CRAHCN-O: A Consistent Reduced Atmospheric Hybrid Chemical Network Oxygen Extension for Hydrogen Cyanide and Formaldehyde Chemistry in CO$_2$-, N$_2$-, H$_2$O-, CH$_4$-, and H$_2$-Dominated Atmospheres

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Abstract: Hydrogen cyanide (HCN) and formaldehyde (H$_2$CO) are key precursors to biomolecules such as nucleobases and amino acids in planetary atmospheres; However, many reactions which produce and destroy these species in atmospheres containing CO$_2$ and H$_2$O are still missing from the literature. We use a quantum chemistry approach to find these missing reactions and calculate their rate coefficients using canonical variational transition state theory and Rice–Ramsperger–Kassel–Marcus/master equation theory at the BHandHLYP/aug-cc-pVDZ level of theory. We calculate the rate coefficients for 126 total reactions, and validate our calculations by comparing with experimental data in the 39% of available cases. Our calculated rate coefficients are most frequently within a factor of 2 of experimental values, and generally always within an order of magnitude of these values. We discover 45 previously unknown reactions, and identify 6 from this list that are most likely to dominate H$_2$CO and HCN production and destruction in planetary atmospheres. We highlight $^1$O + CH$_3$ $\rightarrow$ H$_2$CO + H as a new key source, and H$_2$CO + $^1$O $\rightarrow$ HCO + OH as a new key sink, for H$_2$CO in upper planetary atmospheres. In this effort, we develop an oxygen extension to our consistent reduced atmospheric hybrid chemical network (CRAHCN-O), building off our previously developed network for HCN production in N$_2$-, CH$_4$-, and H$_2$-dominated atmospheres (CRAHCN). This extension can be used to simulate both HCN and H$_2$CO production in atmospheres dominated by any of CO$_2$, N$_2$, H$_2$O, CH$_4$, and H$_2$.

INTRODUCTION

Hydrogen cyanide (HCN) and formaldehyde (H$_2$CO) are key precursors to various biomolecules required for the origin of life. The four nucleobases in RNA, i.e., adenine, guanine, cytosine and uracil, form in aqueous solutions containing one or both of these reactants.$^{1-3}$ Ribose, which pairs with phosphate to make up the backbone of RNA, forms from the oligomerization of H$_2$CO.$^{4,5}$ Amino acids form via Strecker synthesis, which includes both HCN and an aldehyde (H$_2$CO for glycine) as reactants.$^{6,7}$

Given their substantial role in producing biomolecules, HCN and H$_2$CO may be distinguishing atmospheric features of what we call biogenic worlds. These are worlds capable of producing key biomolecules rather than requiring they be delivered (e.g., by meteorites). It is presently unknown whether the early Earth was biogenic.

The redox state of the oldest minerals on the planet suggests the early Earth atmosphere was composed of “weakly reducing” gases, i.e., CO$_2$, N$_2$, and H$_2$O, with relatively smaller amounts of CH$_4$, CO, and H$_2$.$^{8,9,10}$ These atmospheric species are broken up into reactive radicals by UV radiation, lightning, and/or galactic cosmic rays (GCRs), which allows disequilibrium chemistry and the production of HCN and H$_2$CO to occur.$^{11-15}$ The following pathways are possible from the dissociation of these "weakly reducing" species.$^{11-15}$

\[
\text{CO}_2 + h\nu \rightarrow \text{CO} + ^3\text{O} \quad (1)
\]

\[
\rightarrow \text{CO} + ^1\text{O} \quad (2)
\]

\[
\text{N}_2 + h\nu \rightarrow 4\text{N} + 2\text{N} \quad (3)
\]

\[
\text{CH}_4 + h\nu \rightarrow \text{CH}_3 + \text{H} \quad (4)
\]

\[
\rightarrow ^3\text{CH}_2 + 2\text{H} \quad (5)
\]

\[
\rightarrow ^1\text{CH}_2 + \text{H}_2 \quad (6)
\]

\[
\rightarrow \text{CH} + \text{H}_2 + \text{H} \quad (7)
\]

\[
\text{H}_2\text{O} + h\nu \rightarrow \text{OH} + \text{H} \quad (8)
\]

\[
\text{H}_2 + h\nu \rightarrow 2\text{H} \quad (9)
\]

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where the superscripts, $^1$, $^2$, $^3$, and $^4$ refer to the singlet, doublet, triplet and quartet electronic spin states.

One way to better understand the biogenicity of the early Earth, is to use chemical kinetic models to simulate the production of HCN and H$_2$CO in plausible early Earth atmospheres. Atmospheric simulations of these species for primitive Earth conditions have been performed in the past, which make use of collections of reaction rate coefficients typically gathered from various sources the literature (e.g. experiment, theoretical simulations, thermodynamics, similar reactions).

The literature, however, is still missing several reactions between the radicals produced in CO$_2$-, N$_2$-, H$_2$O-, CH$_4$-, and H$_2$-dominated atmospheres, and these reactions may be crucial to understanding HCN and H$_2$CO chemistry in early Earth and other terrestrial environments. The largest gap in rate coefficient data is for reactions involving electronically excited species, e.g. $^1$O, $^2$N, and $^3$CH$_2$, which are directly produced from the dissociation of CO$_2$, N$_2$, and CH$_4$, respectively.

In Pearce et al. and Pearce et al., we developed an accurate and feasible method making use of computational quantum chemistry coupled with canonical variational transition state theory (CVT) and Rice–Ramsperger–Kassel–Marcus/master equation (RRKM/ME) theory to calculate a large network of reaction rate coefficients for one-, two- and three-body reactions. We first used this method to explore the entire field of possible reactions for a list of primary species in N$_2$-, CH$_4$-, and H$_2$-dominated atmospheres, and uncovered 48 previously unknown reactions; many of which were based on excited species such as $^2$N and $^3$CH$_2$. We then built an initial reduced network of 104 reactions based on this exploratory study, and used it to simulate HCN production in Titan’s atmosphere. This approach provided us with a more complete picture of HCN chemistry on Titan, as one of our newly discovered reactions was found to be one of the four dominant channels to HCN production on Titan.

In this work, we use the same theoretical approach to expand upon our initial network, by exploring and calculating all the potential reactions between three key oxygen species present on the early Earth (CO$_2$, H$_2$O, H$_2$CO), their dissociation radicals (CO, $^3$O, $^1$O, OH, and HCO), and all the non-oxygen primary species in our network (see Table 1 for the list of primary species). In this effort, we discover 45 brand new reactions, which are mainly based on HCO, H$_2$CN, $^1$O, $^2$N, $^3$CH$_2$, and CH. We calculate the rate coefficients for a total of 126 reactions, and validate our calculations by comparing with experimental data in the 39% of available cases.

Finally, we build the consistent reduced atmospheric hybrid chemical network oxygen extension (CRAHHCN-O), composed of experimental rate coefficients when available, and our calculated values otherwise. CRAHHCN-O is the amalgamation of the network developed in Pearce et al., and the oxygen reactions explored in this work. This network can be used to accurately simulate HCN and H$_2$CO production in CO$_2$-, N$_2$-, H$_2$O-, CH$_4$-, and H$_2$-dominated atmospheres.

The paper is outlined as follows: In the Methods section, we detail the theoretical and computational approach we use to explore reactions and calculate their rate coefficients. In the Results section, we describe the results of our rate coefficient calculations, including their agreement with any available experiments. We also discuss the limitations of our theoretical approach. In the Discussion section, we highlight 6 new reactions from this work which are potentially key production and destruction pathways to H$_2$CO and HCN in planetary atmospheres. We also summarize CRAHHCN-O and describe how it can be used for other atmospheric models. Finally, in the Conclusions section, we summarize the main conclusions from this work.

The Supporting Information (SI) contains two tables summarizing the new CRAHHCN-O rate coefficient data (the non-oxygen reaction data can be found in Pearce et al., any experimental rate coefficient data for reactions calculated in this work, the Lenard-Jones parameters used for three-body reaction rate coefficient calculations, a breakdown of some of the non-standard reaction calculations, and the quantum chemistry data used in our calculations.

**METHODS**

There are four phases to this work: First we explore all the potential reactions between eight oxygen species (CO$_2$, CO, $^3$O, $^1$O, H$_2$O, OH, H$_2$CO, and HCO) and the primary species in Table 1. These species are the the dominant sources of oxygen in the early Earth atmosphere (CO$_2$ and H$_2$O), a key biomolecule precursor (H$_2$CO) and their dissociation radicals. In this process, we characterize 81 known reactions and discover 45 previously unknown reactions. Second, we calculate the rate coefficients for every reaction that we find at 298 K, and validate the calculations by comparing to experimental data when available (in 39% of cases). Third, we calculate the temperature dependencies for the reactions that have no experimental measurements and have barriers (i.e. strong temperature dependencies from 50–400 K). Last, we gather the experimental and theoretical rate coefficients into the consistent reduced atmospheric hybrid chemical network oxygen extension (CRAHHCN-O), which contains experimental values when available, and our calculated rate coefficients otherwise.
TABLE 1. List of primary molecular species involved in this study and their spin states. Reactions strictly between non-oxygen species (below center line) were explored in Pearce et al. [18] and Pearce et al. [19]. Reactions involving the oxygen species (above center line) are new to this study.

| Species | Spin state | Ground/Excited state |
|---------|------------|----------------------|
| CO₂     | singlet    | ground               |
| H₂CO    | singlet    | ground               |
| HCO     | doublet    | ground               |
| CO      | singlet    | ground               |
| H₂O     | singlet    | ground               |
| OH      | doublet    | ground               |
| ³O      | triplet    | ground               |
| ¹O      | singlet    | excited              |
| H₂CN    | doublet    | ground               |
| HCN     | singlet    | ground               |
| CN      | doublet    | ground               |
| N₂      | singlet    | ground               |
| NH      | triplet    | ground               |
| ²N      | doublet    | excited              |
| ⁴N      | quartet    | ground               |
| CH₄     | singlet    | ground               |
| CH₃     | doublet    | ground               |
| ¹CH₂    | singlet    | excited              |
| ³CH₂    | triplet    | ground               |
| CH      | doublet    | ground               |
| H₂      | singlet    | ground               |
| H       | doublet    | ground               |

Computational Quantum Method and Basis Set

All exploration and rate coefficient calculations are performed with the Becke-Half-and-Half-Lee-Yang-Parr (BHandHLYP) density functional and the augmented correlation-consistent polarized valence double-ζ (aug-cc-pVDZ) basis set [22–26].

We have four key reasons for choosing this level of theory to perform our calculations:

1) We have benchmarked BHandHLYP/aug-cc-pVDZ rate coefficient calculations by comparing with experimental values in the past, and this method most frequently provides the best accuracy with respect to agreement with experimental values in comparison with other widely used, computationally cost effective methods.

In Pearce et al. [19], we compared the accuracy of 3 methods for calculating 12 reaction rate coefficients. We found BHandHLYP/aug-cc-pVDZ rate coefficient calculations give the best, or equal to the best agreement with experiment in 8 out of 12 cases. This is compared to ωB97XD/aug-cc-pVDZ and CCSD/aug-cc-pVTZ, which gave the best, or equal to the best agreement with experiment in 7 out of 12 and 6 out of 12 cases, respectively [19].

In another method-comparison study on a single reaction between BHandHLYP, CCSD, CAM-B3LYP, M06-2x, B3LYP and HF, all with the aug-cc-pVDZ basis set, we found that only BHandHLYP and CAM-B3LYP provide rate coefficients within the experimental range [19].

2) BHandHLYP/aug-cc-pVDZ calculations paired with CVT and RRKM/ME theory typically compute rate coefficients within a factor of two of experimental values, and all calculations generally fall within an order of magnitude of experimental values. This accuracy is consistent with typical uncertainties assigned in large-scale experimental data evaluations [27,28].

For examples in our network, Baulch et al. [27] assign uncertainties of 2–3 to HCO + HCO → H₂CO + CO and ³O + CH → CO + H and order-of-magnitude uncertainties to CO₂ + CH → products, H₂O + CH → products, and H₂CO + CH → products.

3) BHandHLYP/aug-cc-pVDZ calculations are computationally cost effective, and therefore feasible for a large scale exploratory study such as ours.

We have also shown in previous work for 12 rate coefficients, that increasing the basis set to the more computationally expensive aug-cc-pVTZ level does not increase the accuracy of our calculations with respect to agreement with experimental values [19].

4) Finally, using the BHandHLYP/aug-cc-pVDZ level of theory for all the calculations in this oxygen extension allows us to maintain consistency with the calculations in the original network (CRAHCN [18]).

1This hybrid functional uses 50% Hartree-Fock (HF) and 50% density functional theory (DFT) for the exchange energy calculation, offering a compromise between HF, which tends to overestimate energy barriers, and DFT, which tends to underestimate energy barriers.
Reaction Exploration

Using the Gaussian 09 software package, we perform a thorough search for reactions between eight oxygen species (CO$_2$, CO, O, H$_2$O, OH, H$_2$CO, and HCO) and the 22 primary species in this study (see Table 1). The procedure below is carried out for 8 x 22 = 176 pairs of species.

Using the Avogadro molecular visualization software, we placed each species at a handful of different distances and orientations form its reaction partner. We use a bit of chemical intuition when determining the distance between the species, e.g., abstraction reactions in our network tend to occur at short separations (1–2 Å), whereas addition reactions tend to be longer range (2–6 Å).

We then copy the geometries into Gaussian input files, and use the ‘opt=modredundant’ option to freeze the bond distances between one atom of each species. We run the Gaussian simulations with vibrational analyses to allow us to identify whether points along the MEP were found. A point along a MEP is identified by a single negative frequency that oscillates in the direction of the reaction. We run multiple simulations to look for possible abstraction, addition, and bond insertion reactions.

For reactions that form a single product, we continue the exploration of that product by searching for efficient decay and/or isomerization pathways. In many cases, we find the product efficiently decays into other products, sometimes after one or more isomerizations.

For cases where our above approach fails to find a MEP, we have developed a Python program that can be used to perform a more thorough scan of the potential energy surface. This program takes two species geometries as input, selects, e.g., 10 random separations and orientations for those species, and runs those Gaussian simulations in parallel. This program is especially useful for MEPs that turn out to be not strictly intuitive (e.g. OH + 1CH$_2$).

Once we find a point along a MEP, we then characterize the reaction path by doing a coarse-grain scan backwards and forwards from the identified point in intervals of 0.1 Å. We then plot the Gibbs free energies of these optimized points along the reaction path, and analyze the points using Avogadro to find the rough location(s) of the transition state(s). In several cases we find more than one transition state along a reaction path, with one or more stable structures between the reactants and the products.

Rate coefficient calculations

One- and Two-body Reactions

We calculate one- and two-body reaction rate coefficients using canonical variational transition state theory (CVT). This is a statistical mechanics approach which makes use of the canonical ensemble. This method can be used to calculate rate coefficients for reactions with and without energy barriers.

CVT can be explained as follows. There is a point that is far enough along the minimum energy reaction path (MEP), that the reactants that cross over this point are unlikely to cross back. This point is defined as the location where the generalized transition state (GT) rate coefficient is at its smallest value, therefore providing best dynamical bottleneck. This is expressed as:

$$k_{CVT}(T, s) = \min_s \{k_{GT}(T, s)\} \cdot \frac{k_B T}{h} K^0 e^{-\Delta G_{GT}(T, s)/RT},$$

where $k_{GT}(T, s)$ is the generalized transition state theory rate coefficient, $T$ is the temperature, and $s$ is a point along the MEP (e.g. bond distance).

To find the location along the MEP where the rate coefficient is at a minimum, we use the maximum Gibbs free energy criterion. It can be seen from the quasi-thermodynamic equation of transition-state theory that the maximum value for $\Delta G_{GT}(T, s)$ corresponds to a minimum value for $k_{GT}(T, s)$:

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

where $K^0$ is the reaction quotient under standard state conditions (i.e. 1 cm$^3$ for second-order reactions, 1 cm$^6$ for third-order reactions), and $\Delta G_{GT}(T, s)$ is the difference in the Gibbs free energy between transition state and reactants (kJ mol$^{-1}$).

This method offers a compromise of energetic and entropic effects, as $\Delta G$ contains both enthalpy and entropy. To obtain a similar accuracy for all calculations, we refine our coarse grain scans near the Gibbs maxima to a precision of 0.01 Å.

The generalized transition state theory rate coefficient, neglecting effects due to tunneling, can be calculated with the equation:

$$k_{GT}(T, s) = \sigma \frac{k_B T}{h} \prod_{i=1}^{N} Q_i^n(T) e^{-E_0(s)/RT},$$

where $\sigma$ is the reaction path multiplicity, $k_B$ is the Boltzmann constant (1.38 x 10$^{-23}$ J K$^{-1}$), $T$ is temperature (K), $h$ is the Planck constant (6.63 x 10$^{-34}$ J·s), $Q_i^n$ is the partition function of the transition state per unit volume (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 $i$, $n_i$ is the stoichiometric coefficient of species $i$, $N$ is the number of reactant species, $E_0$ is the difference in zero-point energies between the generalized transition state and the reactants (kJ mol$^{-1}$) (0 for barrierless reactions), and $R$ is the gas constant (8.314 x 10$^{-3}$ kJ K$^{-1}$ mol$^{-1}$).

The partition functions per unit volume have four components and are gathered from the Gaussian output files,
\[ Q = \frac{q_t}{V} g_q g_v q_r. \] (13)

where \( V \) is the volume (cm\(^{-3}\)) and the \( t, e, v, \) and \( r \) subscripts stand for translational, electronic, vibrational, and rotational, respectively.

