuperscript{a} Single point energies are based on optimized geometries calculated at the MP2/cc-pVTZ level.}
\text{\textsuperscript{b} Energy barrier scaled by a factor of 1.174.}
\text{\textsuperscript{c} Single point energies are based on optimized geometries calculated at the BHandHLYP/6-31G(d,p) level.}
\text{\textsuperscript{d} Single point energies are based on optimized geometries calculated at the BHandHLYP/cc-pVDZ level.}
\text{\textsuperscript{e} Energy barrier scaled by a factor of 0.86.}
\text{\textsuperscript{f} Single point energies are based on optimized geometries calculated at the MP2/6-31G(d) level.}
\text{\textsuperscript{g} Single point energies are based on optimized geometries calculated at the HF/6-31G(d) level.}
\text{\textsuperscript{h} Single point energies are based on optimized geometries calculated at the UMP2/6-31G** level.}
\text{\textsuperscript{i} Single point energies are based on optimized geometries calculated at the B3LYP/cc-pVTZ level.}
\text{\textsuperscript{j} Values calculated in the high-pressure limit (p \rightarrow \infty).}
\text{\textsuperscript{k} Single point energies are based on optimized geometries calculated at the B3LYP/6-31G* level, and corrections are applied at the CAS+1+2+QC/aug-cc-pVTZ level.}
\text{\textsuperscript{l} CI calculations are based on optimized geometries calculated at the UHF/DZP level.}
\text{\textsuperscript{m} Single point energies are based on optimized geometries calculated at the CASSCF/ANO-L level.}
\text{\textsuperscript{n} Single point energies are based on optimized geometries calculated at the B3LYP/6-311++G(3df,2p) level.}
\text{\textsuperscript{o} Single point energies are based on optimized geometries calculated at the MP2/6-31G(d,p) level.}
\text{\textsuperscript{p} Single point energies are based on optimized geometries calculated at the B3LYP/6-311++G(d,p) level.}
\text{\textsuperscript{q} Single point energies are based on optimized geometries calculated at the FORS-MCSCF(7,6)/6-311++G** level.}

\text{TST: Transition state theory.}
\text{CVT: Canonical variational transition state theory.}
\text{SCT: Small curvature tunneling approximation.}
\text{\muOMT: Microcanonical optimized multidimensional tunneling.}
\text{BEBO: Bond-energy-bond-order method.}
\text{WTC: Wigner tunneling correction.}
\text{RRKM: Rice-Ramsperger-Kassel-Marcus theory.}
\text{\muVT: Microcanonical variational transition state theory.}
\text{SACM/CT: Statistical adiabatic channel model/classical trajectories approach.}
\text{VRC-TST: Variable reaction coordinate transition state theory.}
\text{LTS: Loose transition state model.}
\text{MC: Monte Carlo simulations.}
\text{FTST: Flexible transition state theory.}
\text{QCT: Quasi-classical trajectory method}
\text{CT: Classical trajectory method}

Example Calculation and Computational Methods

Comparison

The \text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2 abstraction reaction has been thoroughly studied both experimentally and theoretically$^{129,131,132,149,152}$. A pair of experiments at 298 K place its rate coefficient between $1.7–3.5 \times 10^{-17}$
However, based on a range of experiments and evaluations over a wider temperature range (300–2000 K), it has been suggested the rate coefficient is closer to $8.2 \times 10^{-19}$ cm$^3$s$^{-1}$.[23] Previous theoretical studies have calculated its rate coefficient to be between $1.8 \times 10^{-21}$ and $2.2 \times 10^{-18}$ cm$^3$s$^{-1}$ (see Table S2).

The geometry of this reaction progresses as follows: A single H atom approaches a CH$_4$ molecule directly in line with one of its H atoms and its central C atom. The H-C bond in methane then stretches until its H atom bonds with the adjacent H atom. The two newly formed molecules, H$_2$ and CH$_3$ then separate. The geometry of the transition state is depicted in Figure S2.

![FIG. S1. Geometry of the conventional transition state for CH$_4$ + H $\rightarrow$ CH$_3$ + H$_2$ at the BH$\text{Hand}$HLYP/aug-cc-pVDZ level of theory. In the reactant state, hydrogen B is 1.09 Å from the central carbon. In the product state hydrogen B is 0.754 Å from hydrogen A.](image)

In Figure S2 we show $\Delta G_{GT}(298.15K, s)$ with the reaction coordinate representing the C-H bond distance. At the BH$\text{Hand}$HLYP/aug-cc-pVDZ level of theory, the maximum $\Delta G$ occurs at a C-H distance of 1.44 Å, which is slightly farther along the reaction coordinate than the conventional transition state (1.409 Å).

We calculate the rate coefficient for this reaction using 6 different computational methods, and display them in Table S3.

Rate coefficient calculations using BH$\text{Hand}$HLYP and CAM-B3LYP methods are within the experimental and suggested range. Calculations using HF grossly overestimate the energy barrier, and provide a rate coefficient several orders of magnitude lower than the experimental and suggested range. M06-2x and CCSD methods also provide values lower than the experimental and suggested range, however only by approximately an order of magnitude. Calculations using B3LYP underestimate the energy barrier, leading to a value approximately an order of magnitude higher than the experimental and suggested range.

The calculated rate coefficient using the BH$\text{Hand}$HLYP functional sits in the middle of the range of experimental and suggested values, whereas he rate coefficient calculated using CAM-B3LYP sits within ~10% of the experimental value at the high end of the range. The BH$\text{Hand}$-LYP result may provide the best compromise between the experimental and suggested rate coefficients for this reaction.

![FIG. S2. Gibbs free energy difference as a function of the reaction coordinate (C-H bond distance) for CH$_4$ + H $\rightarrow$ CH$_3$ + H$_2$ at the BH$\text{Hand}$HLYP/aug-cc-pVDZ level of theory. The maximum $\Delta G$ occurs at 1.44 Å. $\Delta G$ is calculated as the Gibbs free energy at the reaction coordinate minus the Gibbs free energy of the reactants placed 100 Å apart.](image)

| Computational Method | k(298)   | Error factor |
|----------------------|----------|--------------|
| HF                   | $3.5 \times 10^{-25}$ | $2 \times 10^{6}$ |
| M06-2x               | $5.7 \times 10^{-20}$ | 14            |
| CCSD                 | $9.9 \times 10^{-20}$ | 8             |
| BH$\text{Hand}$HLYP | $8.1 \times 10^{-18}$ | 1             |
| CAM-B3LYP            | $3.1 \times 10^{-17}$ | 1             |
| B3LYP                | $3.9 \times 10^{-16}$ | 11            |

TABLE S3. Calculated rate coefficients for CH$_4$ + H $\rightarrow$ CH$_3$ + H$_2$ using 6 different computational methods with the aug-cc-pVDZ basis set. Experimental and suggested values range from $8.2 \times 10^{-19}$ to $3.5 \times 10^{-17}$ cm$^3$s$^{-1}$.[23] The error factor is the multiplicative or divisional factor from the nearest experimental or suggested value; the error factor is 1 if the calculated value is within the range of experimental or suggested values. Rate coefficients have units cm$^3$s$^{-1}$. 
Finally, CCSD provides a fairly accurate rate coefficient within a factor of 8 of the suggested value.

**Theoretical Case Studies**

*Case Study 1: H$_2$CN + H $\rightarrow$ HCN + H$_2$*

Tomeczek and Gradoń used published chemical compositions of the flames of CH$_4$ and O$_2$ + N$_2$ at 2500 to 1850 K to suggest a temperature-independent rate coefficient for H$_2$CN + H $\rightarrow$ HCN + H$_2$. They suggest the value $8.3 \times 10^{-11}$ cm$^3$s$^{-1}$ for this reaction. However, they note that this does not include the effects of an energy barrier. Another way to state this is, they suggest a value much larger than the experimental value for the barrierless reaction. This reaction occurs on the singlet and triplet PES's. Conversely on the triplet PES, where excited $^3$HCN is produced, the effects of the energy barrier are significant.

On the singlet surface, we calculate the reaction rate coefficient at the BHandHLYP/aug-cc-pVDZ level of theory to be $1.8 \times 10^{-11}$ cm$^3$s$^{-1}$. This is less than a factor of 5 larger than the experimental value for the barrierless reaction.

On the triplet surface, the reaction rate coefficient is too small to consider in this study ($k < 10^{-21}$ cm$^3$s$^{-1}$).

*Case Study 2: 2H$_2$CN $\rightarrow$ HCN + H$_2$CNH*

Horne and Norrish calculated the experimental reaction rate coefficient for 2H$_2$CN $\rightarrow$ HCN + H$_2$CNH at 300 K by monitoring the decay of H$_2$CN. The assumption they made was that 2H$_2$CN $\rightarrow$ HCN + H$_2$CNH is the dominant decay pathway of H$_2$CN. The value they obtained was in the range of $3.3-8.3 \times 10^{-12}$ cm$^3$s$^{-1}$.

No theoretical reaction rate coefficients for 2H$_2$CN $\rightarrow$ HCN + H$_2$CNH have been previously published.

We find a direct reaction pathway on the singlet PES that has no energy barrier. However, the simulations did not converge beyond a N-H bond distance of 1.95 Å and the Gibbs maximum was not found. However, choosing the reaction coordinate at a N-H bond distance of 1.95 Å for the calculation provides us with a lower bound estimate of the rate coefficient, which we calculate to be $3.7 \times 10^{-14}$ cm$^3$s$^{-1}$. This value is a factor of 89 smaller than the closest experimental value. The discrepancy between the theoretical and experimental values is expected to be due to these convergence issues.

A higher energy reaction pathway involving two ground state H$_2$CN molecules exists on the triplet surface, however, this reaction produces excited $^3$HCN and is likely much less efficient than the singlet case.

*Case Study 3: CH$_4$ + N $\rightarrow$ products*

Several experiments have measured the rate coefficient of CH$_4$ + $^2$N $\rightarrow$ products by monitoring the decay of $^2$N in the presence of CH$_4$ at 295–300 K. The measured values range from 3.0–5.4 $\times 10^{-12}$ cm$^3$s$^{-1}$. Herron reviewed these experiments and recommended a value of $k(298) = 4.0 \times 10^{-12}$ cm$^3$s$^{-1}$. Umemoto et al. measured the product yields of H and $^3$NH in similar experiments to suggest branching ratios for CH$_4$ + $^2$N $\rightarrow$ H$_2$CNH + H and CH$_4$ + $^2$N $\rightarrow$ CH$_3$ + $^3$NH to be 0.8±0.2 and 0.3±0.1, respectively. Multiplying these branching ratios, the experimental rate coefficients for CH$_4$ + $^2$N $\rightarrow$ H$_2$CNH + H range from 2.4–4.5 $\times 10^{-12}$ cm$^3$s$^{-1}$ and the experimental rate coefficients for CH$_4$ + $^2$N $\rightarrow$ CH$_3$ + $^3$NH range from 0.9–1.7 $\times 10^{-12}$ cm$^3$s$^{-1}$.

Takayanagi et al. used CVT at the CASSCF(5,5)/6-311G** level of theory to calculate the rate coefficient of CH$_4$ + N $\rightarrow$ products to be $8.5 \times 10^{-14}$ cm$^3$s$^{-1}$. They note that their disagreement between experimental and theoretical values is due to the CASSCF calculations estimating too large a barrier. Ouk et al. used TST + WTC at the MRCI+P+Q/aug-cc-pVTZ level of theory to calculate the rate coefficient, and obtained a value closer to the experimental values at $6.8 \times 10^{-12}$ cm$^3$s$^{-1}$. They confirm the results from experiment that suggests a small barrier exists, although no barrier is found using the CCSD(T) and B3LYP levels of theory. The experimental barrier has a height of 6.3 kJ mol$^{-1}$.

In this case study, we analyze the two main branches for the reaction CH$_4$ + $^2$N $\rightarrow$ products. The mechanistic model for these reactions is shown in Figure S3, which displays the conversion of $^2$N to HCN and CH$_3$ + $^3$NH. The reaction pathways for these conversions are depicted in a diagrammatic form.

![Mechanistic models for the production of (a) $^3$H$_2$CNH + H and (b) CH$_3$ + $^3$NH from $^2$N + CH$_4$ on the doublet potential energy surface.](image-url)
TABLE S4. Calculated overall rate coefficients for \( \text{CH}_4 + \text{2N} \rightarrow \text{H}_2\text{CNH} + \text{H} \) and \( \text{CH}_4 + \text{3N} \rightarrow \text{CH}_3 + \text{3NH} \), as well as the intermediate forward and reverse rate coefficients which were used in the calculations. In all simulations, the BHandHLYP method was used with the aug-cc-pVDZ basis set. When using a branching ratio of 0.8 for \( \text{CH}_4 \) + \( \text{2N} \) \( \rightarrow \) \( \text{H}_2\text{CNH} + \text{H} \) \( \rightarrow \) \( \text{CH}_3 + \text{3NH} \), the same experiments provide \( k_a \) values between 2.4 and \( 4.5 \times 10^{-12} \text{ cm}^3\text{s}^{-1} \). Similarly when using a branching ratio of 0.3 for \( \text{CH}_4 + \text{2N} \rightarrow \text{CH}_3 + \text{3NH} \), the same experiments provide \( k_b \) values between 0.9–1.7 \( \times 10^{-12} \text{ cm}^3\text{s}^{-1} \). First-order rate coefficients have units \( \text{s}^{-1} \). Second-order rate coefficients have units \( \text{cm}^3\text{s}^{-1} \).

| Rate coefficient | \( k(298) \) |
|------------------|----------------|
| \( k_a \)        | \( 4.7 \times 10^{-11} \) |
| \( k_b \)        | \( 5.8 \times 10^{-29} \) |
| \( k_1 \)        | \( 4.7 \times 10^{-11} \) |
| \( k_{-1} \)     | \( 3.0 \times 10^{-66} \) |
| \( k_2 \)        | \( 4.9 \times 10^{-13} \) |
| \( k_3 \)        | \( 6.0 \times 10^{-31} \) |

\( ^a \) Simulations did not converge beyond a C-N bond distance of 2.82\( \text{A} \); therefore the rate coefficient is a lower bound.

...theoretical works found the transition state to be at a C-N bond distance of 2.26–2.45 Å. 116-118

We find the barrierless reaction rate coefficient of \( \text{CH}_4 + \text{2N} \rightarrow \text{H}_2\text{CNH} \) at the BHandHLYP/aug-cc-pVDZ level of theory to be \( 6.0 \times 10^{-10} \text{ cm}^3\text{s}^{-1} \), a value two orders of magnitude greater than the closest experimental value. Given that there is likely a small barrier of \( \sim 6.3 \text{ kJ mol}^{-1} \) for this reaction, we insert this experimental barrier into the calculation for \( k \), and obtain a value of \( 4.7 \times 10^{-11} \text{ cm}^3\text{s}^{-1} \). This is only a factor of 9 larger than the nearest experimental value.

... There is only a factor of 9 larger than the nearest experimental value.

...There are several decay pathways for the \( \text{H}_3\text{CNH} \) molecule (e.g.118). Nevertheless, we calculate the upper bound for the rate coefficients of \( \text{CH}_4 + \text{2N} \rightarrow \text{H}_2\text{CNH} + \text{H} \) and \( \text{CH}_4 + \text{2N} \rightarrow \text{CH}_3 + \text{3NH} \) by assuming \( \text{H}_3\text{CNH} \) only decays through these two dominant pathways.

... The steady-state solution of the kinetic rate equations for the above mechanistic models lead to the overall rate constants for a) \( \text{CH}_4 + \text{2N} \rightarrow \text{H}_2\text{CNH} + \text{H} \) and b) \( \text{CH}_4 + \text{2N} \rightarrow \text{CH}_3 + \text{3NH} \) on the doublet PES.

\[
k_a = \frac{k_1 k_2}{k_{-1} + k_2 + k_3} \quad \text{(S1)}
\]

\[
k_b = \frac{k_1 k_3}{k_{-1} + k_2 + k_3} \quad \text{(S2)}
\]

...The values of the reaction rate constants at the BHandHLYP/aug-cc-pVDZ level of theory are listed in Table S3.

...We calculate the overall rate constant for \( \text{CH}_4 + \text{2N} \rightarrow \text{H}_3\text{CNH} \rightarrow \text{H}_2\text{CNH} + \text{H} \) to be the same as the rate constant for \( \text{CH}_4 + \text{2N} \rightarrow \text{H}_3\text{CNH} \). This means the first step is the rate-limiting step. We calculate the value for \( k_a \) to be \( 4.7 \times 10^{-11} \text{ cm}^3\text{s}^{-1} \), which is approximately a factor of 10 smaller than the experimental values. We find the overall rate coefficient for \( \text{CH}_4 + \text{2N} \rightarrow \text{H}_3\text{CNH} \rightarrow \text{CH}_3 + \text{3NH} \) to be inefficient (\( k_b = 5.8 \times 10^{-29} \text{ cm}^3\text{s}^{-1} \)). This is several orders of magnitude smaller than the rate coefficients suggested by the experimental branching ratio.119 However, some theoretical branching ratios for \( \text{CH}_4 + \text{2N} \rightarrow \text{H}_3\text{CNH} \rightarrow \text{CH}_3 + \text{3NH} \) are as low as 0.01, and in every case, \( \text{CH}_4 + \text{2N} \rightarrow \text{H}_3\text{CNH} \rightarrow \text{H}_2\text{CNH} + \text{H} \) is the dominant product. Considering all this, we do not include the inefficient \( \text{CH}_4 + \text{2N} \rightarrow \text{H}_3\text{CNH} \rightarrow \text{CH}_3 + \text{3NH} \) reaction in our network.