In some cases, there are multiple steps (i.e. transition states) to a single reaction, and we must use mechanistic modeling in order to determine the steady-state solution of the overall rate equation. We place an example of a mechanistic model in Case Study 9 in the SI.

Three-body reactions

In the cases where two reactants form a single product, a colliding third body is required to remove excess vibrational energy from the product to prevent it from dissociating.\(^{35} \) This is expressed as,

\[ A + B \rightleftharpoons C_{(v)} \] (14)

\[ C_{(v)} + M \rightarrow C. \] (15)

The rate coefficient for these three-body reactions is expressed as\(^{36} \)

\[ k([M]) = \frac{k_0[M]/k_\infty}{1 + k_0[M]/k_\infty} k_\infty \] (16)

where \( k_0 \) is the third-order low-pressure limit rate coefficient (cm\(^6\)s\(^{-1}\)), \([M]\) is the number density of the colliding third body, and \( k_\infty \) is the second-order high-pressure limit rate coefficient (cm\(^3\)s\(^{-1}\)).

The high-pressure limit rate coefficients are equivalent to the two-body reaction rate coefficients (i.e., \( A + B \rightarrow C \)), and can be calculated using CVT as above. We use the koools code of the Multiwell Program Suite for the high pressure limit rate coefficient calculations.\(^{37,39} \)

The low-pressure limit rate coefficients, on the other hand, require information about the collisional third body for their calculation. To calculate these values, we use the Multiwell Master Equation (ME) code, which employs RRKM theory. The ME contains the probabilities that the vibrationally excited product will be stabilized by a colliding third body.\(^{40} \) Multiwell employs Monte Carlo sampling of the ME to build up a statistical average for the two outcomes of the reaction (i.e., destabilize back into reactants, or stabilize the product).

With the output from these stochastic trials, we calculate the low-pressure limit rate coefficient with the following equation\(^{38,41} \)

\[ k_0([M]) = \frac{k_\infty f_{prod}}{[M]} \] (17)

where \( k_\infty \) is the high-pressure limit rate coefficient, \( f_{prod} \) is the fractional yield of the collisionally stabilized product, and \([M]\) is the simulation number density (cm\(^{-3}\)), which we lower until \( k_0 \) converges.

We simulate three-body reactions using three different colliding bodies, corresponding to potential dominant species in the early Earth atmosphere (\( \text{N}_2, \text{CO}_2, \) and \( \text{H}_2 \)). The energy transfer was treated with a standard exponential-down model with \( < \Delta E \rangle_{\text{down}} = 0.8 \text{T K}^{-1} \text{cm}^{-1} \). The Lennard-Jones parameters for the bath gases and all the products were taken from the literature\(^{42-46} \) and can be found in Table S4.

In some cases, when two reactants come together to form a single product, the vibrationally excited product preferably decays along a different channel into something other than the original reactants (e.g. \( ^1\text{O} + \text{H}_2 \rightarrow \text{H}_2\text{O}_{(v)}; \rightarrow \text{OH} + \text{H} \)). In these cases, we also include the second-order reactions to these favourable decay pathways in our network. We verify the preferred decay pathways of vibrationally excited molecules by looking at previous experimental studies.

Temperature dependencies

For the one- and two-body reactions in this study with barriers, and no experimental measurements, we calculate temperature dependencies for the rate coefficients in the 50–400 K range. Barrierless reaction rate coefficients do not typically vary by more than a factor of \( \sim 3 \) between 50 and 400 K.\(^{44,45} \) To obtain temperature dependencies, we calculate the rate coefficients at 50, 100, 200, 298.15, and 400 K and fit the results to the modified Arrhenius expression

\[ k(T) = \alpha \left( \frac{T}{300} \right)^\beta e^{-\gamma/T}, \] (18)

where \( k(T) \) is the temperature-dependent second-order rate coefficient (cm\(^3\)s\(^{-1}\)), \( \alpha, \beta, \) and \( \gamma \) are fit parameters, and \( T \) is temperature (in K).

RESULTS

Comparison with Experiments

In Table 2 we display the three-body high- and low-pressure limit calculated rate coefficients at 298 K. Out of these 31 reactions, 12 have experimentally measured high-pressure limit rate coefficients. For the low-pressure limit rate coefficients, 9 of the 31 reactions have experimental measurements: However, the bath gases used in the low-pressure experiments often differ from the colliding third bodies in our calculations (i.e. \( \text{N}_2, \text{CO}_2, \) and \( \text{H}_2 \)). When using several different bath gases, low-pressure limit rate coefficients tend to range by \( \sim \) an order of magnitude.\(^{27,28,49} \)
TABLE 2: Lindemann coefficients for the three body reactions in this paper, calculated at 298 K, and valid within the 50–400 K temperature range. $k_\infty$ and $k_0$ are the third-order rate coefficients in the high and low pressure limits, with units cm$^3$s$^{-1}$ and cm$^6$s$^{-1}$, respectively. These values are for usage in the pressure-dependent rate coefficient equation $k = \frac{k_0[M]}{k_0 + k_\infty[M]}$. Calculations are performed at the BHandHLYP/aug-cc-pVDZ level of theory. Low-pressure limit rate coefficients are calculated for three different bath gases (N$_2$, CO$_2$, and H$_2$). Reactions with rate coefficients slower than $k_\infty = 10^{-13}$ cm$^3$s$^{-1}$ are not included in this network. The error factor is the multiplicative or divisional factor from the nearest experimental or suggested value.

| No. | Reaction equation | $k_\infty(298)$ calc. | $k_\infty(298)$ exp. | Error$\infty$ | $k_0(298)$ calc. | $k_0(298)$ exp. | Error$0$ |
|-----|-------------------|------------------------|----------------------|--------------|-----------------|-----------------|----------|
| *1. | CO$_2$ + $^1$O + M $\rightarrow$ CO$_3$ + M | $3.8 \times 10^{-11}$ | $0.1-23 \times 10^{-11}$ | 1 | (M=N$_2$) $3.0 \times 10^{-29}$ | (CO$_2$) $3.1 \times 10^{-29}$ | (H$_2$) $6.7 \times 10^{-29}$ |
| *2. | HCO + $^2$N + M $\rightarrow$ HCON· + M· $\rightarrow$ HCNO + M | $2.0 \times 10^{-11}$ | | | | | |
| *3. | HCO + CH$_3$ + M $\rightarrow$ CH$_3$CHO + M | $5.7 \times 10^{-12}$ | $6.3-44 \times 10^{-12}$ | 1 | (N$_2$) $5.3 \times 10^{-27}$ | (CO$_2$) $6.4 \times 10^{-27}$ | (H$_2$) $1.2 \times 10^{-27}$ |
| 4. | HCO + H + M $\rightarrow$ H$_2$CO + M | $4.9 \times 10^{-11}$ | | | | | |
| *5. | CO + CN + M $\rightarrow$ NCCO + M | $6.0 \times 10^{-12}$ | | | | | |
| 6. | CO + $^1$O + M $\rightarrow$ CO$_2$ + M | $2.8 \times 10^{-11}$ | $0.3-7 \times 10^{-11}$ | 1 | (N$_2$) $2.8 \times 10^{-29}$ | (CO$_2$) $3.0 \times 10^{-29}$ | (H$_2$) $5.9 \times 10^{-30}$ |
| *7. | CO + $^3$CH$_2$ + M $\rightarrow$ CH$_2$CO + M | $1.3 \times 10^{-11}$ | | | | | |
| 8. | CO + CH + M $\rightarrow$ HCCO + M | $4.6 \times 10^{-11}$ | $0.5-17 \times 10^{-11}$ | 1 | (N$_2$) $1.7 \times 10^{-28}$ | (CO$_2$) $1.9 \times 10^{-28}$ | (H$_2$) $3.3 \times 10^{-28}$ |
| 9. | CO + H + M $\rightarrow$ HCO + M | $2.7 \times 10^{-12}$ | | | | | |
| *10. | OH + H$_2$CN + M $\rightarrow$ H$_2$CNOH + M | $6.9 \times 10^{-12}$ | $6.0 \times 10^{-12}$ | 1 | (N$_2$) $6.5 \times 10^{-30}$ | (CO$_2$) $7.4 \times 10^{-30}$ | (H$_2$) $1.3 \times 10^{-29}$ |
| *11. | OH + CN + M $\rightarrow$ HOCN + M | $1.0 \times 10^{-12}$ | | | | | |
| 12. | OH + OH + M $\rightarrow$ H$_2$O$_2$ + M | $2.3 \times 10^{-11}$ | $1.5-6.5 \times 10^{-11}$ | 1 | (N$_2$) $4.9 \times 10^{-32}$ | (CO$_2$) $5.5 \times 10^{-32}$ | (H$_2$) $5.1 \times 10^{-31}$ |
| *13. | OH + $^3$O + M $\rightarrow$ HO$_2$ + M | $7.4 \times 10^{-11}$ | | | | | |
| *14. | OH + $^1$O + M $\rightarrow$ HO$_2$ + M | $1.0 \times 10^{-9}$ | | | | | |
| Reaction                                      | Rate Constant | Efficiency | Collision Factor | Product | Reference |
|-----------------------------------------------|---------------|------------|------------------|---------|-----------|
| 15. OH + NH + M → OH· + NH· + M + M          | 7.0 × 10^{-12} |            |                  |         |           |
| 16. OH + CH₃ + M → OH· + CH₃· + M + M + M + M | 2.0 × 10^{-11}  | 9.3–17 × 10^{-11} | 5               | (CO₂) 4.5 × 10^{-30} | (H₂) 8.3 × 10^{-30} |
| 17. OH + H + M → H₂O + M                     | 2.4 × 10^{-10}  |            |                  | (N₂) 8.5 × 10^{-31} | (CO₂) 9.2 × 10^{-31} |
| 18. ^3O + CN + M → NCO + M                   | 7.1 × 10^{-12}  | 9.4–16 × 10^{-12} | 1               | (N₂) 1.3 × 10^{-30} | (CO₂) 1.5 × 10^{-30} |
| 19. ^3O + ^3O + M → O₂ + M                   | 1.8 × 10^{-11}  |            |                  | (N₂) 3.4 × 10^{-33} | (Ar, O₂) 3.9–100 × 10^{-34} |
| 20. ^3O + Ar + M → NO + M                    | 6.6 × 10^{-11}  |            |                  | (N₂) 1.6 × 10^{-33} | (CO₂) 1.8 × 10^{-33} |
| 21. ^3O + ^3CH₂ + M → H₂CO + M               | 6.7 × 10^{-11}  | 1.9–20 × 10^{-11} | 1              | (N₂) 9.2 × 10^{-29} | (CO₂) 1.1 × 10^{-28} |
| 22. ^3O + CH + M → HCO + M                   | 1.1 × 10^{-10}  | 6.6–9.5 × 10^{-11} | 1             | (N₂) 5.2 × 10^{-30} | (CO₂) 6.2 × 10^{-30} |
| 23. ^3O + H + M → OH + M                     | 3.5 × 10^{-10}  |            |                  | (N₂) 2.6 × 10^{-33} | (CO₂) 2.9 × 10^{-33} |
| 24. ^3O + HCN + M → HCNO + M                 | 3.3 × 10^{-11}  |            |                  | (N₂) 4.0 × 10^{-29} | (CO₂) 4.6 × 10^{-29} |
| 25. ^3O + CN + M → NCO + M                   | 8.9 × 10^{-11}  |            |                  | (N₂) 1.9 × 10^{-29} | (CO₂) 2.1 × 10^{-29} |
| 26. ^3O + ^3O + M → O₂ + M                   | 2.3 × 10^{-10}  |            |                  | (N₂) 8.8 × 10^{-33} | (CO₂) 9.6 × 10^{-33} |
| 27. ^3O + CH₄ + M → CH₃OH + M                 | 5.8 × 10^{-9}   | 1.4–4.0 × 10^{-10} | 15            | (N₂) 3.6 × 10^{-23} | (CO₂) 3.9 × 10^{-23} |
| 28. ^3O + ^3CH₂ + M → H₂CO + M               | 3.3 × 10^{-10}  |            |                  | (N₂) 6.6 × 10^{-27} | (CO₂) 7.7 × 10^{-27} |
| 29. ^3O + CH + M → HCO + M                   | 9.2 × 10^{-11}  |            |                  | (N₂) 4.9 × 10^{-29} | (CO₂) 5.8 × 10^{-29} |
Our calculated high-pressure rate coefficients are within the range of experimental values in 9 out of 12 cases. The other three rate coefficients are factors of 2, 5, and 15 from the nearest experimental values. Typical uncertainties for rate coefficients as assigned in large experimental data evaluations range from factors of 2–10. Therefore, this calculated accuracy is consistent with the levels of uncertainty typically found in the literature.

Each low-pressure limit rate coefficient was calculated for three bath gases (N₂, CO₂, and H₂) and compared to experiments performed with matching bath gases when possible, and any bath gases otherwise. Nine of the reactions had experimentally measured low-pressure limit rate coefficients for one or more bath gases. All of our calculated rate coefficients for these reactions landed within an order of magnitude of the experimental range for the matching bath gas when possible, or another bath gas otherwise. Most commonly (67% of the time), our rate coefficients were within a factor of 3 from the nearest experimental measurement. Larger deviations tended to occur for cases that only have a single experimental measurement for comparison.

In Table 3, we display the 95 one- and two-body reaction rate coefficients calculated at 298 K with any experimental or suggested values. 47 of these reactions have experimental or suggested values, and our calculations are within approximately one order of magnitude of these values in all but one case. In 60% of cases our calculated rate coefficients are within a factor of 2 of experimental values, and in 83% of cases our calculated rate coefficients are within a factor of 6 of experimental values.

In one case, OH + CH₄ → H₂O + CH₃, our calculated rate coefficient has a slightly higher than an order of magnitude deviation from experiment (factor of 54). We attribute this error to the lack of a quantum tunneling correction in our calculations. Bravo-Pérez et al.,[52] performed transition state theory calculations for this reaction at the BHandHLYP/6-311G(d,p) level of theory, and calculated a tunneling factor of 30.56 at 298 K using an Eckart model. If we applied this factor to our calculation, our rate coefficient would be within a factor of two of the experimental range.

| No. | Reaction equation | Forw./Rev. | Barrier? | k(298) calculated | k(298) experimental | Error factor |
|-----|-----------------|------------|---------|-------------------|---------------------|-------------|
| 32  | NCCO → CO + CN  | F          | Y       | 9.4×10⁻¹²         | 0.1–23×10⁻¹¹       | 1           |
| 33  | CO₂ + ³O → ³CO₃ · → ³CO₃ · → CO₂ + ³O | F          |          | 3.8×10⁻¹¹         | 1.8–6.8×10⁻¹³     | 6           |
| 34  | CO₂ + ³N → NCO₂ · → OCNO · → CO + NO | F          | aY      | 3.2×10⁻¹⁴         | 1.5–1.9×10⁻¹³     | 2           |
| 35  | CO₂ + ³CH₂ → ³CH₂CO₂ · → H₂CO + CO | F          |          | 8.0×10⁻¹³         | 1.5–2.1×10⁻¹²     | 1           |
| 36  | CO₂ + CH → CHCO₂ · → HCCO · → HCO + CO | F          | bN      | 3.1×10⁻¹²         | 1.6–4.2×10⁻¹⁰     | 6           |
| 37  | H₂O₂ → OH + OH  | F          |         | 5.1×10⁻⁹         | 1.6–4.2×10⁻¹⁰     | 6           |
| 38  | H₂O + CN → HCN + HCO | F          |         | 1.8×10⁻¹¹         | 1.7×10⁻¹¹         | 1           |
| 39  | H₂O + CH → CH₂HCOH · → trans-HCOHO · + H · → H₂O + CO + H | F          |         | 7.1×10⁻¹⁷         | 1.5–1.9×10⁻¹³     | 2           |
| 40  | H₂O + OH → H₂O₂ · → HO · → H₂O + HCO | F          |         | 1.1×10⁻¹⁰         | 1.5–2.1×10⁻¹⁰     | 6           |
| 41  | H₂O + ³O → HCO + OH | F          |         | 6.8×10⁻¹⁴         | 1.5–1.9×10⁻¹³     | 2           |
| 42  | H₂O + ³O → H₂O₂ · → HCO₂H · → HCO + OH | F          |         | 4.6×10⁻¹⁰         | 1.5–2.1×10⁻¹⁰     | 6           |
| 43  | H₂O + CH₄ → HCO + CH₄ | F          |         | 1.9×10⁻¹⁹         | 2.2–4.2×10⁻¹⁸     | 12          |
| 44  | H₂O + ³CH₂ → HCO + CH₃ | F          |         | 1.1×10⁻¹⁴         | <1.0×10⁻¹⁴        | 1           |
| 45  | H₂O + ³CH₂ → HCO + CH₃ | F          |         | 1.5×10⁻¹²         | 2.0×10⁻¹²         | 1           |
| Reaction | Products | Reaction | Products | Reaction | Products |
|----------|----------|----------|----------|----------|----------|
| H₂O + H  | HCO + H₂ | H₂O + H  | HCO + H₂ | H₂O + H  | HCO + H₂ |
| H₂O + H  | HCO + H₂ | H₂O + H  | HCO + H₂ | H₂O + H  | HCO + H₂ |
| H₂O + H  | HCO + H₂ | H₂O + H  | HCO + H₂ | H₂O + H  | HCO + H₂ |
| H₂O + H  | HCO + H₂ | H₂O + H  | HCO + H₂ | H₂O + H  | HCO + H₂ |
| H₂O + H  | HCO + H₂ | H₂O + H  | HCO + H₂ | H₂O + H  | HCO + H₂ |