...Case Study 4: \( \text{CH}_3 + \text{N} \rightarrow \text{products} \)

...Stief et al.125 experimentally calculated the overall reaction rate constant for \( \text{CH}_3 + \text{N} \rightarrow \text{products} \) at 298 K to be \( 8.6 \times 10^{-11} \text{ cm}^3\text{s}^{-1} \) by monitoring the decay of reactants \( \text{CH}_3 \) and \( \text{N} \) in a volume. Marston et al.126 suggest the three possible branches for the reaction of \( \text{CH}_3 + \text{N} \rightarrow \text{products} \) are:

\[
\text{CH}_3 + \text{N} \rightarrow \text{H}_2\text{CN} + \text{H},
\]

\[
\text{CH}_3 + \text{N} \rightarrow \text{HCN} + \text{H}_2,
\]

...and

\[
\text{CH}_3 + \text{N} \rightarrow \text{HCN} + 2\text{H}.
\]

...Marston et al.126 monitored the production of \( \text{H}_2 \), and \( \text{H} \) in experiments reacting \( \text{CH}_3 \) and \( \text{N} \), and calculated the above reaction branching ratios to be approximately 0.9, 0.1, and 0 respectively. This suggests a preference for the \( \text{CH}_3 + \text{N} \rightarrow \text{H}_2\text{CN} + \text{H} \) pathway by approximately an order of magnitude over the \( \text{CH}_3 + \text{N} \rightarrow \text{HCN} + \text{H}_2 \) pathway. It must be noted that in performing this calculation, Marston et al.126 assumed that \( \text{H}_2 \) and \( \text{H} \) were solely generated through the above pathways. They caution the reader that it is also possible that these products formed through the \( \text{H}_2\text{CN} \) intermediate.

...Miller and Bowman127 suggested the rate coefficient of \( \text{CH}_3 + \text{N} \rightarrow \text{H}_2\text{CN} + \text{H} \) to be \( 5.0 \times 10^{-11} \text{ cm}^3\text{s}^{-1} \) based on thermodynamic calculations.

...There are two main PES’s that the \( \text{CH}_3 \) + \( \text{N} \) reaction evolves on: the triplet and the singlet surfaces. The quintet surface is only possible, however this reaction is much higher in energy and therefore much less likely to occur.124 Both the ground state nitrogen atom (i.e. \( ^4\text{N} \)) and the excited nitrogen atom (i.e. \( ^2\text{N} \)) can react with \( \text{CH}_3 \) on the triplet PES. Only the excited state nitrogen atom can react with \( \text{CH}_3 \) on the singlet PES.
A computational study of the CH$_3$ + N $\rightarrow$ products reaction shows a preference for the CH$_3$ + 4N $\rightarrow$ H$_2$CN + H pathway. This study finds the CH$_3$ + 2N $\rightarrow$ HCN + H$_2$ channel to be negligible. Cimas and Largo suggest that the HCN measured in experiments by Marston et al. formed through the H$_2$CN intermediate, via reaction equations. Chiba and Yoshida alternatively suggest that HCN + H$_2$ may form through the triplet-singlet spin-forbidden process.

Alves et al. and Cimas and Largo analyzed CH$_3$ + N $\rightarrow$ products theoretically using quantum computational simulations at the CCSD(T)/CBS and CCSD(T)/cc-pVTZ levels of theory, and calculated its reaction rate coefficients to be $1.93 \times 10^{-10}$ cm$^3$s$^{-1}$ and $9.1 \times 10^{-12}$ cm$^3$s$^{-1}$, respectively.

In this case study, we analyze the three suggested main branches for CH$_3$ + N $\rightarrow$ products using CVT (see the methods section for full details). Computational studies show that CH$_3$ + 4N $\rightarrow$ products reactions first proceed through a barrierless reaction to H$_3$CN on the triplet surface. We confirm this barrierless reaction (CH$_3$ + 4N $\rightarrow$ 3H$_3$CN) and calculate its rate coefficients at the BHandHLYP/aug-cc-pVDZ level of theory to be $3.3 \times 10^{-11}$ cm$^3$s$^{-1}$. This result is less than a factor of 3 smaller than the experimental result ($8.6 \times 10^{-11}$ cm$^3$s$^{-1}$). Our calculated rate coefficient is also within a factor of 3 of the calculated value by Cimas and Largo at the CCSD(T)/cc-pVTZ level of theory ($9.1 \times 10^{-12}$ cm$^3$s$^{-1}$).

We do not find a direct reaction pathway on the singlet or triplet surface to CH$_3$ + N $\rightarrow$ HCN + 2H.

We display the mechanistic models for forming H$_2$CN + H, and HCN + H$_2$ from CH$_3$ + N in Figure S4. These mechanistic models are similar to that used in Alves et al. Note we do not analyze spin-forbidden processes in these models.

H$_2$CN + H can form directly from 3H$_3$CN, or after isomerization from the intermediate 3H$_2$CNH. Similarly, HCN + H$_2$ can form directly from 1H$_3$CN, or from the intermediate 1H$_2$CNH. On the singlet surface, we find H$_2$CN + H forms from the intermediate 1H$_2$CNH, however we do not find a pathway from 1H$_3$CN. We find a smooth decrease in Gibbs free energy along the MEP for the reaction 1H$_3$CN $\rightarrow$ 1H$_2$CNH, suggesting this reaction has neither an energy barrier nor an entropic barrier. We estimate the rate coefficient for this reaction by choosing the reactant geometry as the transition state. We find the overall rate coefficients for CH$_3$ + N $\rightarrow$ H$_2$CN + H and CH$_3$ + N $\rightarrow$ H$_2$CN + H to be insensitive to this intermediate rate coefficient by varying the latter’s value by over 10 orders of magnitude in both directions. The optimization of 1H$_3$CN does not converge, therefore we use a reactant geometry close to 1H$_2$CN that has vibrational modes for HCN + H$_2$ and 1H$_2$CNH. In any case, we find the values of $k_c$ and $k_d$ are independent of the 1H$_3$CN geometry.

The steady-state solution of the kinetic rate equations

$$k_c = \frac{k_4}{A} \left( \frac{k_6 + \frac{k_5k_7}{k_{5-7}+k_{7-7}}} \right).$$ (S3)

$$k_d = \frac{k_8}{B} \left( \frac{k_6 + \frac{k_5k_7}{k_{5-7}+k_{7-7}}} \right).$$ (S4)

$$k_e = \frac{k_9}{C} \left( \frac{k_{11}k_{13}}{k_{11-13} + k_{12+13}} \right).$$ (S5)

$$k_f = \frac{k_9}{C} \left( \frac{k_{10} + \frac{k_{11}k_{12}}{k_{10-11} + k_{12-13}}}{k_{11} + k_{12} + k_{13}} \right).$$ (S6)
The values of the reaction rate constants using the BHandHLYP method and aug-cc-pVDZ basis set are listed in Table S5.

The rate coefficients of \( k_c, k_d, \) and \( k_e \) are equivalent to those of \( k_4, k_5, \) and \( k_9 \), respectively. Thus the rate-limiting steps for these reactions are the first steps, i.e. \( \text{CH}_3 + \text{N} \rightarrow \text{H}_3\text{CN} \).

On the triplet surface, or theoretical value of \( k_e \), at the BHandHLYP/aug-cc-pVDZ level of theory is a factor of 1.5–2.5 smaller than the values calculated in experiments and suggested by thermodynamics.\[^{25,38,39}\]

On the singlet surface, there is a strong preference to produce \( \text{H}_2\text{CN} + \text{H} \) over \( \text{HCN} \). The rate coefficient of \( \text{CH}_3 + ^{2}\text{N} \rightarrow \text{HCN} + \text{H}_2 \) is less than \( 10^{-21} \) cm\(^3\)s\(^{-1}\), therefore we do not include this reaction in our network.

**Case Study 5: \( \text{CH}_2 + \text{H} \leftrightarrow \text{CH}_3 \cdot \leftrightarrow \text{CH} + \text{H}_2 \)**

There are three spin configurations for this reaction. \(^3\text{CH}_2 + \text{H} \rightarrow \text{CH}_3 \cdot \rightarrow \text{CH} + \text{H}_2 \) and \(^1\text{CH}_2 + \text{H} \rightarrow \text{CH}_3 \cdot \rightarrow \text{CH} + \text{H}_2 \) occur on the doublet PES, and \(^3\text{CH}_2 + \text{H} \rightarrow ^4\text{CH} + \text{H}_2 \) occurs on the quartet PES.

Several experiments have calculated the reaction rate coefficient for \(^3\text{CH}_2 + \text{H} \rightarrow \text{CH} + \text{H}_2 \) at 285–300 K.\[^{28,41}\] Although methodology differs between experiments, they generally involve monitoring the decay of \(^3\text{CH}_3\). The experimental values are as low as \( 8.3 \times 10^{-11} \) cm\(^3\)s\(^{-1}\) and as high as \( 2.7 \times 10^{-10} \) cm\(^3\)s\(^{-1}\). Two studies have reviewed a variety of experiments at a range of temperatures and suggested values of \( 2.7 \times 10^{-10} \) cm\(^3\)s\(^{-1}\) and \( 2.0 \times 10^{-10} \) cm\(^3\)s\(^{-1}\).\[^{52}\]

Although no experiments have been performed for the reaction of \(^1\text{CH}_2 + \text{H} \rightarrow \text{CH} + \text{H}_2 \), Tsang and Hampson\[^{28}\] suggest the value should be near \( 5.0 \times 10^{-11} \) cm\(^3\)s\(^{-1}\) based on thermodynamics.

To date there have been no published theoretical reaction rate coefficients for any spin configuration of this reaction.

On the quartet PES, we find the reaction proceeds directly \(^3\text{CH}_2 + \text{H} \rightarrow ^4\text{CH} + \text{H}_2 \). We calculate the rate coefficient for this reaction at the BHandHLYP/aug-cc-pVDZ level of theory to be \( \sim 10^{-25} \) cm\(^3\)s\(^{-1}\), which is too inefficient to consider in this network.

| Rate coefficient | \( k(298) \) |
|------------------|--------------|
| \( k_c \)        | \( 3.3 \times 10^{-11} \) |
| \( k_d \)        | \( 1.0 \times 10^{-10} \) |
| \( k_e \)        | \( 3.1 \times 10^{-11} \) |
| \( k_f \)        | \( 2.3 \times 10^{-28} \) |
| \( k_g \)        | \( 3.3 \times 10^{-11} \) |
| \( k_h \)        | \( 1.3 \times 10^{-32} \) |
| \( k_i \)        | \( 1.1 \times 10^{-19} \) |
| \( k_j \)        | \( 8.2 \times 10^{-11} \) |
| \( k_k \)        | \( 3.0 \times 10^{-12} \) |
| \( k_l \)        | \( 5.6 \times 10^{-7} \) |
| \( k_m \)        | \( 1.0 \times 10^{-10} \) |
| \( k_n \)        | \( 3.0 \times 10^{-51} \) |
| \( k_o \)        | \( 3.1 \times 10^{-11} \) |
| \( k_p \)        | \( 6.3 \times 10^{-41} \) |
| \( k_q \)        | \( 1.5 \times 10^{-14} \) |
| \( k_r \)        | \( 1.9 \times 10^{13} \) |
| \( k_s \)        | \( 3.9 \times 10^{-57} \) |
| \( k_t \)        | \( 2.0 \times 10^{-56} \) |
| \( k_u \)        | \( 2.9 \times 10^{-39} \) |

*No energy or entropic barrier. Transition state chosen at classical location (the saddle point) instead of the variational location. We find the overall rate coefficients \( k_c, k_d, \) and \( k_e \) to be insensitive to changes in these intermediate coefficients of over 10 orders of magnitude. \( k_f \) is also insensitive to increases in \( k_{12} \) by over 10 orders of magnitude, however, decreasing \( k_{12} \) directly decreases \( k_f \). Because we do not consider reactions with rate coefficients lower than \( 10^{-21} \) cm\(^3\)s\(^{-1}\), we make no attempt to increase the accuracy of \( k_f \). Experiments at 298 K provide a \( k_f \) value of \( 7.7 \times 10^{-11} \) and a \( k_f \) value of \( 8.6 \times 10^{-12} \) cm\(^3\)s\(^{-1}\). First-order rate coefficients have units s\(^{-1}\). Second-order rate coefficients have units cm\(^3\)s\(^{-1}\).*

The doublet PES reactions proceed through the \( \text{CH}_3 \) intermediate. The mechanistic model for these reactions is shown in Figure S5.

Although there are many reaction pathways for the
CH$_3$ molecule, we calculate the upper bound for the rate constants of $^3$CH$_2$ + H $\rightarrow$ CH$_3$ $\cdot$ $\rightarrow$ CH + H$_2$ and $^1$CH$_2$ + H $\rightarrow$ CH$_3$ $\cdot$ $\rightarrow$ CH + H$_2$ by assuming all CH$_3$ reacts to form CH + H$_2$.

The steady-state solutions of the kinetic rate equations for these mechanistic models give us the overall rate constants for $^3$CH$_2$ + H $\rightarrow$ CH + H$_2$ and $^1$CH$_2$ + H $\rightarrow$ CH + H$_2$.

The values of the reaction rate constants using the BHandHLYP method and aug-cc-pVDZ basis set are listed in Table S50.

The theoretical value of $k_h$ is nearly 10 orders of magnitude larger than that of $k_{14}$. Thus the first step is the rate-limiting step. The theoretical value of $k_g$ is nearly the same as that of $k_{14}$, however because the reverse rate coefficient ($k_{-14}$) is comparable to the rate coefficient of the second step ($k_{15}$), the value of $k_g$ is slightly smaller than that of $k_{11}$. We calculate $k_g$ to be $4.3 \times 10^{-10}$ cm$^3$ s$^{-1}$, which is within the range of experimental values for $^3$CH$_2$ + H $\rightarrow$ CH + H$_2$. We calculate $k_h$ to be $8.4 \times 10^{-11}$ cm$^3$ s$^{-1}$, which is less than a factor of 2 larger than the suggested value by Tsang and Hampson. Our calculations show CH$_3$ $\rightarrow$ CH + H$_2$ is inefficient ($k_{15}$ = $\sim 10^{-57}$ s$^{-1}$), therefore we do not consider the second step of this reaction in our study.

The same mechanistic approach can be used for the reverse reaction CH + H$_2$ $\rightarrow$ CH$_3$ $\cdot$ $\rightarrow$ $^3$CH$_2$ + H. This reaction could produce $^1$CH$_2$ + H as well, however $k_{-14}$ is $\sim 10$ orders of magnitude larger than $k_{-16}$, suggesting the dominant pathway would be to produce $^3$CH$_2$ + H.

Several experiments have calculated the rate coefficient of CH + H$_2$ $\rightarrow$ CH$_3$ as 1.0 $\times 10^{-12}$ to 1.6 $\times 10^{-10}$ cm$^3$ s$^{-1}$. Studies reviewing these experiments suggest a rate coefficient of 1.2 $\times 10^{-10}$ cm$^3$ s$^{-1}$. We find no theoretical rate coefficients for the $^1$CH$_2$ + H$_2$ $\rightarrow$ CH$_3$ + H reaction.

This reaction occurs on the singlet and triplet surfaces, as $^1$CH$_2$ + H$_2$ $\rightarrow$ CH$_4$ $\cdot$ $\rightarrow$ CH$_3$ + H and $^3$CH$_2$ + H$_2$ $\rightarrow$ CH$_3$ + H, respectively. We find the first step to be the rate-limiting step, i.e. CH + H$_2$ $\rightarrow$ CH$_3$. We calculate the reverse rate coefficient of this reaction to be 7.9 $\times 10^{-11}$ cm$^3$ s$^{-1}$. This is within the range of experimental values.

We find the second step of the reverse reaction (CH$_3$ $\rightarrow$ CH$_2$ + H) to be too inefficient to consider in this network (i.e. $k < 10^{-21}$ s$^{-1}$).

Case Study 6: CH$_2$ + H$_2$ $\rightarrow$ CH$_3$ + H

Several experiments have calculated the rate coefficient of 3CH$_2$ + H as well as the intermediate forward and reverse rate coefficients which were used in the calculations. In all simulations, the BHandHLYP method was used with the aug-cc-pVDZ basis set. Experiments at 298 K provide $k_g$ values between $8.3 \times 10^{-11}$ and 2.7 $\times 10^{-10}$ cm$^3$ s$^{-1}$. A value of 5.0 $\times 10^{-11}$ cm$^3$ s$^{-1}$ is suggested for $k_g$. First-order rate coefficients have units s$^{-1}$. Second-order rate coefficients have units cm$^3$ s$^{-1}$.

Table S6. Calculated overall rate coefficient for 3CH$_2$ + H $\rightarrow$ CH + H$_2$, and 1CH$_2$ + H $\rightarrow$ CH + H$_2$, as well as the theoretical value of $k_g$. We calculate $k_g$ was used in the calculations. In all simulations, the BHandHLYP method was used with the aug-cc-pVDZ basis set. Experiments at 298 K provide $k_g$ values between $8.3 \times 10^{-11}$ and 2.7 $\times 10^{-10}$ cm$^3$ s$^{-1}$. A value of 5.0 $\times 10^{-11}$ cm$^3$ s$^{-1}$ is suggested for $k_g$. First-order rate coefficients have units s$^{-1}$. Second-order rate coefficients have units cm$^3$ s$^{-1}$.

| Rate coefficient | k(298) |
|------------------|---------|
| $k_g$            | 4.3 $\times 10^{-10}$ |
| $k_h$            | 8.4 $\times 10^{-11}$ |
| $k_{14}$         | 5.6 $\times 10^{-10}$ |
| $k_{-14}$        | 3.7 $\times 10^{-58}$ |
| $k_{15}$         | 1.2 $\times 10^{-57}$ |
| $k_{16}$         | 8.4 $\times 10^{-11}$ |
| $k_{-16}$        | 9.5 $\times 10^{-68}$ |
TABLE S7. Calculated rate coefficients for CH2 + N → H2CN, and H2CN → HCN + H on the doublet and quartet potential energy surfaces. In all simulations, the BHandHLYP method was used with the aug-cc-pVDZ basis set. First-order rate coefficients have units s⁻¹. Second-order rate coefficients have units cm³s⁻¹.

| Reaction | k(298) doublet | k(298) quartet |
|----------|----------------|----------------|
| 1CH2 + 2N → H2CN | 1.5×10⁻¹⁰ | 
| 1CH2 + 4N → H2CN | 1.1×10⁻¹⁰ | 
| 3CH2 + 4N → H2CN | 1.3×10⁻¹⁰ | 
| 3CH2 + 2N → H2CN | 2.7×10⁻¹⁰ | 4.3×10⁻¹⁰ |
| H2CN → HCN + H | 1.6×10⁻¹¹ | 4.6×10⁻²⁴ |

They employed the G2M(RCC2) computational method with B3LYP optimized geometries and obtained a value of 1.5×10⁻¹⁸ cm³s⁻¹.