*Note: The reactions with asterisks are not documented in the text.*
NO + H

*87. OH + 2N → 3OH · N → 3NOH · → F N 1.5×10\(^{-10}\) NO + H

88. OH + CH\(_4\) → H\(_2\)O + CH\(_3\) F Y 1.1×10\(^{-16}\) 5.9–11×10\(^{-15}\) 54
89. OH + CH\(_3\) → 2O + CH\(_4\) F Y 1.1×10\(^{-18}\) 1.8×10\(^{-17}\) 16
90. OH + CH\(_3\) → H\(_2\)O + 3CH\(_2\) F Y 3.5×10\(^{-18}\) 5.9×10\(^{-17}\) 16
91. OH + 3CH\(_2\) → OH · · · CH\(_2\) · → H\(_2\)COH · → F N 4.6×10\(^{-11}\) 3.0×10\(^{-11}\) 2
H\(_2\)CO + H
92. OH + CH\(_2\) → H\(_2\)O + CH F N 7.6×10\(^{-13}\)
93. OH + 3CH\(_2\) → OH · · · CH\(_2\) · → H\(_2\)COH · → F N 4.6×10\(^{-11}\) 5.0×10\(^{-11}\) 1
H\(_2\)CO + H
94. OH + CH → 3OH · CH · → 3HCOH · → F N 3.2×10\(^{-11}\)
3H\(_2\)CO · → HCO + H
95. OH + CH → anti-HCOH\(_{\nu}\) · → F N 6.3×10\(^{-12}\)
H\(_2\)CO\(_{\nu}\) · → CO + H\(_2\)
96. OH + CH → anti-HCOH\(_{\nu}\) · → F N 6.3×10\(^{-12}\)
H\(_2\)CO\(_{\nu}\) · → CO + H + H
97. OH + H\(_2\) → H\(_2\)O + H F Y 1.5×10\(^{-15}\) 5.3–8.5×10\(^{-15}\) 4
98. OH + H → 3O + H\(_2\) F Y 6.5×10\(^{-16}\) 9.9×10\(^{-17}\)–5.6×10\(^{-16}\) 1
*99. 3O + H\(_2\)CN → CH\(_3\)NO · → F Y 4.0×10\(^{-14}\)
HCNO + H
*100. 3O + H\(_2\)CN ↔ CH\(_3\)NO · ↔ F Y 9.8×10\(^{-11}\)
HCNO + H
101. 3O + H\(_2\)CN → CH\(_3\)NO · → F Y 8.3×10\(^{-15}\)
HCNOH · → OH + HCN
102. 3O + HCN → 3NCOH → NCO + H F Y 1.5×10\(^{-18}\)
103. 3O + HCN · ↔ 3NCOH · ↔ NCO + H R Y 2.5×10\(^{-20}\)
104. 3O + CN → 4NCO → CO + 2N F N 1.5×10\(^{-11}\) 2.7×10\(^{-12}\)–3.7×10\(^{-11}\) 1
105. 3O + CN → NCO\(_{\nu}\) · → CO + 2N F N 7.1×10\(^{-12}\) 9.4×10\(^{-12}\)–1.6×10\(^{-11}\) 1
106. 3O + NH → HNO · → NO + H F N 3.1×10\(^{-11}\) 5.0×10\(^{-11}\) 2
107. 3O + NH → OH + 4N F Y 2.2×10\(^{-14}\) <1.7×10\(^{-13}\)–5.0×10\(^{-12}\) 1
108. 3O + CH\(_2\) → OH + CH\(_3\) F Y 1.1×10\(^{-19}\) 6.6×10\(^{-19}\)–6.6×10\(^{-16}\) 6
109. 3O + CH\(_3\) → CH\(_3\)O · → H\(_2\)CO + H F N 9.4×10\(^{-11}\) >3.0×10\(^{-11}\)–1.9×10\(^{-10}\) 1
110. 3O + 3CH\(_2\) → H\(_2\)CO\(_{\nu}\) · → CO + H + H F N 3.4×10\(^{-11}\) \(^{b}\)1.0×10\(^{-11}\)–1.0×10\(^{-10}\) 1
111. 3O + 3CH\(_2\) → H\(_2\)CO\(_{\nu}\) · → CO + H\(_2\) F N 3.4×10\(^{-11}\) \(^{b}\)1.0×10\(^{-11}\)–1.0×10\(^{-10}\) 1
*112. 3O + 3CH\(_2\) → 3H\(_2\)CO · → HCO + H F N 2.1×10\(^{-10}\)
113. 3O + CH → HCO\(_{\nu}\) · → CO + H F N 1.1×10\(^{-10}\) 6.6×10\(^{-11}\) 2
114. 3O + CH → 4HCO · → 4COH · → F N 2.5×10\(^{-10}\)
OH + C
115. 3O + H\(_2\) → OH + H F Y 7.2×10\(^{-19}\) 7.0×10\(^{-18}\)–1.1×10\(^{-17}\) 10
*116. 1O + H\(_2\)CN → CH\(_2\)NO · → F Y 4.5×10\(^{-10}\)
3O + H\(_2\)CN
*117. 1O + H\(_2\)CN → CH\(_2\)NO · → F Y 6.0×10\(^{-13}\)
HCNO + H
*118. 1O + H\(_2\)CN → CH\(_2\)NO · → F Y 1.2×10\(^{-13}\)
HCNOH · → HCN + OH
*119. 1O + CN → NCO\(_{\nu}\) · → CO + 2N F N 8.9×10\(^{-11}\)
120. 1O + CH\(_3\) → CH\(_3\)OH\(_{\nu}\) · → OH + CH\(_3\) F N 5.8×10\(^{-10}\) 1.4–4.0×10\(^{-10}\) 15
*121. 1O + CH\(_3\) → CH\(_2\)O · → H\(_2\)CO + H F N 4.3×10\(^{-10}\)
122. 1O + CH\(_2\) → 3H\(_2\)CO · → HCO + H F N 7.0×10\(^{-10}\)
*123. 1O + 1CH\(_2\) → H\(_2\)CO\(_{\nu}\) · → F N 1.7×10\(^{-10}\)
CO + H + H
*124. 1O + 1CH\(_2\) → H\(_2\)CO\(_{\nu}\) · → CO + H\(_2\) F N 1.7×10\(^{-10}\)
*125. 1O + CH → HCO\(_{\nu}\) · → CO + H F N 9.2×10\(^{-11}\)
126. 1O + H\(_2\) → H\(_2\)O\(_{\nu}\) · → OH + H F N 7.1×10\(^{-10}\) 1.1–3.0×10\(^{-10}\) 2

\(^{a}\) We introduce a barrier of 17.15 kJ mol\(^{-1}\) (half the HF barrier) to this calculation as no barrier is found at the BHandHLYP/aug-cc-pVDZ level of theory (see supplement for more details).

\(^{b}\) We remove the barrier from this calculation as experiment predicts this reaction to be barrierless below 400 K\(^{56}\).

\(^{c}\) We remove the intermediate barriers from this reaction and reduce the barrierless first step by a factor of 3.4 to match the barrier effects at the B3LYP/aug-cc-pVDZ level of theory. Experiments predict this reaction to have little to no barrier\(^{57}\).

\(^{d}\) We remove the barrier from the rate limiting third step of this calculation, as experiment predicts this reaction to be barrierless\(^{54}\).

\(^{e}\) Simulations did not converge beyond a O-O bond distance of 2.90 Å. The rate coefficient is calculated with the variational transition state at
this location, which has the highest $\Delta G$.

We remove the barrier from the rate limiting third step of this calculation, as data evaluations suggest little to no barrier for this reaction\cite{22}.

$^9$ This rate coefficient is one half of the calculated rate coefficient for $\text{OH} + \text{CH} \rightarrow \text{anti-} \text{HCOH}_2$ as both $\text{CO} + \text{H}_2$ and $\text{CO} + \text{H} + \text{H}$ are equally probable decay pathways for anti- HCOH$_2$.\cite{23,25,26,27,28,59}

$^b$ Experimental values are for $^3\text{O} + ^3\text{CH}_2 \rightarrow$ products divided by 2. As both product channels CO + H + H and CO + H$_2$ are suggested to be equally likely,\cite{27,25,26,28,59}

Method Limitations

Occasionally computational methods misdiagnose reaction energy barriers. In other words, a method may calculate a barrier when experiments suggest the reaction is barrierless, or a method may calculate no barrier when experiments suggest a small-to-modest-sized barrier ($\sim$1–20 kJ mol$^{-1}$) exists. We find this to be biggest limitation of applying a consistent computational quantum method to a large number of reactions. This is the main reason for taking a hybrid approach to building CRAHCN-O. Experiments are the most accurate method to calculate rate coefficients, therefore experimental values will always be used when possible. However, for the large number of reactions without experimentally measured rate coefficients, we must use a robust and feasible computational method to calculate and include these reactions in the network.

In four cases (noted in Table 3), our chosen computational method (BHandHLYP/aug-cc-pVDZ) predicts barriers at the first step or an intermediate step of reactions that are expected to be barrierless. In one other case, this method predicts a reaction had no barrier, when experiment suggests a barrier of 17.15 kJ mol$^{-1}$\cite{60}. For these few cases, we artificially remove the barriers from these calculations, or introduce an experimental barrier. Based on the calculations in this paper, we find this method correctly diagnoses barriers $\sim$92% of the time.

Comparing the barrier diagnosis capabilities of BHandHLYP/aug-cc-pVDZ with two other widely used method in past work\cite{43}, we find CCSD/aug-cc-pVTZ and $\omega$B97XD/aug-cc-pVDZ share these limitations. For 11 chosen reactions, BHandHLYP/aug-cc-pVDZ misdiagnosed 4 barriers, CCSD/aug-cc-pVTZ misdiagnosed 5 barriers, and $\omega$B97XD/aug-cc-pVDZ misdiagnosed 2 barriers.

A second limitation of our method is that we do not include a correction factor for quantum mechanical tunneling. This may not be a big concern at 298 K, where our rate coefficient calculations are typically within a factor of two of experimental values, and generally always within an order of magnitude of experimental values. However, tunneling is most relevant at lower temperatures\cite{61}

Given the lack of experimental low temperature ($\lesssim$ 230 K) rate coefficient data for the reactions in this study, we cannot obtain a valid statistical sense of the accuracy of our method for calculating low temperature rate coefficients. However, it is a reasonable assumption that our treatment leads to larger uncertainties at the lower end of our temperature range (50–200 K), where tunneling plays a greater role; possibly up to two orders of magnitude.

DISCUSSION

Highlighted New Reactions

As we have already noted, we have discovered 45 previously unknown reactions and provide the first calculations of their rate coefficients. In Table 4, we highlight 6 of these reactions. These reactions are potentially key pathways for the production and destruction of HCN or $\text{H}_2\text{CO}$ in planetary atmospheres due to their high rate coefficients at 298 K, and the reasonably high abundances of their reactants in atmospheres.

Different reactions tend to dominate in different regions of an atmosphere. In the diffuse upper atmosphere (thermosphere), incoming UV radiation breaks apart dominant atmospheric species to produce radicals. In the dense lower atmosphere (troposphere), radicals can be transported from the upper atmosphere via turbulent mixing, or produced by lightning and/or GCRs. In this lower region, there is also sufficient pressure to collisionally deexcite the vibrationally excited intermediates in three-body reactions.

One newly discovered reaction with a great potential to produce substantial amounts $\text{H}_2\text{CO}$ in upper atmospheres is $^1\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$. Firstly, there will likely be high concentrations of reactants $^1\text{O}$ and $\text{CH}_3$ in the upper atmospheres of planets containing CO$_2$ and CH$_4$, as the former are the direct photodissociation fragments of the latter. Secondly, this reaction has a barrierless rate coefficient of $k(298 \text{ K}) = 4.3 \times 10^{-10}$ cm$^3$s$^{-1}$, which is in the 94th percentile for highest two-body reaction rate coefficients in this study. For these reasons, we expect this reaction to be a dominant source of $\text{H}_2\text{CO}$ in CO$_2$-rich and CH$_4$-containing atmospheres such as the early Earth. At the CCSD/aug-cc-pVDZ level of theory, we calculate this rate coefficient to be only 14% lower (3.7 $\times$ 10$^{-10}$ cm$^3$s$^{-1}$), suggesting this calculation is not very sensitive to the choice of computational method.

In lower planetary atmospheres, we find two new three-body reactions that may be important pathways to $\text{H}_2\text{CO}$. These reactions are $^3\text{O} + ^3\text{CH}_2 + \text{M} \rightarrow \text{H}_2\text{CO} + \text{M}$ and $^3\text{O} + ^3\text{CH}_2 + \text{M} \rightarrow \text{H}_2\text{CO} + \text{M}$. These reactions are most favourable at the high-pressure limit, where their rate coefficients are $k_\infty(298 \text{ K}) = 3.3 \times 10^{-10}$ and 6.7 $\times$ 10$^{-11}$ cm$^3$s$^{-1}$, respectively. The pressures at which these reaction rate coefficients reach 90% of $k_\infty(298 \text{ K})$ in a N$_2$ bath gas are 0.61 bar and 7.1 bar, respectively.
TABLE 4. Highlighted newly discovered reactions in this work, listed with their calculated rate coefficients at 298 K and potential for importance in atmospheres. For simplicity, reaction intermediates are not listed here. See Tables 2 and 3 for full details of reaction intermediates. Second-order rate coefficients have units cm³ s⁻¹. Third-order rate coefficients have units cm⁶ s⁻¹.

| Reaction                                      | k(298) calculated | Importance                                      |
|-----------------------------------------------|-------------------|------------------------------------------------|
| ¹O + CH₃ → H₂CO + H                           | 4.3×10⁻¹⁰         | H₂CO production in upper atmospheres           |
| ¹O + ²CH₂ + M → H₂CO + M                      | k∞ = 3.3×10⁻¹⁰    | H₂CO production in lower atmospheres           |
|                                              | k₀(N₂) = 6.6×10⁻²⁷|                                                |
|                                              | k₀(CO₂) = 7.7×10⁻²⁷|                                                |
|                                              | k₀(H₂) = 1.2×10⁻²⁶ |                                                |
| ³O + ³CH₂ + M → H₂CO + M                      | k∞ = 6.7×10⁻¹¹    | H₂CO production in lower atmospheres           |
|                                              | k₀(N₂) = 9.2×10⁻²⁹|                                                |
|                                              | k₀(CO₂) = 1.1×10⁻²⁸|                                                |
|                                              | k₀(H₂) = 1.7×10⁻²⁸ |                                                |
| ¹O + H₂CN → HCN + OH                         | 1.2×10⁻¹³         | HCN production in upper atmospheres            |
| H₂CO + ¹O → HCO + OH                         | 4.6×10⁻¹⁰         | H₂CO destruction in upper atmospheres         |
| ¹O + HCN + M → HCNO + M                      | k∞ = 3.3×10⁻¹¹    | HCN destruction in lower atmospheres           |
|                                              | k₀(N₂) = 4.0×10⁻²⁹|                                                |
|                                              | k₀(CO₂) = 4.6×10⁻²⁹|                                                |
|                                              | k₀(H₂) = 8.0×10⁻²⁹ |                                                |

Such pressures would have been present in the evolving early Earth atmosphere ~4.5 billion years ago.²²

For new potentially important routes to HCN, we find ¹O + H₂CN → HCN + OH, which has a rate coefficient of k(298 K) = 1.2×10⁻¹³ cm³ s⁻¹. This reaction has the potential to be an important source of HCN in upper atmospheres with high CO₂ mixing ratios, and low H₂ and CH₄ mixing ratios. The reason for this is that there is a direct competing reaction for HCN production from H₂CO + N → HCN + H₂, which has a rate coefficient of k(298 K) = 2.2×10⁻¹¹ cm³ s⁻¹. Therefore, the ¹O/H ratio in upper atmospheres will determine which of these two reactions dominates. We note also that this reaction has a complex reaction scheme, with two other favourable channels from the H₂CNO intermediate: HCNO + H and ³O + H₂CN. Our calculations of this reaction rate coefficient using two other computational methods (ωB97XD, CCSD) suggests the channel to HCN + OH may be more favourable than our BHandHLYP calculation implies, up to a factor of ~700 (see theoretical case study 9 in the SI for more details). Given these discrepancies, and the novelty of this reaction, we recommend experimental measurements be performed for the three product channels of ¹O + H₂CN.

A new reaction with a great potential to destroy H₂CO is H₂CO + ¹O → HCO + OH, which has a barrierless rate coefficient of 4.6×10⁻¹⁰ cm³ s⁻¹ at 298 K. As with the main new production pathway to H₂CO, this rate coefficient is one of the highest two-body rate coefficients in this study, and likely plays a role of attenuating H₂CO in upper atmospheres. At the CCSD/aug-cc-pVDZ level of theory, we calculate this rate coefficient to be only 50% lower (2.3×10⁻¹⁰ cm³ s⁻¹) than the value at the BHandHLYP/aug-cc-pVDZ level of theory.

Lastly, we highlight a new HCN destruction pathway in lower atmospheres, ¹O + HCN + M → HCNO + M. This reaction may be particularly important in attenuating HCN abundances in the troposphere, which is the region where HCN dissolves in rain droplets and makes its way into surface water. This reaction rate coefficient reaches 90% of k∞(298 K) in a N₂ bath gas at 3 bar.

CRAHCN-O

CRAHCN-O is a chemical reaction network that can be used to simulate the production of HCN and H₂CO in atmospheres ranging from ~50–400 K dominated by any of the following gases: CO₂, N₂, H₂O, CH₄, and H₂. CRAHCN-O is the amalgamation of the CRAHCN network developed in Pearce et al.²⁸ and the oxygen extension developed in this work. CRAHCN-O contains experimental rate coefficients (when available), and our consistently calculated theoretical rate coefficients from this work otherwise.

We summarize the oxygen extension in Tables S1 and S2 in the supplementary materials. In addition to the 126 reactions explored in this work, we include one experimental spin-forbidden collisionally induced intersystem crossing reaction (¹O + M → ³O + M), whose rate coefficient cannot be calculated using our theoretical method.

The original CRAHCN network can be found in the
appendices of Pearce et al. [13].

CONCLUSIONS

In this work, we use a novel technique making use of computational quantum chemistry and experimental data to build a consistent reduced atmospheric hybrid chemical network oxygen extension (CRAHCN-O). This network can be used to simulate HCN and H$_2$CO chemistry in planetary atmospheres dominated by CO$_2$, N$_2$, H$_2$O, CH$_4$, and H$_2$.

The oxygen extension contains 127 reactions, and is made up of approximately 30% experimental and 70% consistently calculated theoretical rate coefficients. Below are the main conclusions of this work in bullet point.

- We discover 45 previously unknown reactions, and are the first to calculate their rate coefficients. These new reactions typically involve electronically excited species (e.g., $^1$O, $^1$CH$_2$, $^2$N).

- The majority (~62%) of our calculated rate coefficients are accurate to within a factor of two of experimental measurements. ~84% are accurate to within a factor of 6 of experimental values, and the rest are accurate to within about an order of magnitude of experimental values. This level of accuracy is consistent with the uncertainties assigned in large scale experimental data evaluations.

- We identify 6 potentially key new production and destruction pathways for H$_2$CO and HCN from these previously unknown reactions.

- The high, barrierless rate coefficient of $^1$O + CH$_3$ $\rightarrow$ H$_2$CO + H ($k$(298 K) = 4.3 x 10$^{-10}$ cm$^3$s$^{-1}$) likely makes it a key source of formaldehyde in upper atmospheres where $^1$O and CH$_3$ are produced from the UV photodissociation of CO$_2$ and CH$_4$, respectively.

- Conversely, the high, barrierless rate coefficient of H$_2$CO + $^1$O $\rightarrow$ HCO + OH ($k$(298 K) = 4.6 x 10$^{-10}$ cm$^3$s$^{-1}$) likely makes it a key sink for formaldehyde in upper atmospheres.

- $^1$O + H$_2$CN $\rightarrow$ HCN + OH is less efficient than the known HCN source, H$_2$CN + H $\rightarrow$ HCN + H$_2$; However the former may dominate HCN production in CO$_2$-rich upper atmospheres with high $^1$O/H ratios from CO$_2$ photodissociation.

- In lower atmospheres (i.e. high partial pressures), H$_2$CO may form via new reactions between $^1$O + $^1$CH$_2$ and $^3$O + $^3$CH$_2$, which require a collisional third body at the high pressures present in these regions. HCN may be efficiently removed in this region via $^1$O + HCN + M $\rightarrow$ HCN + M.

Having now filled in the missing chemical data relevant to HCN and H$_2$CO production in CO$_2$- and H$_2$O-rich atmospheres, we intend to couple CRAHCN-O to a 1D chemical kinetic model to simulate the atmosphere of the early Earth.

SUPPORTING INFORMATION

Rate coefficient data, experimental data, Lennard-Jones parameters, theoretical case studies, and quantum chemistry data.

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REFERENCES

[1] Oró, J. Mechanism of Synthesis of Adenine from Hydrogen Cyanide under Possible Primitive Earth Conditions. *Nature* **1961**, *191*, 1193–1194.

[2] Larowe, D. E.; Regnier, P. Thermodynamic Potential for the Abiotic Synthesis of Adenine, Cytosine, Guanine, Thymine, Uracil, Ribose, and Deoxyribose in Hydrothermal Systems. *Orig. Life Evol. Biosph.* **2008**, *38*, 383–397.

[3] Ferus, M. et al. Prebiotic synthesis initiated in formaldehyde by laser plasma simulating high-velocity impacts. *Astron. Astrophys.* **2019**, *626*, A52.

[4] Butlerow, A. Bildung einer zuckerartigen Substanz durch Synthese. *Ann. Chem. Pharm.* **1861**, *120*, 295–298.

[5] Breslow, R. On the mechanism of the formose reaction. *Tetrahedron Letts.* **1959**, *1*, 22–26.

[6] Strecker, A. Ueber einen neuen aus AldehydAmmoneiak und Blausäure entstehenden Körper. *Liebigs Ann. Chem.* **1854**, *91*, 339–351.

[7] Miller, S. L.; Van Trump, J. E. In *Origin of Life*; Wolman, Y., Ed.; Reidel: Dordrecht, The Netherlands, 1981; pp 135–141.
[42] Gong, C.-M.; Ning, H.-B.; Li, Z.-R.; Li, X.-Y. Theoretical and kinetic study of reaction C$_2$H + C$_2$H$_4$ on the C$_2$H$_4$ potential energy surface. Theor. Chem. Acc. 2015, 134, 1599.

[43] Zhao, L.; Ye, L.; Zhang, F.; Zhang, L. Thermal Decomposition of 1-Pentanol and Its Isomers: A Theoretical Study. J. Phys. Chem. A 2012, 116, 9238-9244.

[44] Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. The Properties of Gases and Liquids, Third Edition; McGraw-Hill, Inc: New York, 1977; p 683.

[45] Welty, J. R.; Wicks, C. E.; Wilson, R. E.; Rorrer, G. L. Chemical Rate Coefficients for the Reactions of H + CH$_3$ and H + CH$_2$; CRC Press, 2008; p 711.

[46] Wang, H.; Dames, E.; Sirjean, B.; Sheen, D. A.; Tango, R.; Violi, A.; Lai, J. Y. W.; Egolfopoulos, F. N.; Davidson, D. F.; Hanson, R. X.; et al., JetSurf version 2.0; 2010.

[47] Clary, D. C. Fast Chemical Reactions: Theory Challenges Experiments. Annu. Rev. Phys. Chem. 1990, 41, 61–90.

[48] Li, H.; Chen, B.-Z.; Huang, M.-B. CASPT2 investigation of reaction of O($^3$P) + H$_2$O and O($^3$P) + CO$_2$ by collisions with N$_2$, NO, O$_2$, CO, and NO$_2$ at 296 K and with CO$_2$ at 296 ± T/K ≤ 873. J. Chem. Soc., Faraday Trans. 1996, 92, 2335–2341.

[49] Blitz, M. A.; Pesa, M.; Pilling, M. J.; Seakins, P. W. Reaction of CH with H$_2$O: Temperature Dependence and Isotope Effect. J. Phys. Chem. A 1999, 103, 5699–5704.

[50] Cohen, N.; Westberg, K. R. Chemical Kinetic Data Sheets for High-Temperature Reactions. Part II. J. Phys. Chem. Ref. Data 1991, 20, 1211–1311.

[51] Schaub, W. M.; Hsu, D. S. Y.; Lin, M. C. Dynamics and mechanisms of CO production from the reactions of CH$_2$ radicals with O(3$^P$) and O$_2$. Eighteenth Symposium (International) on Combustion. Seattle, 1981; pp 811–818.

[52] Husain, D.; Mitra, S. K.; Young, A. N. Kinetic Study of Electronically Excited Nitrogen Atoms, N($^2$D$_J$, $^2$P$_J$), by Attenuation of Atomic Resonance Radiation in the Vacuum Ultra-violet. J. Chem. Soc., Faraday Trans. 2 1974, 70, 1721–1731.

[53] Meiners, J.; Kästner, J. Atom Tunneling in Chemistry. Angew Chem Int Ed Engl 2016, 55, 5400–5413.

[54] Zahnle, K.; Arndt, N.; Cockell, C.; Halliday, A.; Nisbet, E.; Selvis, F.; Sleep, N. H. Emergence of a Habitable Planet. Space Sci Rev 2007, 129, 35–78.

[55] Clerc, M.; Barat, F. Kinetics of CO Formation Studied by Faruv Flash Photolysis of CO$_2$. J. Chem. Phys. 1967, 46, 107–110.

[56] Hochanadel, C. J.; Sworski, T. J.; Ogren, P. J. Ultraviolet spectrum and reaction kinetics of the fornyl radical. J. Phys. Chem. 1980, 84, 231–235.

[57] Nizamov, B.; Dagdigian, P. J. Spectroscopic and Kinetic Investigation of Methylene Amido in Cavity Ring-Down Spectroscopy. J. Phys. Chem. A 2003, 107, 2256–2263.

[58] Campbell, I. M.; Thrush, B. A. Behaviour of carbon dioxide and nitrous oxide in active nitrogen. Trans. Faraday Soc. 1966, 62, 3366–3374.

[59] Dunlea, E. J.; Ravishankara, A. R. Kinetic studies of the reactions of O($^1$D) with several atmospheric molecules. Phys. Chem. Chem. Phys. 2004, 6, 2152–2161.

[60] Yu, T.; Yang, D. L.; Lin, M. C. Kinetics of CN radical reactions with formaldehyde and 1,3,5trioxane. Int. J. Chem. Kinet. 1993, 25, 1053–1064.

[61] Yee Quee, M. J.; Thynne, J. C. J. The Photolysis of 3-Pentanol and Its Isomers: A Theoretical Investigation of Ethane Dissociation and Methyl Recombination. J. Am. Chem. Soc. 1977, 99, 2916–2920.

[62] Phillips, L. F. Rate of Reaction of OH with HCN Between 298 and 563 K. Aust. J. Chem. 1979, 32, 2571–2577.

[63] Dunlea, E.-J.; Ravishankara, A. R. Kinetic studies of the reactions of O(1$^D$) with several atmospheric molecules. Phys. Chem. Chem. Phys. 2004, 6, 2152–2161.

[64] Phillips, L. F. Rate of Reaction of OH with HCN Between 298 and 563 K. Aust. J. Chem. 1979, 32, 2571–2577.

[65] Dunlea, E.-J.; Ravishankara, A. R. Kinetic studies of the reactions of O(1$^D$) with several atmospheric molecules. Phys. Chem. Chem. Phys. 2004, 6, 2152–2161.

[66] Vranckx, S.; Peeters, J.; Carl, S. Kinetics of O(1$^D$) + H$_2$O and O(1$^D$) + H$_2$: absolute rate coefficients and O(3$^P$) yields between 227 and 453 K. Phys. Chem. Chem. Phys. 2016, 18, 9213–9221.

[67] Manion, J. A.; Huie, R. E.; Levin, R. D.; Burgess Jr., D. R.; Orkin, V. L.; Tsang, W.; McGiver, W. S.; Huddens, J. W.; Knyasev, V. D.; Atkinson, D. B.; et al., NIST Chemical Kinetics Database; NIST Standard Reference Database Number 17, Version 7.0 (Web Version), Release 1.6.8, Data version 2015.09, National Institute of Standards and Technology: Gaithersburg, MD, http://kinetics.nist.gov/; (retrieved May 10, 2018).

[68] Yu, T.; Yang, D. L.; Lin, M. C. Kinetics of CN radical reactions with formaldehyde and 1,3,5trioxane. Int. J. Chem. Kinet. 1993, 25, 1053–1064.

[69] Yee Quee, M. J.; Thynne, J. C. J. The Photolysis of 3-Pentanol and Its Isomers: A Theoretical Investigation of Ethane Dissociation and Methyl Recombination. J. Am. Chem. Soc. 1977, 99, 2916–2920.

[70] Phillips, L. F. Rate of Reaction of OH with HCN Between 298 and 563 K. Aust. J. Chem. 1979, 32, 2571–2577.

[71] Dunlea, E.-J.; Ravishankara, A. R. Kinetic studies of the reactions of O(1$^D$) with several atmospheric molecules. Phys. Chem. Chem. Phys. 2004, 6, 2152–2161.

[72] Vranckx, S.; Peeters, J.; Carl, S. Kinetics of O(1$^D$) + H$_2$O and O(1$^D$) + H$_2$: absolute rate coefficients and O(3$^P$) yields between 227 and 453 K. Phys. Chem. Chem. Phys. 2010, 12, 9213–9221.

[73] Manion, J. A.; Huie, R. E.; Levin, R. D.; Burgess Jr., D. R.; Orkin, V. L.; Tsang, W.; McGiver, W. S.; Huddens, J. W.; Knyasev, V. D.; Atkinson, D. B.; et al., NIST Chemical Kinetics Database; NIST Standard Reference Database Number 17, Version 7.0 (Web Version), Release 1.6.8, Data version 2015.09, National Institute of Standards and Technology: Gaithersburg, MD, http://kinetics.nist.gov/; (retrieved May 10, 2018).

[74] Young, R. A.; Black, G.; Slanger, T. G. Reaction and Deactivation of O(1$^D$)−. J. Chem. Phys. 1968, 49, 4758–4768.

[75] Blitz, M. A.; Dillon, T. J.; Heard, D. E.; Pilling, M. J.; Trought, I. D. Laser induced fluorescence studies of the
reactions of $O(^1D_2)$ with $N_2$, $O_2$, $N_2O$, $CH_4$, $H_2$, $CO_2$, $Ar$, $Kr$ and $n-C_2H_5O$. *Phys. Chem. Chem. Phys.* **2004**, 6, 2162–2171.

[76] Wine, P. H.; Ravishankara, A. R. Kinetics of $O(^3D)$ interactions with the atmospheric gases $N_2$, $N_2O$, $H_2O$, $H_2$, $CO_2$, and $O_3$. *Chem. Phys. Lett.* **1981**, 77, 103–109.

[77] Young, R. A.; Ung, A. Y.-M. Optical Studies of the Photoysis of $CO_2$ at 1470 *A*. *J. Chem. Phys.* **1966**, 44, 3038–3040.

[78] Heidner, III, R. F.; Husain, D.; Wiesenfeld, J. R. Kinetic Investigation of Electronically Excited Oxygen Atoms, $O(2^3D_2)$, by Time-resolved Attenuation of Atomic Resonance Radiation in the Vacuum Ultra-violet. *J. Chem. Soc., Faraday Trans. 2* **1973**, 69, 927–938.

[79] Amimoto, S. T.; Force, A. P.; Gulotty, Jr., R. G.; Wiesenfeld, J. R. Collisional deactivation of $O(2^3D_2)$ by the atmospheric gases. *J. Chem. Phys.* **1979**, 71, 3640–3647.

[80] Davidson, J. A.; Sadowski, C. M.; Schiff, H. I.; Streit, G. E.; Howard, C. J.; Jenkins, A. L., D. A. Schmeltekopf Absolute rate constant determinations for the deactivation of $O(^1D)$ by time resolved decay of $O(^1D) \rightarrow O(^3P)$ emission. *J. Chem. Phys.* **1976**, 64, 57–62.

[81] Fell, B.; Rivas, I. V.; McFadden, D. L. Kinetic Study of Electronically Metastable Nitrogen Atoms, $N(2^3D_2)$, by Electron Spin Resonance Absorption. *J. Phys. Chem.* **1981**, 85, 224–228.

[82] Black, G.; Slanger, T. G.; St. John, G. A.; Young, R. A. Vacuum-Ultraviolet Photolysis of $N_2O$. IV. Deactivation of $N(^2D)$. *J. Chem. Phys.* **1969**, 51, 116–121.

[83] Lin, C.-L.; Kaufman, F. Reactions of Metastable Nitrogen Atoms. *J. Chem. Phys.* **1971**, 55, 3760–3770.

[84] Piper, L. G.; Donahue, M. E.; Rawlins, W. T. Rate Coefficients for $N(^2D)$ Reactions. *J. Phys. Chem.* **1987**, 91, 3883–3888.

[85] Laufer, A. H.; Bass, A. M. Reaction between triplet methylene and $CO_2$: rate constant determination. *Chem. Phys. Lett.* **1977**, 46, 151–155.

[86] Butler, J. E.; Fleming, J. W.; Goss, L. P.; Lin, M. C. Kinetics of CH Radical Reactions Important to Hydrocarbon Combustion Systems. **1980**.

[87] Butler, J. E.; Fleming, J. W.; Goss, L. P.; Lin, M. C. Kinetics of CH radical reactions with selected molecules at room temperature. *Chem. Phys.* **1981**, 56, 355–365.

[88] Berman, M. R.; Fleming, J. W.; Harvey, A. B.; Lin, M. C. Temperature dependence of CH radical reactions with $O_2$, NO, CO and $CO_2$. **1982**.

[89] Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. An Fourier transform infrared study of the kinetics and mechanism for the reaction of hydroxyl radical with formaldehyde. *J. Phys. Chem.* **1984**, 88, 5342–5344.

[90] Temps, F.; Wagner, H. G. Rate Constants for the Reactions of OHRadicals with $CH_2O$ and $HCO$. *Ber. Bunsenges. Phys. Chem.* **1984**, 88, 415–418.

[91] Yetter, R. A.; Rabitz, H.; Dryer, F. L. Evaluation of the rate constant for the reaction $OH + H_2CO$: Application of modeling and sensitivity analysis techniques for determination of the product branching ratio. *J. Chem. Phys.* **1989**, 91, 4088–4097.