We calculate the rate coefficient of 3CH2 + H2 → CH3 + H to be 2.5×10⁻¹⁶ cm³s⁻¹. This value agrees with the upper bounds for the rate coefficient from experiments.

We find the reverse rate coefficient, CH3 + H → 3CH2 + H2 to have a value of 1.4×10⁻²⁰ cm³s⁻¹. We include this reverse reaction in our network as its rate coefficient is within the threshold of what we define to be a fast reaction (i.e. k > 10⁻²¹ cm³s⁻¹).

Case Study 7: CH2 + N → HCN + H

Catling and Kasting suggest CH2 + N → HCN + H is one of the main pathways forming HCN in the early atmosphere. They note however that the rate constant for this reaction has not yet been studied experimentally.

Herbst et al. performed quantum dynamics simulations to calculate the rate coefficient of 3CH2 + 4N → H2CN · → HCN + H. They calculated a value of 7.9×10⁻¹¹ cm³s⁻¹.

We find no direct reaction pathway for CH2 + N → HCN + H on the doublet, quartet, or sextet PES’s. We do however find two-step reactions CH2 + N → H2CN and H2CN → HCN + H on the doublet and quartet surfaces.

We list the calculated reaction rate coefficients on the doublet and quartet energy surfaces in Table S7.

All spin configurations of CH2 + N → H2CN are barrierless and have efficient reaction rate coefficients. H2CN → HCN + H, however, is only efficient on the doublet surface. We distinguish between the quartet and doublet H2CN molecules in our network, as the deexcitation of H2CN to H2CN is spin-forbidden, and we can’t assume H2CN will efficiently decay into its ground state in an atmosphere.

Our calculated rate coefficient for 3CH2 + 4N → H2CN is approximately a factor of 1.5 greater than the previous theoretical value.[59]

We include all CH2 + N → H2CN reaction spin configurations as well as the efficient doublet H2CN → HCN + H reaction in our network.

Case Study 8: 2CH2 → C2H4 · → products

There are three spin configurations for this reaction on a total of two PES’s. On the singlet surface, there is 3CH2 + 3CH2 → 1C2H4 · → C2H2 · + H · → C2H2 + 2H and 1CH2 + 1CH2 → 1C2H4 · → products, and on the triplet PES there is 3CH2 + 3CH2 → 3C2H4 · → products.

Braun et al. monitored the decay of 3CH2 and the production of C2H2 in experiments to measure the rate coefficient of 3CH2 + 3CH2 → C2H2 + product at 298 K. This measurement was 5.3×10⁻¹¹ cm³s⁻¹. Braun et al. assumed that molecular hydrogen was produced along with C2H2 in this reaction, however Becerra et al. modeled the reaction network starting from the decomposition of ketene and found that 3CH2 + 3CH2 → C2H2 + 2H was more likely. Becerra et al. found that 3CH2 + H → CH + H2 can account for the molecular hydrogen observed in reactions of this kind.

Braun et al. suggest that the reaction of 3CH2 with 3CH2 passes through the C2H4 intermediate.

Jasper et al. calculate the theoretical rate coefficient for 3CH2 + 3CH2 → C2H4 · → C2H2 + 2H using variable reaction coordinate transition state theory. Their value is 1.5×10⁻⁰⁷ cm³s⁻¹.

There is no experimental data for 1CH2 + 1CH2 → C2H4 · → products, however it is expected to proceed rapidly, and yield the same products as 3CH2 + 3CH2 → C2H4 · → C2H2 + 2H. Tsang and Hampson recommend a value of 5.0×10⁻¹⁰ cm³s⁻¹ for this reaction.

Similarly, there is no experimental data for 3CH2 + 1CH2 → 3C2H4 · → products, however it is also expected to be rapid. Conversely, it is suggested that the preferred products for this reaction are 3CH2 + 1CH2 → 3C2H4 · → 3C2H2 + H2. Tsang and Hampson suggest a value of 3.0×10⁻¹¹ cm³s⁻¹ for this reaction.

To our knowledge there have been no theoretical reaction rate coefficients for 1CH2 + 1CH2 → C2H2 + 2H, or 1CH2 + 3CH2 → 3C2H2 + H2 produced to date.

Because in some of the other reactions in our network, C2H4 is a stable product, i.e. CH + CH4 → C2H5 · → C2H4 + H, CH2 + CH3 → C2H5 · → C2H4 + H, we only include the first steps of these reactions in our network (i.e. 2CH2 → C2H4). We find the first steps of reactions 3CH2 + 3CH2 → C2H4 · → C2H2 + 2H and 1CH2 + 1CH2 → C2H4 · → C2H2 + 2H to be the rate-limiting
TABLE S8. Calculated rate coefficients for $2\text{CH}_2 \longrightarrow \text{C}_2\text{H}_4$

on the singlet and triplet potential energy surfaces. These rate coefficients are compared with the experimental rate coefficient of the multi-step reaction $3\text{CH}_2 + 3\text{CH}_2 \longrightarrow \text{C}_2\text{H}_4$. $\longrightarrow \text{C}_2\text{H}_2 + 2\text{H}$ as well as the suggested rate coefficients for $1\text{CH}_2 + 1\text{CH}_2 \longrightarrow \text{C}_2\text{H}_4$. $\longrightarrow \text{C}_2\text{H}_2 + 2\text{H}$, and $1\text{CH}_2 + 3\text{CH}_2 \longrightarrow 3\text{C}_2\text{H}_4$. $\longrightarrow \text{products}$ in the literature. We find the first steps of the reactions of $3\text{CH}_2 + 3\text{CH}_2 \longrightarrow \text{C}_2\text{H}_4$. $\longrightarrow \text{C}_2\text{H}_2 + 2\text{H}$ to be the rate-limiting steps and assume the same for $1\text{CH}_2 + 3\text{CH}_2 \longrightarrow 3\text{C}_2\text{H}_4$. $\longrightarrow \text{products}$. In all simulations, the BHHandHLYP method was used with the aug-cc-pVDZ basis set. Rate coefficients have units cm$^3$ s$^{-1}$.

| Reaction                | $k_{\text{calc}}(298)$ | $k_{\text{fit}}(298)$ | $k_{\text{fit}}$ (S12) | $k_{\text{fit}}$ (S13) |
|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| $3\text{CH}_2 + 3\text{CH}_2$ | $4.2 \times 10^{-11}$  | $9.9 \times 10^{-12}$  | $3.5 \times 10^{-11}$  |                        |
| $1\text{CH}_2 + 3\text{CH}_2$ | $5.3 \times 10^{-11}$  | $5.0 \times 10^{-11}$  | $3.0 \times 10^{-11}$  |                        |

$^a$ Simulations did not converge beyond a C-C bond distance of 3.52 Å. Therefore the calculated rate coefficient is a lower bound.

steps, and assume the same for $1\text{CH}_2 + 3\text{CH}_2 \longrightarrow 3\text{C}_2\text{H}_4$. $\longrightarrow \text{products}$.

We list the calculated reaction rate coefficients on the singlet and triplet energy surfaces in Table S8.

Our calculated $k(298)$ value for $3\text{CH}_2 + 3\text{CH}_2 \longrightarrow \text{C}_2\text{H}_4$ is within 30% of the experimental value for $3\text{CH}_2 + 3\text{CH}_2 \longrightarrow \text{C}_2\text{H}_2 + 2\text{H}$. The $k(298)$ value for $1\text{CH}_2 + 1\text{CH}_2 \longrightarrow \text{C}_2\text{H}_4$ is a factor of 5 smaller than the suggested value. Simulations did not converge for $1\text{CH}_2 + 3\text{CH}_2 \longrightarrow 3\text{C}_2\text{H}_4$ beyond a C-C reaction coordinate of 3.52 Å, however using this location for the variational transition state leads to a calculated rate coefficient that is within 20% of the suggested value.

Case Study 9: $\text{CH}_2 + \text{CH}_3 \longrightarrow \text{C}_2\text{H}_5$. $\longrightarrow \text{C}_2\text{H}_4 + \text{H}$

This is a two step reaction, passing through the $\text{C}_2\text{H}_5$ intermediate. On the doublet surface, both $3\text{CH}_2$ and $1\text{CH}_2$ can react with $\text{CH}_3$ to produce the $\text{C}_2\text{H}_5$ intermediate. On the quartet surface, $3\text{CH}_2$ reacts with $\text{CH}_3$ to produce excited $^4\text{C}_2\text{H}_5$. However this reaction is higher in energy than the doublet reactions, and has a very slow rate coefficient ($\sim 10^{-54}$ cm$^3$ s$^{-1}$).