[92] Vandooren, J.; Van Tiggelen, P. J. Reaction mechanisms of combustion in low pressure acetylene-oxygen flames. Sixteenth Symposium (International) on Combustion. 1977; pp 1133–1144.

[93] Chang, J. S.; Barker, J. R. Reaction rate and products for the reaction oxygen($^3P$) + $H_2O$. *J. Phys. Chem.* **1979**, 83, 3059–3064.

[94] Klemm, R. B. Absolute rate parameters for the reactions of formaldehyde with $O$ atoms and $H$ atoms over the temperature range 250–500 K. *J. Chem. Phys.* **1979**, 71, 1987–1993.

[95] Klemm, R. B.; Skolnik, E. G.; Michael, J. V. Absolute rate parameters for the reaction of $O(^3P)$ with $H_2CO$ over the temperature range 250 to 750 K. *J. Chem. Phys.* **1980**, 72, 1256–1264.

[96] Herron, J. T.; Penzhorn, R. D. Mass spectrometric study of the reactions of atomic oxygen with ethylene and formaldehyde. *J. Phys. Chem.* **1969**, 73, 191–196.

[97] Mack, G. P. R.; Thrush, B. A. Reaction of oxygen atoms with carbonyl compounds. Part 1.–Formaldehyde. *J. Chem. Soc., Faraday Trans. 1* **1973**, 69, 208–215.

[98] Zabarnick, S.; Fleming, J. W.; Lin, M. C. Temperature dependence of CH radical reactions with $H_2O$ and $CH_2O$. **1988**.

[99] Ridley, B. A.; Davenport, J. A.; Stief, L. J.; Welge, K. H. Absolute Rate Constant for the Reaction $H+H_2CO$. *J. Chem. Phys.* **1972**, 57, 520–523.

[100] Brennen, W. R.; Gay, I. D.; Glass, G. P.; Niki, H. Reactions of atomic hydrogen with formaldehyde. *J. Chem. Phys.* **1965**, 43, 2569–2570.

[101] Oehler, C.; Wagner, H. G.; Ziemer, H.; Dóbé, S. An Investigation of the D/H AdditionElimination and H Atom Abstraction Channels in the Reaction $D + H_2CO$ in the Temperature Range $296 K \leq T \leq 780 K$. *J. Phys. Chem.* **2000**, 104, 10500–10510.

[102] Vandooren, J.; Oldenhove de Guertechin, L.; Van Tiggelen, P. J. Kinetics in a lean formaldehyde flame. *Combust. Flame* **1986**, 64, 127–139.

[103] Westenberg, A. A.; DeHaas, N. Measurement of the rate constant for $H + H_2CO \rightarrow H_2 + HCO$ at 297–652K. *J. Phys. Chem.* **1972**, 76, 2213–2214.

[104] Stoeckel, F.; Schuh, M. D.; Goldstein, N.; Atkinson, G. H. Time-resolved intracavity laser spectroscopy: 266 nm photodissociation of acetaldehyde vapor to form HCO. *Chem. Phys.* **1985**, 95, 135–144.

[105] Baggott, J. E.; Frey, H. M.; Lightfoot, P. D.; Walsh, R. The absorption cross section of the HCO radical at 614.59 nm and the rate constant for $HCO+HCO \rightarrow H_2CO+CO$. *Chem. Phys. Lett.* **1986**, 132, 225–230.

[106] Reilly, J. P.; Clark, J. H.; Moore, J. B.; Fimnetel, G. C. HCO production, vibrational relaxation, chemical kinetics, and spectroscopy following laser photolysis of
formaldehyde. J. Chem. Phys. 1978, 69, 4381–4394.

Friedrichs, G.; Herbon, J. T.; Davidson, D. F.; Hanson, R. K. Quantitative detection of HCO behind shock waves: The thermal decomposition of HCO. Phys. Chem. Chem. Phys. 2002, 4, 5778–5788.

Veyret, B.; Roussel, P.; Lesclaux, R. Absolute rate constant for the disproportionation reaction of formyl radicals from 295 to 475 K. Chem. Phys. Lett. 1984, 103, 389–392.

Vedeneev, V.; Sviridenkov, E.; Nadtoczenko, V.; Ceskis, S.; Sarkisov, O. Spectroscopic study of elementary reactions involving HCO, NH2 and HNO. J. Chem. Phys. 1984, 4, 111–120.

Mulenko, S. A. Investigation of the recombination of the hco radical in an atmosphere of argon and helium by the method of internal resonator laser spectroscopy. J. Appl. Spectrosc. 1980, 33, 688–694.

Ziemer, H.; Debê, S.; Wagner, H. G.; Olzman, M.; Viskolcz, B.; Temp, F. Kinetics of the reactions of HCO with H and D atoms. Ber. Bunsenges. Phys. Chem. 1998, 102, 897–905.

Frost, M. J.; Sharkey, P.; Smith, I. W. M. Reaction between OH (OD) radicals and CO at temperatures down to 80 K: experiment and theory. J. Phys. Chem. 1993, 97, 12254–12259.

Vohra, B.; Zetsch, C. Formation of HO2 from OH and C2H2 in the presence of O2. J. Chem. Soc., Faraday Trans. 1998, 94, 1203–1210.

Herron, J. T. Reaction kinetics involving ground X2Π and excited AΣ+ hydroxyl radicals. Part 1–Quenching kinetics of OH AΣ+ and rate constants for reactions of OH X2Π with CH3CCl3 and CO. J. Chem. Soc., Faraday Trans. 2 1979, 75, 569–581.

Hussain, D.; Plane, J. M. C.; Slater, N. K. H. Kinetic investigation of the reactions of OH(X2Π) with the hydrogen halides, HCl, DCI, HBr and DBr by time-resolved resonance fluorescence (AΣ+–X2Π) . J. Chem. Soc., Faraday Trans. 2 1981, 77, 1949–1962.

Lissianski, V.; Yang, H.; Qin, Z.; Mueller, M. R.; Shin, K. S.; Gardiner Jr., W. C. High-temperature measurements of the rate coefficient of the H + CO2 → CO + OH reaction. Chem. Phys. Lett. 1995, 240, 57–62.

Ravishankara, A. R.; Thompson, R. L. Kinetic study of the reaction of OH with CO from 250 to 1040 K. Chem. Phys. Lett. 1983, 99, 377–381.

Frost, M. J.; Sharkey, P.; Smith, I. W. M. Energy and structure of the transition states in the reaction OH + CO → H + CO2. Faraday Discuss. Chem. Soc. 1991, 91, 305–317.

Herron, J. T. Mass-Spectrometric Study of the Rate of the Reaction CO + OH. J. Chem. Phys. 1966, 45, 1854–1855.

Davidson, J. A.; Schiff, H. I.; Brown, T. J.; Howard, C. J. Temperature dependence of the deactivation of O(1D) by CO from 113–333 K. J. Chem. Phys. 1978, 69, 1216–1217.

Noxon, J. F. Optical Emission from O(1D) and O2(b2Σg) in Ultraviolet Photolysis of O2 and CO2. J. Chem. Phys. 1970, 52, 1852–1873.

Le Picard, S. D.; Canosa, A.; Rowe, B. R.; Brownsword, R. A.; Smith, I. W. M. Determination of the limiting low pressure rate constants of the reactions of CH with N2 and CO: A CRESU measurement at 53 K. J. Chem. Soc., Faraday Trans. 1998, 94, 2889–2893.

Brownsword, R. A.; Herbert, L. B.; Smith, I. W. M.; Stewart, D. W. A. Pressure and temperature dependence of the rate constants for the association reactions of CH radicals with CO and N2 between 202 and 584 K. J. Chem. Soc., Faraday Trans. 1996, 92, 1087–1094.

Fulle, D.; Hippler, H.; Striebl, F. The high-pressure range of the reaction CH(^2Π)+CO+M→HCCO+M. J. Chem. Phys. 1998, 108, 6709–6716.

Taatjes, C. A. Association and isotopic exchange reactions of CH(CD)^([X]^2Π)+CO . J. Chem. Phys. 1997, 106, 1786–1795.

Bosnali, M. W.; Perner, D. Notizen: Reaktionen von pulsradiolytisch erzeugtem CH(Π) mit Methan und anderen Substanzen. Z. Naturforsch. 1971, 26, 1768–1769.

Bennett, J. E.; Blackmore, D. R. Rates of gas-phase hydrogen-atom recombination at room temperature in the presence of added gases. Thirteenth Symposium (International) on Combustion. Seattle, 1971; pp 51–59.

Wang, H. Y.; Eyre, J. A.; Dorfman, L. M. Activation energy for the gas phase reaction of hydrogen atoms with carbon monoxide. J. Chem. Phys. 1973, 59, 5199–5200.

Hikida, T.; Eyre, J. A.; Dorfman, L. M. Pulse Radiolysis Studies. XX. Kinetics of Some Addition Reactions of Gaseous Hydrogen Atoms by Fast Lyman Absorption Spectrophotometry . J. Chem. Phys. 1971, 54, 3422–3428.

Alam, J. A.; Michael, J. V.; Osborne, D. T. Pressure Dependence and Third Body Effects on the Rate Constants for H+O2,H+NO, and H+CO. J. Chem. Phys. 1975, 57, 3736–3745.

Gauthier, M. J. E.; Snelling, D. R. La photolyse de l’ozone a 253.7 nm: Desactivation de O(1D) et de O2(1Σg) par les gaz de l’atmosphere. J. Photochem. 1975, 4, 27–50.

Lee, L. C.; Sanger, T. G. Atmospheric OH production-The O(1D) + H2O reaction rate. Geophys. Res. Lett. 1979, 6, 165–166.

Davidson, J. A.; Schiff, H. I.; Streit, G. E.; McAfee, J. R.; Schmeltekopf, A. L.; Howard, C. J. Temperature dependence of O(1D) rate constants for reactions with N2,O2,H2,CH4,HCl and NH3. J. Chem. Phys. 1977, 67, 5021–5025.

Streit, G. E.; Howard, C. J.; Schmeltekopf, A. L.; Davidson, J. A.; Schiff, H. I. Temperature dependence of O(1D) rate constants for reactions with O2, N2, CO2, O3, and H2O. J. Chem. Phys. 1976, 65, 4761–4764.

Dunlea, E.-J.; Ravishankara, A. R. Measurement of the rate coefficient for the reaction of O(1D) with H2O and re-evaluation of the atmospheric OH production rate. Phys. Chem. Chem. Phys. 2004, 6, 3333–3340.

Gerickce, K.-H.; Comes, F. J. Energy partitioning in the reaction O(1D) + H2O → OH + OH: The influence of O(1D) translational energy on the reaction rate constant. Chem. Phys. Lett. 1981, 81, 218–222.
[143] Fritz, B.; Lorenz, K.; Steinert, W.; Zellner, R. Laboratory Kinetic Investigations of the Tropospheric Oxidation of Selected Industrial Emissions. Physico-Chemical Behaviour of Atmospheric Pollutants. Dordrecht, 1982.

[144] Zellner, R.; Ewig, F.; Paschke, R.; Wagner, G. Pressure and temperature dependence of the gas-phase recombination of hydroxyl radicals. J. Phys. Chem. 1988, 92, 4184–4190.

[145] Sangwan, M.; Chesnokov, E. N.; Krasnoperov, L. N. Reaction OH + OH Studied over the 298-834 K Temperature and 1 - 100 bar Pressure Ranges. J. Phys. Chem. A 2012, 116, 6282–6294.

[146] Trainor, D. W.; von Rosenberg Jr., C. W. Energy partitioning in the products of elementary reactions involving OH-radicals. Fifthteenth Symposium (International) on Combustion. 1975; pp 755–764.

[147] Trainor, D. W.; von Rosenberg Jr., C. W. Flash photolysis study of the gas phase recombination of hydroxyl radicals. J. Chem. Phys. 1974, 61, 1010–1015.

[148] Greiner, N. R. Hydroxyl radical kinetics by kinetic spectroscopy. III. Reactions with hydrogen peroxide in the range 300–458 K. J. Phys. Chem. 1968, 72, 406–410.

[149] Fulle, D.; Hamann, H. F.; Hippler, H.; Troe, J. High pressure range of the addition of HO to HO. III. Saturated laserinduced fluorescence measurements between 200 and 700 K. J. Chem. Phys. 1996, 105, 1001–1006.

[150] Dixon-Lewis, G.; Wilson, W. E.; Westenberg, A. A. Studies of Hydroxyl Radical Kinetics by Quantitative ESR. J. Chem Phys. 1966, 44, 2877–2884.

[151] Westenberg, A. A.; de Haas, N. Rate of the Reaction OH + OH → H2O + O. J. Chem Phys. 1973, 58, 4066–4071.

[152] Farquharson, G. K.; Smith, R. H. Rate constants for the gaseous reactions OH + C2H4 and OH + CH4. Aust. J. Chem. 1980, 33, 1425–1435.

[153] Clyne, M. A. A.; Down, S. Kinetic behaviour of OH X2Π and A2σ+ using molecular resonance fluorescence spectrometry. J. Chem Soc., Faraday Trans. 2 1974, 70, 253–266.

[154] Sangwan, M.; Krasnoperov, L. N. Disproportionation Channel of Self-Reaction of Hydroxyl Radical, OH + OH → H2O + O, Studied by Time-Resolved Oxygen Atom Trapping. J. Phys. Chem. A 2012, 116, 11817–11822.

[155] Bedjanian, Y.; Le Bras, G.; Poulet, G. Kinetic Study of OH + OH and OD + OD Reactions. J. Phys. Chem. A 1999, 103, 7017–7025.

[156] Wagner, G.; Zellner, R. Temperature Dependence of the Reaction OH + OH → H2O + O. Ber. Bunsenges. Phys. Chem. 1981, 85, 1122–1128.

[157] Breen, J. E.; Glass, G. P. Rate of Some Hydroxyl Radical Reactions. Combust. Flame 1970, 52, 1082–1086.

[158] Smith, I. W. M.; Stewart, D. W. A. Low-temperature kinetics of reactions between neutral free radicals. Rate constants for the reactions of OH radicals with N atoms (103 ≤ T/K ≤ 294) and with O atoms (158 ≤ T/K ≤ 294). J. Chem. Soc., Faraday Trans. 1994, 90, 3221–3227.

[159] Howard, M. J.; Smith, I. W. M. Direct Rate Measurements on the Reactions N + OH → NO + H and O + OH → O2 + H from 250 to 515 K. J. Chem Soc., Faraday Trans. 2 1981, 77, 997–1008.

[160] Westenberg, A. A.; De Haas, N.; Roscoe, J. M. Radical reactions in an electron spin resonance cavity homogeneus reactor. J. Phys. Chem. 1970, 74, 3431–3438.

[161] Howard, M. J.; Smith, I. W. M. Direct rate measurements on the reactions N + OH → NO + H And O + OH → O2 + H. Chem. Phys. Lett. 1980, 69, 40–44.

[162] Robertson, R.; Smith, G. P. Temperature Dependence of O + OH at 136-377 K Using Ozone Photoysis. J. Phys. Chem. A 2006, 110, 6673–6679.

[163] Robertson, R.; Smith, G. P. Photolytic measurement of the O + OH rate constant at 295 K. Chem. Phys. Lett. 2002, 358, 157–162.

[164] Brune, W. H.; Schwab, J. J.; Anderson, J. G. Laser magnetic resonance, resonance fluorescence, and resonance absorption studies of the reaction kinetics of O + OH → H + O2, O + HO2 → OH + O2, N + OH → H + NO, and N + HO2 → products at 300 K between 1 and 5 torr. J. Phys. Chem. 1983, 87, 4503–4514.

[165] Lewis, R. S.; Watson, R. T. Temperature dependence of the reaction O(^1P) + OH(^3Π) → O2 + H. J. Phys. Chem. 1980, 84, 3495–3503.

[166] Kurzius, S. C.; Boudart, M. Kinetics of the branching step in the hydrogen-oxygen reaction. Combust. Flame 1968, 12, 477–491.

[167] Wilson, W. E.; Westenberg, A. A. Study of the reaction of hydroxyl radical with methane by quantitative ESR. Eleventh Symposium (International) on Combustion. 1967; pp 1143–1150.

[168] Wilson, W. E.; Westenberg, A. A. Direct measurements of the rate coefficient for the reaction OH + CH4 → CH3 + H2O over 300-1500 K. Twentieth Symposium (International) on Combustion. 1984; pp 703–713.

[169] Sharkey, P.; Smith, I. W. M. Kinetics of elementary reactions at low temperatures: rate constants for the reactions of OH with HCl (298 ≥ T/K ≥ 138), CH4 (298 ≥ T/K ≥ 178) and C2H6 (298 ≥ T/K ≥ 138). J. Chem. Soc., Faraday Trans. 1993, 89, 631–637.

[170] Mellouki, A.; Téton, S.; Laverdet, G.; Quilgars, A.; Le Bras, G. Kinetic studies of OH reactions with H2O2, C2H4 and CH4 using the pulsed laser photolysis - laser induced fluorescence method. J. Chim. Phys. 1994, 91, 473–487.

[171] Bryukov, M. G.; Knyazev, V. D.; Lomnicki, S. M.; McFerrin, C. A.; Dellinger, B. Temperature-Dependent Kinetics of the Gas-Phase Reactions of OH with Cl2, CH4, and C2H6. J. Phys. Chem. A 2004, 108, 10464–10472.

[172] Bonard, A.; Daële, V.; Delfau, J.-L.; Vovelle, C. Kinetics of OH Radical Reactions with Methane in the Temperature Range 295-660 K and with Dimethyl Ether and Methyl-tert-butyl Ether in the Temperature Range 295-618 K. J. Phys. Chem. A 2002, 106, 4384–4389.

[173] Gierczak, T.; Talukdar, R. K.; Herndon, S. C.; Vaghjiani, G. L.; Ravishankara, A. R. Rate Coefficients for the Reactions of Hydroxyl Radicals with Methane and Deuterated Methanes. J. Phys. Chem. A 1997, 101, 3125–3134.

[174] Vaghjiani, G. L.; Ravishankara, A. R. New measurement of the rate coefficient for the reaction of OH with methane. Nature 1992, 350, 406–409.

[175] Dunlop, J. R.; Tully, F. P. A kinetic study of OH radical reactions with methane and perdeuterated methane. J. Phys. Chem. 1993, 97, 11148–11150.

[176] Finlayson-Pitts, B. J.; Ezell, M. J.; Jayaweera, T. M.; Berko, H. N.; Lai, C. C. Kinetics of the reactions of OH with methyl chloroform and methane: Implications for global tropospheric OH and the methane budget. Geophys. Res. Lett. 1992, 19, 1371–1374.
[177] Fagerström, K.; Lund, A.; Mahmoud, G.; Jodkowski, J. T.; Ratajczak, E. Kinetics of the cross reaction between methyl and hydroxyl radicals. Chem. Phys. Lett. 1993, 204, 226–234.

[178] Humphfer, R.; Oser, H.; Grotheer, H.-H.; Just, T. The reaction system CH₃+OH at intermediate temperatures. Appearance of a new product channel. Twenty-Fifth Symposium (International) on Combustion. 1994; pp 721–731.

[179] Fagerström, K.; Lund, A.; Mahmoud, G.; Jodkowski, J. T.; Ratajczak, E. Pressure and temperature dependence of the gas-phase reaction between methyl and hydroxyl radicals. Chem. Phys. Lett. 1994, 224, 43–50.

[180] Oser, H.; Stothard, N. D.; Humphfer, R.; Grotheer, H.-H. Direct measurement of the reaction CH₃ + OH at ambient temperature in the pressure range 0.3–6.2 mbar. J. Phys. Chem. 1992, 96, 5359–5363.

[181] Oser, H.; Stothard, N. D.; Humphfer, R.; Grotheer, H.-H.; Just, T. Direct measurement of the reaction CH₃+OH and its pathways between 300 and 480 K. Twenty-Fourth Symposium (International) on Combustion. 1992; pp 597–604.

[182] Anastasi, C.; Beverton, S.; Ellermann, T.; Pagsberg, P.; Fagerström, K.; Lund, A.; Mahmoud, G.; Jodkowski, J. T.; Ratajczak, E. Pressure and temperature dependence of the gas-phase reaction between methyl and hydroxyl radicals. Chem. Phys. Lett. 1994, 224, 43–50.

[183] Orkin, V. L.; Kozlov, S. N.; Poskrebyshev, G. A.; Overend, R. P.; Paraskevopoulos, G.; Cvetanović, R. J. Rates of OH Radical Reactions. I. Reactions with CH₄, C₂H₆, and C₂H₈ at 295K. Can. J. Chem. 1975, 53, 3374–3382.

[184] Trainor, D. W.; von Rosenberg Jr., C. W. Energy partitioning in the products of elementary reactions involving OH-radicals. Fifteenth Symposium (International) on Combustion. Seattle, 1975; pp 755–764.

[185] Kaufman, F.; Del Greco, F. P. Fast reactions of OH radicals. 1963.

[186] Cohen, N.; Westberg, K. R. Chemical Kinetic Data Sheets for High-Temperature Chemical Reactions. J. Phys. Chem. Ref. Data 1985, 12, 531–590.

[187] Titarchuk, T. A.; Halpern, J. B. kinetics of CN reactions with O(3P) and SO₂. Chem. Phys. Lett. 1995, 232, 192–196.

[188] Schacke, H.; Schmatjko, K. J.; Wolfrum, J. Reaktionen von Molekülen in definierten Schwingungszuständen (I) Die Reaktionen CN(v”) + O und CN(v”) + O₂. Ber. Bunsenges. Phys. Chem. 1973, 77, 248–253.

[189] Schmatjko, K. J.; Wolfrum, J. Direct determination of the product energy distribution in the reaction of O-atoms with CN radicals. Sixteenth Symposium (International) on Combustion. Seattle, 1977; pp 819–827.

[190] Tsang, W. Chemical Kinetic Data Base for Propellant Combustion. II. Reactions Involving CN, NCO, and HNCO. J. Phys. Chem. Ref. Data 1992, 21, 753–791.

[191] Morgan, J. E.; Elias, L.; Schiff, H. I. Recombination of Oxygen Atoms in the Absence of O₂. J. Chem. Phys. 1960, 33, 930–931.

[192] Tchen, H. Étude cinétique par R. P. E. des atomes d’oxygène 3p dans la post-drécha. Rev. Phys. Appl. 1972, 7, 205–212.

[193] Campbell, I. M.; Gray, C. N. Rate constants for O(3P) recombination and association with N(4S). Chem. Phys. Lett. 1973, 18, 607–609.

[194] Marshall, T. C. Studies of Atomic Recombination of Nitrogen, Hydrogen, and Oxygen by Paramagnetic Resonance. Phys. Fluids 1962, 5, 743–753.

[195] Campbell, I.; Thrus, B. A. The association of oxygen atoms and their combination with nitrogen atoms. Proc. R. Soc. Lond. A Math. Phys. Sci. 1967, 296, 222–232.

[196] Reeves, R. R.; Mannella, G.; Hartwick, P. Rate of Recombination of Oxygen Atoms. J. Chem. Phys. 1960, 32, 632–633.

[197] Kondratiev, V. N.; Nikitin, E. E. Rate Constants for the Process O₂ + Ar ↔ O + O + Ar. J. Chem. Phys. 1966, 45, 1078–1079.

[198] Hack, W.; Wagner, H. G.; Zasypkin, A. Elementary reactions of NH (a1Δ) and NH(X3Σ) with N, O and NO. Ber. Bunsenges. Phys. Chem. 1994, 98, 156–164.

[199] Kretschmer, C. B.; Petersen, H. L. Kinetics of Three-Body Atom Recombination. J. Chem. Phys. 1963, 39, 1772–1778.

[200] Mavroyannis, C.; Winkler, C. A. The reaction of nitrogen atoms with oxygen atoms in the absence of oxygen molecules. Can. J. Chem. 1961, 39, 1601–1607.

[201] Froben, F. W. Die Reaktion von Oatom-en mit Methan, Chloroform und Tetrachlorkohlenstoff. Ber. Bunsenges. Phys. Chem. 1968, 72, 996–998.

[202] Westenberg, A. A.; de Haas, N. AtomMolecule Kinetics at High Temperature Using ESR Detection. Technique and Results for O + H₂, O + CH₄, and O + C₂H₆. J. Chem. Phys. 1967, 46, 490–501.

[203] Falconer, J. W.; Hoare, D. E.; Overend, R. Photolysis of carbon dioxide and methane mixtures at 873 and 293 K with 163.3 nm light. J. Chem. Soc., Faraday Trans.
[212] Slagle, I. R.; Pruss, Jr., F. J.; Gutman, D. Kinetics into the steady state. I. study of the reaction of oxygen atoms with methyl radicals. *Int. J. Chem. Kinet.* 1974, 6, 111–123.

[213] Slagle, I. R.; Sarzyński, D.; Gutman, D. Kinetics of the reaction between methyl radicals and oxygen atoms between 294 and 900 K. *J. Phys. Chem.* 1987, 91, 4375–4379.

[214] Washida, N. Reaction of methyl radicals with O(3P), O2 and NO. *J. Chem. Phys.* 1980, 73, 1665–1672.

[215] Washida, N.; Bayes, K. D. The rate of reaction of methyl radicals with atomic oxygen. *Chem. Phys. Lett.* 1973, 23, 373–375.

[216] Zellner, R.; Hartmann, D.; Karthäuser, J.; Rhäsä, D.; Wehring, G. A laser photolysis/LIF study of the reactions of O(3P) atoms with CH₃ and CH₂O₂ radicals. *J. Chem. Soc., Faraday Trans.* 2 1988, 84, 549–568.

[217] Plumb, I. C.; Ryan, K. R. Kinetics of the reactions of CH3 with O(3P) and O₂ at 295 K. *Int. J. Chem. Kinet.* 1982, 14, 861–874.

[218] Washida, N.; Bayes, K. D. The reactions of methyl radicals with atomic and molecular oxygen. *Int. J. Chem. Kinet.* 1976, 8, 777–794.

[219] Senkina, S. W.; Leone, S. R. A laser flash photolysis/time-resolved FTIR emission study of a new channel in the reaction of methyl + oxygen atom: production of carbon monoxide(v). *J. Phys. Chem.* 1992, 96, 4478–4485.

[220] Morris, J., E. D.; Niki, H. Reaction of methyl radicals with atomic oxygen. *Chem. Phys. Lett.* 1973, 35, 47–53.

[221] Niki, H.; Daby, E. E.; Weinstock, B. Mass spectrometric study of the kinetics and mechanism of the ethylene-oxygen reaction by the discharge-flow technique at 300 K. 1969.

[222] Böhlund, T.; Temps, F.; Wagner, H. G. Direct Investigation of the Reaction CH2(X3B1) + O(3P) with the LMR. *Ber. Bunsenges. Phys. Chem.* 1984, 88, 1222–1228.

[223] Vinckier, C.; Debruyne, W. Reactions of methylene in the oxidation process of acetylene with oxygen atoms at 295 K. 1979.

[224] Messing, I.; Filseth, S. V.; Sadowski, C. M.; Carrington, D. Absolute rate constants for the reactions of CH with O and N atoms. *J. Chem. Phys.* 1981, 74, 3874–3881.

[225] Messing, I.; Carrington, D.; Filseth, S. V.; Sadowski, C. M. Absolute rate constant for the CH + O reaction. *Chem. Phys. Lett.* 1980, 74, 56–57.

[226] Zhu, Y.-F.; Arepalli, S.; Gordon, R. J. The rate constant for the reaction O(3P)+D₂ at low temperatures. *J. Chem. Phys.* 1989, 90, 183–188.

[227] Presser, N.; Gordon, R. J. The kinetic isotope effect in the reaction of O(3P) with H₂, D₂, and HD. *J. Chem. Phys.* 1985, 82, 1291–1297.

[228] Light, G. C.; Matsumoto, J. H. Experimental measurement of the rate of the reaction O(3P) + H₂ (v = 0) → OH (v = 0) + H at T = 298 K. *Int. J. Chem. Kinet.* 1980, 12, 451–468.

[229] Baulch, D. L.; Drysdale, D. D.; Horne, D. G.; Lloyd, A. C. Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H₂-O₂ Systems; Butterworths: London, 1972.

[230] Matsumi, Y.; Tomokura, K.; Inagaki, Y.; Kawasaki, M. Isotopic branching ratios and translational energy release of hydrogen and deuterium atoms in reaction of oxygen (1D) atoms with alkanes and alkyl chlorides. *J. Phys. Chem.* 1993, 97, 6816–6821.

[231] Vranckx, S.; Peeters, J.; Carl, S. A temperature dependence kinetic study of O(1D) + CH₄: overall rate coefficient and product yields. *Phys. Chem. Chem. Phys.* 2008, 10, 5714–5722.

[232] Dillon, T. J.; Horowitz, A.; Crowley, J. N. Absolute rate coefficients for the reactions of O(1D) with a series of n-alkanes. *Chem. Phys. Lett.* 2007, 443, 12–16.

[233] Cvetanović, R. J. Excited State Chemistry in the Stratosphere. *Can. J. Chem.* 1974, 52, 1452–1464.

[234] Koppe, S.; Laurent, T.; Naik, P. D.; Volpp, H.-R.; Wolfrum, J.; Arusi-Parpar, T.; Rosenwaks, S. Absolute rate constants and reactive cross sections for the reactions of O(1D) with molecular hydrogen and deuterium. *Chem. Phys. Lett.* 1993, 214, 546–552.

[235] Stief, L. J.; Payne, W. A.; Klemm, R. B. A flash photolysis-resonance fluorescence study of the formation of O(1D) in the photoysis of water and the reaction of O(1D) with H₂, Ar, and He. *J. Chem. Phys.* 1975, 62, 4000–4008.

[236] Tabakdar, R. K.; Ravishankara, A. R. Rate coefficients for O(1D) + H₂ D₂, HD reactions and H atom yield in O(1D) + HD reaction. *Chem. Phys. Lett.* 1986, 125, 177–183.

[237] Ogren, P. J.; Sworski, T. J.; Hochanadel, C. J.; Casel, J.-M. Flash Photolysis of O₃ in O₂ and O₂ + H₂ Mixtures. *J. Phys. Chem.* 1992, 86, 238–242.

[238] Nuñez-Reyes, D.; Hickson, K. M. Kinetics of the Gas-Phase O(1D) + CO₂ and O(1D) + CO₂ Reactions over the 50296 K Range. *J. Phys. Chem. A* 2018, 112, 4002–4008.

[239] Mebel, A. M.; Hayashi, M.; Kislov, V. V.; Lin, S. H. Theoretical Study of Oxygen Isotope Exchange and Quenching in the O(1D) + CO₂ Reaction. *J. Phys. Chem. A* 2004, 108, 7983–7994.

[240] Zhu, L.; Kreutz, T. G.; Hewitt, S. A.; Flynn, G. W. Diode laser probing of vibrational, rotational, and translational excitation of CO₂ following collisions with O(1D). I. Inelastic scattering. *J. Chem. Phys.* 1990, 93, 3277–3288.

[241] Sedlacek, A. J.; Harding, D. R.; Weston, R. E.; Kreutz, T. G.; Flynn, G. W. Probing the O(1D)+CO₂ reaction with second-derivative modulated diode laser-spectroscopy. *J. Chem. Phys.* 1989, 91, 7550–7556.

[242] Shortridge, R. G.; Lin, M. C. CO vibrational population distributions in the reactions of COS with O(3P,j) and O(1D₂) atoms. *Chem. Phys. Lett.* 1975, 35, 146–150.

[243] Tully, J. C. Reactions of O(1D) with atmospheric molecules. *J. Chem. Phys.* 1975, 62, 1893–1898.

[244] Clark, I. D.; Noxon, J. F. Optical Emission from O(1D) and O₂(b1Σg) in Ultraviolet Photoysis of O₂ and CO₂. II. *J. Chem. Phys.* 1972, 57, 1033–1038.

[245] Zipf, E. C. The collisional deactivation of metastable atoms and molecules in the upper atmosphere. *Can. J. Chem.* 1969, 47, 1863–1870.

[246] Paraskevopoulos, G.; Cvetanovic, R. Competitive Reactions of the Excited Oxygen Atoms, O(1D)³P. *J. Am. Chem. Soc.* 1969, 91, 7572–7577.
Herron, J. T. Evaluated Chemical Kinetics Data for Reactions of N(1D), N(1P) and N2(A3Σg+) in the Gas Phase. J. Phys. Chem. Ref. Data 1999, 28, 1453–1483.

Darwin, D. C.; Moore, C. B. Reaction Rate Constants (295 K) for 3CH2 with H2S, SO2, and NO2: Upper Bounds for Rate Constants with Less Reactive Partners. J. Phys. Chem. 1995, 99, 13467–13470.

Kovacs, D.; Jackson, J. E. CH2 + CO2 → CH2O + CO, One-Step Oxygen Atom Abstraction or Addition/Fragmentation via α-Lactone? J. Phys. Chem. A 2001, 105, 7579–7587.

Krasnoperov, L. N.; Chesnokov, E. N.; Stark, H.; Ravishankara, A. R. Elementary reactions of formyl (HCO) radical studied by laser photolysis/absorption spectroscopy. Proc. Combust. Inst. 2005, 30, 935–943.

Saheb, V.; Nazari, A. Products of the Self-Reaction of HCO Radicals: Theoretical Kinetics Studies. Phys. Chem. Res. 2019, 7, 81–94.

Li, J.; Wang, Y.; Jiang, B.; Ma, J.; Dawes, R.; Xie, D.; Bowman, J. M.; Guo, H. Communication: A chemically accurate global potential energy surface for the HO + CO → H + CO2 reaction. J. Chem. Phys. 2012, 136, 041103.

Skinner, D. E.; Germann, T. C.; Miller, W. H. Quantum Mechanical Rate Constants for O + OH = H + O2 for Total Angular Momentum J > 0. J. Phys. Chem. A 1998, 102, 3828–3834.

Lique, F.; Jorfi, M.; Honvault, P.; Halvick, P.; Lin, S. Y.; Guo, H.; Xie, D. Q.; Dagdigian, P. J.; Klos, J.; Alexander, M. H. O + OH → O2 + H: A key reaction for interstellar chemistry. New theoretical results and comparison with experiment. J. Chem. Phys. 2009, 131, 221104.