Pilling and Robertson$^{103}$ and Laufer and Bass$^{102}$ experimentally measured the production of various products (e.g. $\text{C}_2\text{H}_3$, $\text{C}_2\text{H}_4$, $\text{C}_2\text{H}_5$) to model the reaction network spanned by reactions between $3\text{CH}_2$ and $\text{CH}_3$. Their models led to reaction rate coefficients of $5.0 \times 10^{-11}$ and $1.0 \times 10^{-10}$ cm$^3$ s$^{-1}$, respectively. Wang and Fockenberg$^{27}$ performed similar experiments but used the $3\text{CH}_2$ decay profile for their calculation, and obtained a rate of $2.1 \times 10^{-10}$ cm$^3$ s$^{-1}$ at 300 K. Deters et al.$^{101}$ measured the decay of both $3\text{CH}_2$ and $\text{CH}_3$ in a similar experiment to obtain a rate coefficient of $1.1 \times 10^{-10}$ cm$^3$ s$^{-1}$ at 298 K. Baulch et al.$^{102}$ and Tsang and Hampson$^{80}$ reviewed various experiments and suggest a value of $7.0 \times 10^{-11}$ cm$^3$ s$^{-1}$ for the $3\text{CH}_2 + \text{CH}_3 \longrightarrow \text{C}_2\text{H}_5$. $\longrightarrow \text{C}_2\text{H}_4 + \text{H}$ rate coefficient.

Conversely, there is no experimental data for $1\text{CH}_2 + \text{CH}_3 \longrightarrow \text{C}_2\text{H}_5$. $\longrightarrow \text{C}_2\text{H}_4 + \text{H}$, however the reaction is thought to proceed rapidly and suggested to have a rate coefficient near $3.0 \times 10^{-11}$ cm$^3$ s$^{-1}$.

There have been no published theoretical reaction rate coefficients for $\text{CH}_2 + \text{CH}_3 \longrightarrow \text{C}_2\text{H}_4 + \text{H}$.

We find the first steps of these reactions, $3\text{CH}_2 + \text{CH}_3 \longrightarrow \text{C}_2\text{H}_5$ and $1\text{CH}_2 + \text{CH}_3 \longrightarrow \text{C}_2\text{H}_5$, do not have barriers. The second step however ($\text{C}_2\text{H}_5 \longrightarrow \text{C}_2\text{H}_4 + \text{H}$), has a barrier. The mechanistic model for the reaction, involving the triplet and singlet $\text{CH}_2$ molecule, is shown in Figure S6.

FIG. S6. Mechanistic model for the production of $\text{C}_2\text{H}_4 + \text{H}$ from i) $3\text{CH}_2 + \text{CH}_3$ and j) $1\text{CH}_2 + \text{CH}_3$ on the doublet surface.

We calculate the upper bounds for the rate constants by assuming all $\text{C}_2\text{H}_5$ reacts to form $\text{C}_2\text{H}_4 + \text{H}$.

The steady-state solutions of the kinetic rate equations for this mechanistic model gives us the overall rate constant for $\text{CH}_2 + \text{CH}_3 \longrightarrow \text{C}_2\text{H}_4 + \text{H}$.

$$k_i = \frac{k_{18}k_{17}}{k_{17} + k_{18}}$$ (S12)

$$k_j = \frac{k_{18}k_{19}}{k_{19} + k_{18}}$$ (S13)

We list the calculated reaction rate coefficients for this mechanistic model in Table S9.

The theoretical values of $k_i$ and $k_j$ are equal to the values of $k_{17}$ and $k_{19}$, respectively. Thus the first steps of these reactions are the rate-limiting steps. At the BHHandHLYP/aug-cc-pVDZ level of theory, we calculate $k_i$ to be $8.8 \times 10^{-12}$ cm$^3$ s$^{-1}$. This value is approximately a factor of 6 slower than the slowest experimental value. Similarly, we calculate $k_j$ to be $2.3 \times 10^{-11}$ cm$^3$ s$^{-1}$, which is within order unity of the suggested value.

Case Study 10: $\text{CH}_2 + \text{CH}_4 \longrightarrow 2\text{CH}_3$

This reaction occurs on the singlet PES as $1\text{CH}_2 + \text{CH}_4 \longrightarrow \text{C}_2\text{H}_6$. $\longrightarrow 2\text{CH}_3$, and on the triplet PES.
TABLE S9. Calculated overall rate coefficient for $^3\text{CH}_2 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{H}$ and $^1\text{CH}_2 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{H}$, as well as the intermediate forward and reverse rate coefficients which were used in the calculation. In all simulations, the BHandHLYP method was used with the aug-cc-pVDZ basis set. Experiments at 298 K provide a $k_i$ value in the range of $5.0 \times 10^{-11}$ to $2.1 \times 10^{-10}$ cm$^3$ s$^{-1}$. $k_j$ is suggested to have a rate coefficient near $3.0 \times 10^{-11}$ cm$^3$ s$^{-1}$. First-order rate coefficients have units s$^{-1}$. Second-order rate coefficients have units cm$^3$ s$^{-1}$.

| Rate coefficient $k$(298) | $k_i$ | $8.8 \times 10^{-12}$ |
|---------------------------|------|----------------------|
| $k_j$ | $2.3 \times 10^{-11}$ |
| $k_{17}$ | $8.8 \times 10^{-12}$ |
| $k_{1-17}$ | $1.4 \times 10^{-12}$ |
| $k_{18}$ | $4.0 \times 10^{-15}$ |
| $k_{19}$ | $2.3 \times 10^{-11}$ |
| $k_{-19}$ | $3.0 \times 10^{-57}$ |

as $^3\text{CH}_2 + \text{CH}_4 \rightarrow 2 \text{CH}_3$.

Experimentalists have measured the rate coefficient of $^1\text{CH}_2 + \text{CH}_4 \rightarrow \text{C}_2\text{H}_6 \cdot \rightarrow 2 \text{CH}_3$ at 295–298 K by measuring the decay of $^1\text{CH}_2$ or the production of $\text{C}_2\text{H}_3$. These values range from $1.9 \times 10^{-12}$ to $7.3 \times 10^{-11}$ cm$^3$ s$^{-1}$.

Tsang and Hampson\cite{86} reviewed these experiments and suggested a value of $7.1 \times 10^{-11}$ cm$^3$ s$^{-1}$. We find no published theoretical rate coefficients for this reaction.

We find the reaction on the singlet PES proceeds through the $\text{C}_2\text{H}_5$ intermediate and that the first step of this reaction is the rate-limiting step. We calculate its rate coefficient to be $6.1 \times 10^{-13}$ cm$^3$ s$^{-1}$, which is a factor of 3 smaller than the closest experimental value. Because $\text{C}_2\text{H}_5$ is a stable product in other reactions in our network (e.g. $2 \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$), we only consider the first step of this reaction in our network. The second step of this reaction $\text{C}_2\text{H}_6 \rightarrow 2 \text{CH}_3$ is too slow to consider in this network ($k \sim 10^{-55}$ s$^{-1}$).

Böhland et al.\cite{14} performed experiments on the reaction of $^3\text{CH}_2$ with n-hexane at $T = 413$–707 K to estimate the rate coefficient for $^3\text{CH}_2 + \text{CH}_4 \rightarrow 2 \text{CH}_3$ at 298 K. They calculated a value of $3.1 \times 10^{-19}$ cm$^3$ s$^{-1}$. Braun et al.\cite{55} placed an upper bound on the rate coefficient by considering the effect of various gases on the $^3\text{CH}_2$ molecule. They estimate a value of $<3.1 \times 10^{-14}$ cm$^3$ s$^{-1}$. Tsang and Hampson\cite{86} suggest an upper bound of $3.0 \times 10^{-19}$ cm$^3$ s$^{-1}$ based on the results of a photolysis study of the $\text{CH}_3\text{CHO}$ system. We find no theoretical rate coefficients for the $^3\text{CH}_2 + \text{CH}_4 \rightarrow 2 \text{CH}_3$ reaction.

We calculate $^3\text{CH}_2 + \text{CH}_4 \rightarrow 2 \text{CH}_3$ to have a rate coefficient of $1.4 \times 10^{-16}$ cm$^3$ s$^{-1}$. This value agrees with the upper bound from Braun et al.\cite{55} and is a couple orders of magnitude higher than the experimental value from Böhland et al.\cite{14}.

Case Study 11: $\text{CH} + \text{N} \rightarrow \text{HCN} \rightarrow \text{CN} + \text{H}$

There are two spin configurations for this reaction on the triplet surface, which pass through the excited $^3\text{HCN}$ intermediate: $\text{CH} + 4\text{N} \rightarrow 3\text{HCN} \rightarrow \text{CN} + \text{H}$ and $\text{CH} + 2\text{N} \rightarrow 3\text{HCN} \rightarrow \text{CN} + \text{H}$. There is also potentially a reaction of $\text{CH} + 2\text{N}$ on the singlet surface to produce ground state $\text{HCN}$, however we were unable to obtain a convergent solution for such a reaction. Moreover, there is no experimental or past theoretical work for a singlet surface reaction of $\text{CH} + 2\text{N}$ to suggest it occurs efficiently. For these reasons, we only consider the two spin configurations on the triplet surface in this network.

A few experiments have measured the rate coefficient of $\text{CH} + 4\text{N} \rightarrow \text{CN} + \text{H}$ at 296–298 K by monitoring the decay of $\text{CH}$ and/or the production of $\text{CN}$.\cite{50,12,113}

The experimental values of the rate coefficient range from $2.1 \times 10^{-11}$ to $1.6 \times 10^{-10}$ cm$^3$ s$^{-1}$.

Daranlot et al.\cite{60} performed quantum dynamics calculations to obtain a theoretical rate coefficient for $\text{CH} + 4\text{N} \rightarrow 3\text{HCN} \rightarrow \text{CN} + \text{H}$. They calculate a value of $k(298) = 1.2 \times 10^{-10}$ cm$^3$ s$^{-1}$.

We find no experimental or theoretical rate coefficients for $\text{CH} + 2\text{N} \rightarrow 3\text{HCN} \rightarrow \text{CN} + \text{H}$.

Our theoretical calculations show both $\text{CH} + 4\text{N}$ and $\text{CH} + 2\text{N}$ react without a barrier to form the $^3\text{HCN}$ intermediate. We find the first step for both of these reactions to be the rate-limiting step. The second step of this reaction, i.e., the decay of $^3\text{HCN}$ into $\text{CN} + \text{H}$, is extremely efficient ($k = 3.6 \times 10^9$ s$^{-1}$).

We calculate the rate coefficient for $\text{CH} + 4\text{N} \rightarrow 3\text{HCN} \rightarrow \text{CN} + \text{H}$ to be $1.1 \times 10^{-10}$ cm$^3$ s$^{-1}$. This value is within the range of experimental values, and agrees well with the previous calculated theoretical value.\cite{60}

We calculate the rate coefficient for $\text{CH} + 2\text{N} \rightarrow 3\text{HCN} \rightarrow \text{CN} + \text{H}$ to be $2.7 \times 10^{-10}$ cm$^3$ s$^{-1}$.

Case Study 12: $\text{CH} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_5 \cdot \rightarrow \text{C}_2\text{H}_4 + \text{H}$

This reaction occurs on the doublet surface. Several experiments have calculated the rate coefficient for this reaction at 295–298 K by monitoring the production of $\text{C}_2\text{H}_4$ or the decay of $\text{CH}$.\cite{50,113,114,119} The experimental rate coefficient ranges from $2.0 \times 10^{-12}$ to $3.0 \times 10^{-10}$ cm$^3$ s$^{-1}$.

A pair of theoretical studies have been performed on this reaction, however theoretical rate coefficients were not calculated.\cite{172,174}

At the BHandHLYP/aug-cc-pVDZ level of theory, we find this reaction to have a small barrier ($E_0 = 11.5$ kJ mol$^{-1}$). This is smaller than the barrier predicted by Yu et al.\cite{172} ($E_0 = 57.3$ kJ mol$^{-1}$), who used the Moller-Plesset perturbation theory (MP) method with geometries optimized using the Hartree-Fock method. However, Wang et al.\cite{175} calculated the reaction to be barri-
erless (-1.3 kJ mol\(^{-1}\)) using the MP method with MP optimized geometries. Experiments suggest the reaction is barrierless, with an activation energy of -1.7 kJ mol\(^{-1}\). At the B3LYP/aug-cc-pVQZ level of theory, we find this reaction to be barrierless, with an activation energy of -18.2 kJ mol\(^{-1}\). Because experiment predicts this reaction to be barrierless\cite{Adam116,Adam117,Adam119}, and the existence of the theoretical barrier is dependent on the computational method, we artificially remove the barrier from our calculation of the rate coefficient at the BHandHLYP/aug-cc-pVQZ level of theory.

We find the first step of this reaction \(\text{CH} + \text{CH}_4 \longrightarrow \text{C}_2\text{H}_5\) to be the rate-limiting step, with a barrierless rate coefficient of \(3.8 \times 10^{-13} \text{ cm}^3\text{s}^{-1}\). This is a factor of 5 slower than the nearest experimental value. We calculate the rate coefficient of second step of this reaction \(\text{C}_2\text{H}_5 \longrightarrow \text{C}_2\text{H}_4 + \text{H}\) to be \(1.8 \times 10^{-11} \text{ s}^{-1}\), suggesting the \(\text{C}_2\text{H}_5\) intermediate is fairly unstable. Thus we include this two-step reaction in our network as a single step \(\text{CH} + \text{CH}_4 \longrightarrow \text{C}_2\text{H}_4 + \text{H}\).

**Case Study 13: \(\text{NH} + \text{H} \leftrightarrow \text{N} + \text{H}_2\)**

This reaction has two spin configurations on the doublet PES, \(1\text{NH} + \text{H} \longrightarrow 2\text{N} + \text{H}_2\) and \(3\text{NH} + \text{H} \longrightarrow 2\text{N} + \text{H}_2\), and one spin configuration on the quartet PES, \(5\text{NH} + \text{H} \longrightarrow 2\text{N} + \text{H}_2\).

Adam et al.\cite{Adam120} calculated the experimental rate coefficient of \(3\text{NH} + \text{H} \longrightarrow 4\text{N} + \text{H}_2\) at 298 K by monitoring the decay of \(3\text{NH}\). They found the rate coefficient to have a value of \(3.2 \times 10^{-12} \text{ cm}^3\text{s}^{-1}\).

Adam et al.\cite{Adam120} also used the classical trajectory method to calculate the theoretical rate coefficient for \(\text{NH} + \text{H} \longrightarrow \text{N} + \text{H}_2\) at the MRCI/aug-cc-pVQZ level of theory. They found this reaction proceeds directly, rather than through the \(\text{NH}_3\) intermediate. They calculated the rate coefficient to be \(1.5 \times 10^{-12} \text{ cm}^3\text{s}^{-1}\). Other theoretical works calculated the rate coefficient with CVT and QCT to range from \(2.0 \times 10^{-13}\) to \(5.2 \times 10^{-12} \text{ cm}^3\text{s}^{-1}\)\cite{Adam120,Adam116}.

We find no published experimental or theoretical rate coefficients for the two spin configurations on the doublet PES.

On the quartet surface, we calculate the \(3\text{NH} + \text{H} \longrightarrow \text{H}_2 + 4\text{N}\) configuration to be \(1.4 \times 10^{-11} \text{ cm}^3\text{s}^{-1}\). This is a factor of 4 greater than the experimental value reported by Adam et al.\cite{Adam120}.

On the doublet surface, we do not calculate the \(1\text{NH} + \text{H} \longrightarrow \text{H}_2 + 2\text{N}\) configuration as \(1\text{NH}\) is not efficiently produced in this reaction network.

We find the \(5\text{NH} + \text{H} \longrightarrow \text{H}_2 + 2\text{N}\) configuration to proceed through the \(\text{NH}_2\) intermediate. This is consistent with theoretical studies of the reverse reaction\cite{Adam120,Adam116}. We find the total forward rate coefficient to be too slow to consider in this study (\(~10^{-86} \text{ cm}^3\text{s}^{-1}\))

Regarding the reverse reaction, various experiments have been performed on the deactivation of \(2\text{N}\) by \(\text{H}_2\) at 295–300 K\cite{Kobayashi165, Pederson166, Rand1124, Adam120}. The rate coefficients have been measured by monitoring the decay of \(2\text{N}\) and range from \(1.7–5.0 \times 10^{-12} \text{ cm}^3\text{s}^{-1}\). Donovan and Hussy\cite{Donovan124} indicate that \(2\text{N} + \text{H}_2\) should readily undergo chemical reaction into \(3\text{NH} + \text{H}\) via a direct path on the doublet PES. However, theoretical works suggest this reaction will proceed through the \(\text{NH}_2\) intermediate\cite{Pederson166}. Herron\cite{Herron116} reviewed the deactivation experiments and suggested a rate coefficient of \(2.2 \times 10^{-12} \text{ cm}^3\text{s}^{-1}\) for \(2\text{N} + \text{H}_2 \longrightarrow 3\text{NH} + \text{H}\).

Theoretical rate coefficient calculations of the reaction \(2\text{N} + \text{H}_2 \longrightarrow 3\text{NH} + \text{H}\) have been performed using QC\cite{Pederson166}, quantum dynamics\cite{Kobayashi165}, and CVT\cite{Kobayashi165} with the CASSCF and MRCI computational methods. Kobayashi et al.\cite{Kobayashi165} and Pederson et al.\cite{Pederson166} suggest this reaction proceeds through the \(\text{NH}_2\) intermediate. Pederson et al.\cite{Pederson166} find the \(\text{H}_2\) molecule approaches the \(\text{N}\) atom perpendicularly, and that there is no collinear reaction path. The calculated theoretical rate coefficients range from \(8.9 \times 10^{-13}–3.3 \times 10^{-12} \text{ cm}^3\text{s}^{-1}\).

Experimental and theoretical studies both suggest \(2\text{N} + \text{H}_2 \longrightarrow 3\text{NH} + \text{H}\) has a small energy barrier. The experimental value is 7.3 kJ mol\(^{-1}\)\cite{Donovan124}.

We find no published experimental or theoretical rate coefficients for the two other reverse reaction spin configurations (\(2\text{N} + \text{H}_2 \longrightarrow 1\text{NH} + \text{H}\) and \(2\text{N} + \text{H}_2 \longrightarrow 5\text{NH} + \text{H}\)).