TABLE S1: Lindemann coefficients for the three-body oxygen reactions in the consistent reduced atmospheric hybrid chemical network oxygen extension (CRAHCN-O), valid within the 50–400 K temperature range. Experimental values are used when available, and calculated rate coefficients from this work are used otherwise. k∞ is the second-order rate coefficient in the high pressure limit with units cm6 s−1. k0 is the third-order rate coefficient in the low pressure limit with units cm8 s−1. These values fit into the pressure-dependent rate coefficient equation k = k∞(M/M∞)k0(298)k∞.

| No. | Reaction equation | k∞(298) | Avg. of exper. vals, This work | Source(s) |
|-----|-------------------|---------|--------------------------------|-----------|
| 1.  | CO2 + 1O + M →→ CO3 + M | 1.6×10−10 | (M=N2) 3.0×10−29  (CO2) 3.1×10−29  (H2) 6.7×10−29  (N2) 5.0×10−30  (CO2) 5.6×10−30  (H2) 9.7×10−30  (N2) 5.3×10−27  (CO2) 6.4×10−27  (H2) 1.2×10−27  (N2) 7.4×10−30  (CO2) 9.5×10−30  (H2) 1.4×10−29  (N2) 6.2×10−31  (CO2) 6.8×10−31  (H2) 1.3×10−30  (N2) 2.8×10−29  (CO2) 2.8×10−29  (H2) 2.8×10−29  (N2) 1.7×10−28  (CO2) 1.9×10−28  (H2) 3.3×10−28  (N2) 1.2×10−29  | Tsang and Hampson [23], This work |
| 2.  | HCO + 2N + M →→ HCON · + M · →→ HCNO + M | 2.0×10−11 | | This work |
| 3.  | HCO + CH3 + M →→ CH3CHO + M | 3.0×10−11 | | This work |
| 4.  | HCO + H + M →→ H2CO + M | 4.9×10−11 | | This work |
| 5.  | CO + CN + M →→ NCCO + M | 6.0×10−12 | | This work |
| 6.  | CO + 1O + M →→ CO2 + M | 4.6×10−11 | | This work |
| 7.  | CO + 3CH2 + M →→ CH2CO + M | 1.3×10−11 | | This work |
| 8.  | CO + CH + M →→ HCCO + M | 4.3×10−11 | | This work |

[SUPPORTING INFORMATION]

CRAHCN-O

In Tables S1 and S2, we display the Lindemann and the Arrhenius coefficients for the new oxygen reactions in CRAHCN-O. These rate coefficients consist of experimental values when available, and our consistently calculated theoretical values otherwise.
9. \( \text{CO} + \text{H} + \text{M} \rightarrow \text{HCO} + \text{M} \) \(2.7 \times 10^{-12}\) \(\text{(CO}_2\times 1.3 \times 10^{-29}\) \(\text{(H}_2\times 2.4 \times 10^{-29}\) \(\text{(N}_2\times 1.0 \times 10^{-34}\) \(\text{(CO}_2\times 9.9 \times 10^{-35}\) \(\text{(H}_2\times 1.0 \times 10^{-34}\) \(\text{(N}_2\times 6.5 \times 10^{-30}\)

10. \( \text{OH} + \text{H}_2\text{CN} + \text{M} \rightarrow \text{H}_2\text{CNOH} + \text{M} \) \(6.0 \times 10^{-12}\)

11. \( \text{OH} + \text{CN} + \text{M} \rightarrow \text{HOCN} + \text{M} \) \(1.0 \times 10^{-12}\)

12. \( \text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M} \) \(1.5 \times 10^{-11}\)

13. \( \text{OH} + \ \text{O} + \text{M} \rightarrow \text{HO}_2 + \text{M} \) \(7.4 \times 10^{-11}\)

14. \( \text{OH} + \ \text{O} + \text{M} \rightarrow \text{HO}_2 + \text{M} \) \(1.0 \times 10^{-9}\)

15. \( \text{OH} + \text{NH} + \text{M} \rightarrow \text{OH} \cdot \text{NH} \cdot + \text{M} \cdot \rightarrow \) \(7.0 \times 10^{-12}\)

16. \( \text{OH} + \text{CH}_3 + \text{M} \rightarrow \text{OH} \cdot \text{CH}_3 \cdot + \text{M} \cdot \rightarrow \) \(1.3 \times 10^{-10}\)

17. \( \text{OH} + \text{H} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M} \) \(2.4 \times 10^{-10}\)

18. \( \text{O} + \text{CN} + \text{M} \rightarrow \text{NCO} + \text{M} \) \(7.1 \times 10^{-12}\)

19. \( \text{O} + \ \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M} \) \(1.8 \times 10^{-11}\)

20. \( \text{O} + \ \text{O} + \text{M} \rightarrow \text{NO} + \text{M} \) \(6.6 \times 10^{-11}\)

21. \( \text{O} + \text{CH}_2 + \text{M} \rightarrow \text{H}_2\text{CO} + \text{M} \) \(1.9 \times 10^{-11}\)

22. \( \text{O} + \text{CH} + \text{M} \rightarrow \text{HCO} + \text{M} \) \(6.6 \times 10^{-11}\)

23. \( \text{O} + \text{H} + \text{M} \rightarrow \text{OH} + \text{M} \) \(3.5 \times 10^{-10}\)

24. \( \text{O} + \text{HCN} + \text{M} \rightarrow \text{H}_{\text{CNO}} + \text{M} \) \(3.3 \times 10^{-11}\)

25. \( \text{O} + \text{CN} + \text{M} \rightarrow \text{NCO} + \text{M} \) \(8.9 \times 10^{-11}\)

26. \( \text{O} + \ \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M} \) \(2.3 \times 10^{-10}\)

27. \( \text{O} + \text{CH}_4 + \text{M} \rightarrow \text{CH}_3\text{OH} + \text{M} \) \(2.2 \times 10^{-10}\)

28. \( \text{O} + \ \text{CH}_2 + \text{M} \rightarrow \text{H}_2\text{CO} + \text{M} \) \(3.3 \times 10^{-10}\)
| No. | Reaction equation | Form./Rev. | α  | β  | γ  | Source          |
|-----|------------------|-----------|----|----|----|----------------|
| 29. | $^{17}$O + CH + M $\rightarrow$ HCO + M | $9.2 \times 10^{-11}$ | (H$_{2}$) 1.2×10$^{-26}$ | This work |
|     |                  |           | (N$_{2}$) 4.9×10$^{-29}$ | This work |
|     |                  |           | (CO$_{2}$) 5.8×10$^{-29}$ | This work |
|     |                  |           | (H$_{2}$) 9.1×10$^{-29}$ | This work |
| 30. | $^{17}$O + H$_{2}$ + M $\rightarrow$ H$_{2}$O + M | $2.1 \times 10^{-10}$ | (N$_{2}$) 1.2×10$^{-29}$ | Avg. of exper. vals, This work |
|     |                  |           | (CO$_{2}$) 1.4×10$^{-29}$ | This work |
|     |                  |           | (H$_{2}$) 2.0×10$^{-29}$ | This work |
| 31. | $^{17}$O + H + M $\rightarrow$ OH + M | $1.1 \times 10^{-9}$ | (N$_{2}$) 1.4×10$^{-32}$ | This work |
|     |                  |           | (CO$_{2}$) 1.5×10$^{-32}$ | This work |
|     |                  |           | (H$_{2}$) 2.3×10$^{-32}$ | This work |

**TABLE S2:** Arrhenius coefficients for the one- and two-body oxygen reactions in the consistent reduced atmospheric hybrid chemical network oxygen extension (CRAHCN-O). Experimental values are used when available, and calculated rate coefficients from this work are used otherwise. For the reactions with barriers from this work, rate coefficients are calculated at 50, 100, 200, 298, and 400 K, and are fit to the modified Arrhenius expression $k(T) = \alpha \left( \frac{T}{298} \right)^{\beta} e^{-\gamma/T}$. Barrierless reaction rate coefficients do not typically vary by more than a factor of 1-3 for temperatures between 50 and 400 K. Intermediate molecules are labelled with a bullet, and are included to describe the precise reaction pathway for multi-step reactions. First- and second-order reactions with rate coefficients slower than $k(298 \text{ K}) = 10^{-21}$ are not included in this network. First-order rate coefficients have units s$^{-1}$. Second-order rate coefficients have units cm$^3$ s$^{-1}$.
97. OH + H → 3\text{O} + H₂
98. HCO + \text{N} → 3\text{NCOH} → \text{HCO} + \text{H}
F 2.8 \times 10^{-11} 0 0 This work
99. HCO + \text{N} → \text{CO} + \text{NH}
F 2.2 \times 10^{-11} 0 0 This work
100. HCO + \text{N} → 3\text{NCOH} → \text{NCO} + \text{H}
F 6.6 \times 10^{-11} 0 0 This work
101. HCO + \text{N} → \text{CO} + \text{NH}
F 4.8 \times 10^{-11} 0 0 This work
102. HCO + \text{CH}_₃ → \text{CO} + \text{CH}_₂
F 2.0 \times 10^{-10} 0 0 Tsang and Hampson 23
103. HCO + 3\text{CH}_₂ → \text{CH}_₃ + \text{CO}
F 2.1 \times 10^{-11} 0 0 This work
104. HCO + \text{CH}_₂ → \text{CH}_₃\text{HCO} → \text{CH}_₂\text{CO} → \text{CH}_₃ + \text{CO}
F 1.2 \times 10^{-11} 0 0 This work
105. HCO + \text{CH}_₂ → \text{CH}_₂\text{HCO} → \text{CH}_₃\text{CO} → \text{CH}_₃ + \text{CO}
F 1.5 \times 10^{-11} 0 0 This work
106. HCO + \text{CH} → \text{CO} + \text{CH}_₂
F 4.6 \times 10^{-12} 0 0 This work
107. HCO + \text{CH} → \text{CO} + \text{CH}_₂
F 1.5 \times 10^{-10} 0 0 Baulch et al. 24
108. HCO + \text{H} → H₂\text{CO} → \text{CO} + \text{H}_₂
F 2.4 \times 10^{-11} 0 0 This work
109. HCO → \text{CO} + \text{H} + \text{H}
F 1.7 \times 10^{-13} 1.14 10219 This work
110. CO + OH → \text{OH} \cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\·
99. $^{3}\text{O} + \text{H}_2\text{CN} \rightarrow \text{CH}_2\text{NO} \cdot \rightarrow$
$\text{HCNOH} \cdot \rightarrow \text{HCNO} + \text{H}$
$5.7 \times 10^{-13}$ $1.72$ $788$ This work

100. $^{3}\text{O} + \text{H}_2\text{CN} \leftrightarrow \text{CH}_2\text{NO} \cdot \leftrightarrow$
$\text{HCNO} + \text{H}$
$9.8 \times 10^{-11}$ $0$ $0$ This work

101. $^{3}\text{O} + \text{H}_2\text{CN} \rightarrow \text{CH}_2\text{NO} \cdot \rightarrow$
$\text{HCNOH} \cdot \rightarrow \text{HCN} + \text{OH}$
$3.7 \times 10^{-13}$ $0.86$ $1127$ This work

102. $^{3}\text{O} + \text{HCN} \rightarrow ^{3}\text{NCOH} \rightarrow \text{NCO} + \text{H}$
$1.3 \times 10^{-11}$ $0.96$ $4040$ This work

103. $^{3}\text{O} + \text{HCN} \leftrightarrow ^{3}\text{NCOH} \leftrightarrow \text{NCO} + \text{H}$
$1.3 \times 10^{-10}$ $0.20$ $5743$ This work

104. $^{3}\text{O} + \text{CN} \rightarrow ^{4}\text{NCO} \rightarrow \text{CO} + ^{4}\text{N}$
$7.6 \times 10^{-12}$ $0$ $0$ Baulch et al. [24]

105. $^{3}\text{O} + \text{CN} \rightarrow ^{4}\text{NCOH}_\nu \rightarrow \text{CO} + ^{4}\text{N}$
$9.4 \times 10^{-12}$ $0$ $0$ Baulch et al. [24]

106. $^{3}\text{O} + \text{NH} \rightarrow ^{4}\text{NNO} \rightarrow \text{NO} + \text{H}$
$3.1 \times 10^{-11}$ $0$ $0$ This work

107. $^{3}\text{O} + \text{NH} \rightarrow ^{4}\text{NOH} \rightarrow \text{OH} + ^{4}\text{N}$
$4.5 \times 10^{-12}$ $0.54$ $1589$ This work

108. $^{3}\text{O} + \text{CH}_3 \rightarrow ^{3}\text{CH}_3\cdot \rightarrow ^{3}\text{CH}_2\cdot \rightarrow ^{3}\text{H}_2\text{CO} + \text{H}$
$1.4 \times 10^{-10}$ $0$ $0$ Baulch et al. [24]

109. $^{3}\text{O} + \text{CH}_3 \rightarrow ^{3}\text{CH}_3\cdot \rightarrow ^{3}\text{CH}_2\cdot \rightarrow ^{3}\text{H}_2\text{CO} + \text{H}$
$1.4 \times 10^{-10}$ $0$ $0$ Baulch et al. [24]

110. $^{3}\text{O} + \text{CH}_3 \rightarrow ^{3}\text{CH}_3\cdot \rightarrow ^{3}\text{CH}_2\cdot \rightarrow ^{3}\text{H}_2\text{CO} + \text{H}$
$1.4 \times 10^{-10}$ $0$ $0$ Baulch et al. [24]

111. $^{3}\text{O} + ^{1}\text{CH}_2 \rightarrow ^{3}\text{H}_2\text{CO}_\nu \rightarrow ^{3}\text{H}_2\text{CO} + ^{1}\text{H}_2$
$8.0 \times 10^{-11}$ $0$ $0$ Baulch et al. [24]

112. $^{3}\text{O} + ^{1}\text{CH}_2 \rightarrow ^{3}\text{H}_2\text{CO}_\nu \rightarrow ^{3}\text{H}_2\text{CO} + ^{1}\text{H}_2$
$2.1 \times 10^{-10}$ $0$ $0$ This work

113. $^{3}\text{O} + ^{1}\text{CH}_2 \rightarrow ^{3}\text{H}_2\text{CO}_\nu \rightarrow ^{3}\text{H}_2\text{CO} + ^{1}\text{H}_2$
$2.1 \times 10^{-10}$ $0$ $0$ Baulch et al. [24]

114. $^{3}\text{O} + ^{1}\text{CH}_2 \rightarrow ^{3}\text{H}_2\text{CO}_\nu \rightarrow ^{3}\text{H}_2\text{CO} + ^{1}\text{H}_2$
$2.8 \times 10^{-10}$ $0$ $0$ This work

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 S3.

| Technique Temp. (K) | Pressure (Torr) | Reference(s) |
|---------------------|----------------|--------------|
| M 300               | 20             | Young et al. [24] |
| M 295               | 25-250         | Blitz et al. [24] |
| M 297               | 40             | Wine and Ravishankara [24] |
| M                   | 0-0.01         | Aminoto et al. [24] |

TABLE S3: All available experimental or recommended reaction rate coefficients for the reactions in this study. For brevity, only the 10 most recent measurements of OH + CH₄ → H₂O + CH₃, OH + H₂ → H₂O + H, and O + CH₃ → H₂CO + H are included; for a complete listing, we refer the reader to the NIST Chemical Kinetics Database [24]. First-order rate coefficients have units s⁻¹. Second-order rate coefficients have units cm³s⁻¹. Third-order rate coefficients have units cm⁶s⁻¹.
\[
\begin{align*}
1.2 \times 10^{-10} & \quad \text{M} \quad 298 \quad 1.1 \times 10^{-10} \quad \text{M} \quad 298 \quad 5-50 \\
\text{CO}_2 + ^2\text{N} & \rightarrow \text{CO} + \text{NO} \quad \text{Dunlea and Ravishankara}\quad \text{M} \quad 300 \quad 6 \quad \text{Fell et al.}\quad \text{M} \quad 300 \quad 2-5 \quad \text{Black et al.}\quad \text{M} \quad 300 \quad 7-15 \quad \text{Lin and Kaufman}\quad \text{M} \quad 300 \quad 1-3 \quad \text{Piper et al.}\quad \text{M} \quad 300 \quad 26 \quad \text{Husain et al.}\quad \text{M} \quad 300 \quad 2 \quad \text{Laufer and Bass}\quad \text{M} \quad 300 \quad 20 \quad \text{Mehlmann et al.}\quad \text{M} \quad 300 \quad 100 \quad \text{Butler et al.}\quad \text{M} \quad 300 \quad 100 \quad \text{Berman et al.}\quad \text{M} \quad 300 \quad 3 \quad \text{Baulch et al.}\quad \text{M} \quad 300 \quad 40 \quad \text{Vandooren and Van Tiggelen}\quad \text{M} \quad 300 \quad 1.6 \quad \text{Chang and Barker}\quad \text{M} \quad 300 \quad 50-200 \quad \text{Klemm et al.}\quad \text{M} \quad 300 \quad 1.7-4.4 \quad \text{Klemm et al.}\quad \text{M} \quad 300 \quad 2 \quad \text{Herron and Penzhorn}\quad \text{M} \quad 300 \quad 0.9-1.1 \quad \text{Mack and Thrush}\quad \text{M} \quad 300 \quad 2 \quad \text{Baulch et al.}\quad \text{M} \quad 300 \quad 20-300 \quad \text{Tsang and Hampson}\quad \text{M} \quad 300 \quad 100-450 \quad \text{Klemm et al.}\quad \text{M} \quad 297 \quad 25-116 \quad \text{Ridley et al.}\quad \text{M} \quad 298 \quad 1-2 \quad \text{Brennen et al.}\quad \text{M} \quad 298 \quad 1-5 \quad \text{Oehlers et al.}\quad \text{M} \quad 298 \quad 22.5 \quad \text{Vandooren et al.}\quad \text{M} \quad 298 \quad 0.8-2.1 \quad \text{Westenberg and DeHaas}\quad \text{M} \quad 298 \quad 1 \quad \text{Baulch et al.}\quad \text{M} \quad 298 \quad 0.1-1 \quad \text{Stoeckel et al.}\quad \text{M} \quad 298 \quad 26 \quad \text{Yee Quee and Thynne}\quad \text{M} \quad 298
\end{align*}
\]
HCO + HCO $\rightarrow$ H$_2$CO + CO
\[7.5 \times 10^{-11}\] M 295 10–30 Baggott et al. [109]
\[6.3 \times 10^{-11}\] M 298 10 Reilly et al. [110]
\[4.5 \times 10^{-11}\] M 298 210–1425 Friedrichs et al. [111]
\[3.4 \times 10^{-11}\] M 298 10–20 Veyret et al. [112]
\[3.0 \times 10^{-11}\] M 298 Vedeneev et al. [113]