At the BHandHLYP/aug-cc-pVQZ level of theory, we find the first step of the reverse reaction, \(\text{H}_2 + 2\text{N} \longrightarrow \text{NH}_2\), to be barrierless. This step is also the rate-limiting step. Similarly to Pederson et al.\cite{Pederson166}, we find the \(\text{H}_2\) molecule approaches the \(\text{N}\) atom perpendicularly. The second step, \(\text{NH}_2 \longrightarrow 3\text{NH} + \text{H}\), proceeds through a barrier. We calculate the overall barrierless rate coefficient to be \(9.7 \times 10^{-10} \text{ cm}^3\text{s}^{-1}\). This value is over 2 orders of magnitude larger than the experimental values. This disagreement with experiment is due to the lack of a barrier calculated when using the BHandHLYP method. For this reason, we introduce the experimental barrier of 7.3 kJ mol\(^{-1}\)\cite{Donovan124} to our calculation to obtain an overall rate coefficient of \(5.1 \times 10^{-10} \text{ cm}^3\text{s}^{-1}\). This value is only 1 order of magnitude larger than the experimental value.

We expect the remaining discrepancy to be a result of our chosen computational method, as our reaction geometry is the same as other theoretical works\cite{Pederson166,Adam116}.

We find the other two reverse rate coefficients (\(2\text{N} + \text{H}_2 \longrightarrow 1\text{NH} + \text{H}\) and \(2\text{N} + \text{H}_2 \longrightarrow 5\text{NH} + \text{H}\)) to be too inefficient to consider in this study (\(k < 10^{-21} \text{ cm}^3\text{s}^{-1}\)).

**Case Study 14: \(\text{NH} + \text{N} \longrightarrow \text{N}_2\text{H}^- \longrightarrow \text{N}_2 + \text{H}\)**

This reaction occurs on the doublet PES. There are three possible spin configurations: \(3\text{NH} + 4\text{N}\).
N\textsubscript{2}H\cdot \rightarrow \text{N}_2 + \text{H}, \; ^3\text{NH} + \text{N} \rightarrow \text{N}_2\cdot, \; \text{and} \; ^1\text{NH} + \text{N} \rightarrow \text{N}_2\cdot \rightarrow \text{N}_2 + \text{H}. \; \text{Because} \; ^1\text{NH} \; \text{is not produced efficiently by any reaction in this study, we only analyze the two spin configurations involving} \; ^3\text{NH}.

Hack \textit{et al.}\textsuperscript{121} experimentally measured the rate coefficient of $^3\text{NH} + \text{N} \rightarrow \text{products}$ at 298 K by monitoring the decay profile of $^3\text{NH}$. They measured the value to be $2.5 \times 10^{-11}$ cm\textsuperscript{3}s\textsuperscript{-1}.

Konnov and De Ruyck\textsuperscript{122} used the experimental value from Hack \textit{et al.}\textsuperscript{121}, as well as a suggested $T^{0.5}$ dependence to estimate a value of $2.6 \times 10^{-11}$ cm\textsuperscript{3}s\textsuperscript{-1}.

Caridade \textit{et al.}\textsuperscript{161} calculated the theoretical rate coefficient of $^3\text{NH} + \text{N} \rightarrow \text{N}_2\cdot \rightarrow \text{N}_2 + \text{H}$ to be $1.9 \times 10^{-11}$ cm\textsuperscript{3}s\textsuperscript{-1} using quasi-classical trajectory theory at the MRCI/aug-cc-pVQZ level of theory.

We find no published experimental or theoretical rate coefficients for $^3\text{NH} + \text{N} \rightarrow \text{N}_2\cdot \rightarrow \text{N}_2 + \text{H}$.

Consistent with a previous theoretical study, we find the $^3\text{NH} + \text{N} \rightarrow \text{N}_2\cdot \rightarrow \text{N}_2 + \text{H}$ reaction proceeds through the N\textsubscript{2}H intermediate. We find the rate-limiting step to be $^3\text{NH} + \text{N} \rightarrow \text{N}_2\text{H}$, with a rate coefficient of $4.0 \times 10^{-11}$ cm\textsuperscript{3}s\textsuperscript{-1}. This value is only a factor of 1.5 larger than the experimental value, and a factor of 2 larger than the theoretical value.

### Reaction Path Symmetry Numbers

The reaction path symmetry number, or reaction path multiplicity, can be calculated with the following equation.

$$\sigma = \frac{\prod_{i=1}^{N} \sigma_i}{\sigma^\dagger} \quad \text{(S14)}$$

where $\sigma$ is the reaction path symmetry number, $\sigma_i$ is the rotational symmetry number of reactant $i$, and $\sigma^\dagger$ is the rotational symmetry number of the transition state.

In Table S10, we list the reaction path symmetry numbers for all the reactions in our network, as well as the rotational symmetry numbers of the reactants and products used in the calculation.
TABLE S10. Reaction path symmetry numbers for each reaction ($\sigma$), as well as the rotational symmetry numbers of the reactants ($\sigma_i$) and transition states ($\sigma^\dagger$) used in the calculation. All steps in multi-step reactions are included. Spins are labeled only if reaction spin configurations have different reaction path symmetry numbers. $\sigma = \frac{\prod N_i \sigma_i}{\sigma^\dagger}.$

| Reaction Equation | $\sigma_1$ | $\sigma_2$ | $\sigma^\dagger$ | $\sigma$ |
|-------------------|-----------|-----------|-----------------|----------|
| H$_2$CN $\rightarrow$ HCN + H | 2 | 1 | 2 |
| HCN + H $\rightarrow$ H$_2$CN | 1 | 1 | 1 |
| H$_2$CN + H $\rightarrow$ HCN + H$_2$ | 2 | 1 | 1 | 2 |
| H$_2$CN + N $\rightarrow$ HCN + NH | 2 | 1 | 1 | 2 |
| 2H$_2$CN $\rightarrow$ HCN + H$_2$CNH | 2 | 2 | 1 | 4 |
| CH$_4$ + H $\rightarrow$ CH$_3$ + H$_2$ | 12 | 1 | 3 | 4 |
| CH$_4$ + N $\rightarrow$ H$_3$CNH | 12 | 1 | 1 | 12 |
| H$_3$CNH $\rightarrow$ H$_2$CNH + H | 1 | 1 | 1 |
| CH$_3$ + H $\rightarrow$ CH$_4$ | 6 | 1 | 3 | 2 |
| CH$_3$ + H$_2$ $\rightarrow$ CH$_4$ + H | 6 | 2 | 3 | 4 |
| CH$_3$ + N $\rightarrow$ H$_3$CN | 6 | 1 | 3 | 2 |
| H$_3$CN $\rightarrow$ H$_2$CN + H | 3 | 1 | 3 |
| H$_3$CNH $\rightarrow$ H$_2$CNH | 3 | 1 | 3 |
| H$_2$CNH $\rightarrow$ H$_2$CN + H | 1 | 1 | 1 |
| 2CH$_3$ $\rightarrow$ C$_2$H$_6$ | 6 | 6 | 6 |
| 2CH$_3$ $\rightarrow$ CH$_2$ + CH$_4$ | 6 | 6 | 1 | 36 |
| CH$_2$ + H $\rightarrow$ CH$_3$ | 2 | 1 | 1 |
| CH$_2$ + H$_2$ $\rightarrow$ CH$_4$ | 2 | 2 | 1 | 4 |
| CH$_2$ + H$_2$ $\rightarrow$ CH$_3$ + H | 2 | 2 | 2 |
| CH$_2$ + N $\rightarrow$ H$_2$CN | 2 | 1 | 1 |
| H$_2$CN $\rightarrow$ H$_2$CNH | 2 | 1 | 1 |
| 1CH$_2$ + 1CH$_2$ $\rightarrow$ C$_2$H$_4$ | 2 | 2 | 1 | 4 |
| 1CH$_2$ + 3CH$_2$ $\rightarrow$ C$_2$H$_4$ | 2 | 2 | 1 | 4 |
| 3CH$_2$ + 3CH$_2$ $\rightarrow$ C$_2$H$_4$ | 2 | 2 | 2 |
| CH$_2$ + CH$_3$ $\rightarrow$ C$_2$H$_5$ | 2 | 6 | 1 | 12 |
| C$_2$H$_5$ $\rightarrow$ C$_2$H$_4$ + H | 1 | 1 | 1 |
| CH$_2$ + CH$_4$ $\rightarrow$ C$_2$H$_6$ | 2 | 12 | 1 | 24 |
| CH$_2$ + CH$_4$ $\rightarrow$ 2CH$_3$ | 2 | 12 | 1 | 24 |
| CH + H$_2$ $\rightarrow$ CH$_3$ | 1 | 2 | 1 |
| CH + N $\rightarrow$ HCN | 1 | 1 | 1 |
| HCN $\rightarrow$ CN + H | 1 | 1 | 1 |
| 2CH $\rightarrow$ C$_2$H$_2$ | 1 | 1 | 1 |
| CH + CH$_4$ $\rightarrow$ C$_2$H$_5$ | 1 | 12 | 1 | 12 |
| NH + H $\rightarrow$ H$_2$ + N | 1 | 1 | 1 |
| N + H$_2$ $\rightarrow$ NH$_2$ | 1 | 2 | 2 | 1 |
| NH$_2$ $\rightarrow$ NH + H | 2 | 1 | 2 |
| NH + N $\rightarrow$ N$_2$H | 1 | 1 | 1 |
| N$_2$H $\rightarrow$ N$_2$ + H | 1 | 1 | 1 |