Yee Quee and Thynne [69]

HCO + OH $\rightarrow$ H$_2$O + CO
\[3.6 \times 10^{-11}\] M 298 6–75 Baulch et al. [27]
\[1.8 \times 10^{-10}\] M 298 1425–10000 Baulch et al. [27]
\[1.7 \times 10^{-10}\] S 300 Baulch et al. [27]
\[5.0 \times 10^{-11}\] S 300 Baulch et al. [27]

Temps and Wagner [94]

HCO + CH$_3$ $\rightarrow$ CH$_3$HCO
\[4.4 \times 10^{-11}\] M 298 60–76 Mulenko [114]
\[6.3 \times 10^{-12}\] M 298 60–76 Mulenko [114]
\[3.0 \times 10^{-11}\] S 298 Baulch et al. [27]

Yee Quee and Thynne [69]

CO + OH $\rightarrow$ CO$_2$ + H
\[9.7 \times 10^{-13}\] M 300 750–112500 Forster et al. [116]
\[2.3 \times 10^{-13}\] M 299 700 Niki et al. [117]
\[1.3–1.9 \times 10^{-13}\] M 296–297 5–10 Frost et al. [118]
\[1.7 \times 10^{-13}\] M 298 150 Bohn and Zetzsch [119]
\[1.6 \times 10^{-13}\] M 298 2 Bohn and Zetzsch [119]
\[1.5 \times 10^{-13}\] M 300 24 Hussain et al. [121]
\[1.4 \times 10^{-13}\] M 300 24 Lissianski et al. [122]
\[1.4 \times 10^{-13}\] M 298 100 Ravishankara and Thompson [123]
\[1.3 \times 10^{-13}\] M 297 5 Herron [124]
\[8.5 \times 10^{-14}\] M 300 1.8 Herron [124]
\[1.3 \times 10^{-13}\] S 298 Baulch et al. [124]

Ravishankara and Thompson [123]

CO + CH + M $\rightarrow$ HCCO + M
\[k_0(\text{CO}_2) = 2.8 \times 10^{-29}\] M 300 Clerc and Barat [23]

CO + CH + M $\rightarrow$ HCCO + M
\[k_0(\text{Ar}) = 4.2 \times 10^{-30}\] M 298 10–100 Mehmann et al. [125]
\[k_0(\text{Ar}) = 4.1 \times 10^{-30}\] M 298 0.4–4.5 Le Picard et al. [126]

CO + CH + M $\rightarrow$ HCCO + M
\[k_0(\text{Ar}) = 4.2 \times 10^{-30}\] M 298 10–100 Mehmann et al. [125]
\[k_0(\text{Ar}) = 4.1 \times 10^{-30}\] M 298 0.4–4.5 Le Picard et al. [126]

CO + CH + M $\rightarrow$ HCCO + M
\[k_0(\text{Ar}) = 4.2 \times 10^{-30}\] M 298 10–100 Mehmann et al. [125]
\[k_0(\text{Ar}) = 4.1 \times 10^{-30}\] M 298 0.4–4.5 Le Picard et al. [126]
k₀(Ar) = 4.1 \times 10^{-30} \quad M \quad 298 \quad 4–400 \quad Brownsworth et al. [129]
k₀(He) = 4.1 \times 10^{-30} \quad M \quad 298 \quad 10–7500 \quad Fulle et al. [130]
k₀(He) = 3.9 \times 10^{-30} \quad M \quad 298 \quad 10–100 \quad Mehlmann et al. [169]
k₀(He) = 2.4 \times 10^{-30} \quad M \quad 293 \quad 12.5–500 \quad Taatjes [117]

CO + CH $\longrightarrow$ HCCO

1.7 \times 10^{-10} \quad M \quad 298 \quad 10–7500 \quad Fulle et al. [130]
5.9 \times 10^{-11} \quad M \quad 298 \quad high-pressure limit \quad Mehlmann et al. [169]
3.0 \times 10^{-11} \quad M \quad 298 \quad 0.4–4.5 \quad Le Picard et al. [129]
2.1 \times 10^{-11} \quad M \quad 298 \quad 100 \quad Butler et al. [54]
8.3 \times 10^{-12} \quad M \quad 298 \quad 100 \quad Berman et al. [68]
6.9 \times 10^{-12} \quad M \quad 298 \quad 100 \quad Taatjes [117]
4.8 \times 10^{-12} \quad M

CO + H + M $\longrightarrow$ HCO + M

k₀(H₂) < 3.3 \times 10^{-34} \quad M \quad 298 \quad 50–250 \quad Bennett and Blackmore [121]
k₀(CH₄, H₂O) = 1.6 \times 10^{-34} \quad M \quad 298 \quad 760 \quad Hochanadel et al. [23]
k₀(He) = 1.1 \times 10^{-34} \quad M \quad 298 \quad Wang et al. [133]
k₀(H₂) = 1.1 \times 10^{-34} \quad M \quad 298 \quad 800–1220 \quad Hikida et al. [135]
k₀(H₂) = 1.0 \times 10^{-34} \quad M \quad 298 \quad 760 \quad Hochanadel et al. [23]
k₀(H₂O) = 9.9 \times 10^{-35} \quad M \quad 298 \quad 760 \quad Hochanadel et al. [23]
k₀(He) = 7.2 \times 10^{-35} \quad M \quad 298 \quad 800–1220 \quad Hikida et al. [135]
k₀(H₂) = 8.0 \times 10^{-35} \quad M \quad 298 \quad 52–601 \quad Ahumada et al. [159]
k₀(H₂) = 6.9 \times 10^{-35} \quad M \quad 298 \quad 52–601 \quad Ahumada et al. [159]
k₀(He) = 6.2 \times 10^{-35} \quad M \quad 298 \quad 52–601 \quad Ahumada et al. [159]
k₀(He) = 6.0 \times 10^{-35} \quad M \quad 298 \quad 52–601 \quad Ahumada et al. [159]
k₀(N₂) = 4.8 \times 10^{-35} \quad M \quad 298 \quad 52–601 \quad Ahumada et al. [159]

H₂O + ^1O $\longrightarrow$ OH + OH

3.7 \times 10^{-10} \quad M \quad 300 \quad 11 \quad Gauthier and Snelling [139]
3.0 \times 10^{-11} \quad M \quad 300 \quad 15–26 \quad Heidner, III et al. [105]
2.6 \times 10^{-10} \quad M \quad 300 \quad 3–5 \quad Lee and Slanger [129]
2.3 \times 10^{-10} \quad M \quad 298 \quad 10–30 \quad Davidson et al. [129]
2.3 \times 10^{-10} \quad M \quad 298 \quad 1–12 \quad Streit et al. [129]
1.8–2.3 \times 10^{-10} \quad M \quad 295 \quad 20–36 \quad Dunlea and Ravishankara [111]
1.9–2.2 \times 10^{-10} \quad M \quad 298 \quad 7–47 \quad Gericke and Comes [132]
2.1 \times 10^{-10} \quad M \quad 298 \quad 1–30 \quad Davidson et al. [129]

H₂O + CH $\longrightarrow$ products

1.3 \times 10^{-11} \quad M \quad 293 \quad 200 \quad Blitz et al. [57]
4.5 \times 10^{-11} \quad M \quad 293 \quad 200 \quad Bosnali and Perner [122]

OH + HCN $\longrightarrow$ H₂CNOH

6.0 \times 10^{-12} \quad M \quad 298 \quad 120–200 \quad Nizamov and Dagdigian [65]

OH + HCN $\longrightarrow$ products

3.1 \times 10^{-14} \quad M \quad 298 \quad 75–375 \quad Fritz et al. [143]
1.0 \times 10^{-16} \quad M \quad 298 \quad 10 \quad Phillips [26]

OH + OH + M $\longrightarrow$ H₂O₂ + M

k₀(H₂O) = 1.8 \times 10^{-29} \quad M \quad 298 \quad 100 \quad Caldwell and Back [52]
k₀(O₂) = 5.1 \times 10^{-30} \quad M \quad 298 \quad 100 \quad Caldwell and Back [52]
k₀(CO₂) = 4.2 \times 10^{-30} \quad M \quad 298 \quad 100 \quad Caldwell and Back [52]
k₀(H₂O) = 4.0 \times 10^{-30} \quad M \quad 298 \quad 0.08–105 \quad Zellner et al. [144]
k₀(N₂) = 3.3 \times 10^{-30} \quad M \quad 298 \quad 100 \quad Caldwell and Back [24]
k₀(Xe) = 1.3 \times 10^{-30} \quad M \quad 298 \quad 100 \quad Caldwell and Back [24]
k₀(He) = 9.7 \times 10^{-31} \quad M \quad 298 \quad 100 \quad Caldwell and Back [24]
k₀(He) = 9.2 \times 10^{-31} \quad M \quad 298 \quad 750–7500 \quad Sangwan et al. [127]
k₀(He) = 8.5 \times 10^{-31} \quad M \quad 298 \quad 100 \quad Caldwell and Back [24]
k₀(N₂) = 6.9 \times 10^{-31} \quad M \quad 298 \quad 20–825 \quad Zellner et al. [144]
k₀(H₂O) = 2.8 \times 10^{-31} \quad M \quad 298 \quad 200 \quad Black and Porter [53]
k₀(N₂) = 2.5 \times 10^{-31} \quad M \quad 298 \quad 1 \quad Trainor and von Rosenberg Jr. [146]
k₀(N₂) = 2.5 \times 10^{-31} \quad M \quad 298 \quad 1 \quad Trainor and von Rosenberg Jr. [146]
k₀(O₂) = 7.9 \times 10^{-32} \quad M \quad 298 \quad 200 \quad Black and Porter [53]
k₀(CO₂) = 6.4 \times 10^{-32} \quad M \quad 298 \quad 200 \quad Black and Porter [53]
k₀(N₂) = 5.1 \times 10^{-32} \quad M \quad 298 \quad 200 \quad Black and Porter [53]
\[
\text{OH} + \text{CH} \rightarrow \text{OH} + \text{NH}_2
\]

\[
\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2
\]

\[
6.5 \times 10^{-11} \quad \text{M} \quad 300 \quad 1 \quad \text{Greiner et al.}\]

\[
2.6 \times 10^{-11} \quad \text{M} \quad 298 \quad 75000 \quad \text{Fulle et al.}\]

\[
2.4 \times 10^{-11} \quad \text{M} \quad 298 \quad 750-7500 \quad \text{Sangwan et al.}\]

\[
2.2 \times 10^{-11} \quad \text{M} \quad 298 \quad 750-112500 \quad \text{Forster et al.}\]

\[
1.5 \times 10^{-11} \quad \text{M} \quad 298 \quad 20-825 \quad \text{Zellner et al.}\]

\[
1.5 \times 10^{-11} \quad \text{S} \quad 298 \quad \text{Baulch et al.}\]

\[
\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + ^3\text{O}_2
\]

\[
2.6 \times 10^{-12} \quad \text{M} \quad 300 \quad 1 \quad \text{Dixon-Lewis et al.}\]

\[
2.3 \times 10^{-12} \quad \text{M} \quad 298 \quad 1-4 \quad \text{Westenberg and deHaas}\]

\[
2.1 \times 10^{-12} \quad \text{M} \quad 298 \quad 23-78 \quad \text{Trainor and von Rosenberg Jr.}\]

\[
2.1 \times 10^{-12} \quad \text{M} \quad 298 \quad 1 \quad \text{Trainor and von Rosenberg Jr.}\]

\[
1.7 \times 10^{-12} \quad \text{M} \quad 298 \quad \text{Farquharson and Smith}\]

\[
1.3-1.5 \times 10^{-12} \quad \text{M} \quad 298 \quad 1-2 \quad \text{Clyne and Down}\]

\[
1.4 \times 10^{-12} \quad \text{M} \quad 298 \quad 2250-7500 \quad \text{Sangwan and Krasnoperov}\]

\[
1.4 \times 10^{-12} \quad \text{M} \quad 298 \quad 1 \quad \text{Bedjanian et al.}\]

\[
1.4 \times 10^{-12} \quad \text{M} \quad 298 \quad \text{Wagner and Zellner}\]

\[
8.4 \times 10^{-13} \quad \text{M} \quad 298 \quad 1 \quad \text{Breen and Glass}\]

\[
2.0 \times 10^{-12} \quad \text{S} \quad 298 \quad \text{Tsang and Hampson}\]

\[
1.4 \times 10^{-12} \quad \text{S} \quad 298 \quad \text{Baulch et al.}\]

\[
\text{OH} + ^3\text{O} \rightarrow \text{O}_2 + \text{H}
\]

\[
4.3 \times 10^{-11} \quad \text{M} \quad 298 \quad 1 \quad \text{Breen and Glass}\]

\[
4.2 \times 10^{-11} \quad \text{M} \quad 298 \quad 2.5-4 \quad \text{Smith and Stewart}\]

\[
3.9 \times 10^{-11} \quad \text{M} \quad 298 \quad 4 \quad \text{Howard and Smith}\]

\[
2.3-3.8 \times 10^{-11} \quad \text{M} \quad 298 \quad 0.6-0.9 \quad \text{Westenberg et al.}\]

\[
3.8 \times 10^{-11} \quad \text{M} \quad 298 \quad 3.75 \quad \text{Howard and Smith}\]

\[
3.3 \times 10^{-11} \quad \text{M} \quad 298 \quad 40 \quad \text{Robertson and Smith}\]

\[
3.2 \times 10^{-11} \quad \text{M} \quad 298 \quad 40 \quad \text{Robertson and Smith}\]

\[
3.1 \times 10^{-11} \quad \text{M} \quad 300 \quad 1-5 \quad \text{Brune et al.}\]

\[
2.9 \times 10^{-11} \quad \text{M} \quad 298 \quad \text{Lewis and Watson}\]

\[
2.8 \times 10^{-11} \quad \text{M} \quad 300 \quad 2-8 \quad \text{Kurzius and Boudart}\]

\[
3.9 \times 10^{-15} \quad \text{S} \quad 298 \quad \text{Tsang and Hampson}\]

\[
2.9 \times 10^{-11} \quad \text{S} \quad 298 \quad \text{Baulch et al.}\]

\[
\text{OH} + \text{NH} \rightarrow \text{HNO} + \text{H}
\]

\[
3.3 \times 10^{-11} \quad \text{S} \quad 298 \quad \text{Cohen and Westberg}\]

\[
\text{OH} + \text{NH} \rightarrow \text{H}_2\text{O} + ^4\text{N}
\]

\[
5.1 \times 10^{-12} \quad \text{S} \quad 298 \quad \text{Cohen and Westberg}\]

\[
\text{OH} + ^4\text{N} \rightarrow \text{NO} + \text{H}
\]

\[
5.3 \times 10^{-11} \quad \text{M} \quad 298 \quad 4 \quad \text{Howard and Smith}\]

\[
5.2 \times 10^{-11} \quad \text{M} \quad 294 \quad 2.5-6 \quad \text{Smith and Stewart}\]

\[
5.0 \times 10^{-11} \quad \text{M} \quad 298 \quad 3.75 \quad \text{Howard and Smith}\]

\[
4.2 \times 10^{-11} \quad \text{M} \quad 300 \quad 1-5 \quad \text{Brune et al.}\]

\[
\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3
\]

\[
1.1 \times 10^{-14} \quad \text{M} \quad 300 \quad 1 \quad \text{Wilson and Westenberg}\]

\[
8.5 \times 10^{-15} \quad \text{M} \quad 298 \quad 99 \quad \text{Wilson and Westenberg}\]

\[
7.6 \times 10^{-15} \quad \text{M} \quad 298 \quad 100 \quad \text{Sharkey and Smith}\]

\[
6.9 \times 10^{-15} \quad \text{M} \quad 298 \quad 100 \quad \text{Mellouki et al.}\]

\[
6.6 \times 10^{-15} \quad \text{M} \quad 298 \quad 151 \quad \text{Bryukov et al.}\]

\[
6.4 \times 10^{-15} \quad \text{M} \quad 298 \quad 100 \quad \text{Bonard et al.}\]

\[
6.4 \times 10^{-15} \quad \text{M} \quad 298 \quad 100 \quad \text{Gierczak et al.}\]

\[
6.2-6.3 \times 10^{-15} \quad \text{M} \quad 298 \quad 100-300 \quad \text{Vaghjiani and Ravishankara}\]

\[
6.2 \times 10^{-15} \quad \text{M} \quad 298 \quad 400-750 \quad \text{Dunlop and Tully}\]

\[
5.9 \times 10^{-15} \quad \text{M} \quad 298 \quad 1 \quad \text{Finlayson-Pitts et al.}\]
\[
\begin{align*}
8.0 \times 10^{-15} & \quad S \quad 298 & \quad \text{Baulch et al.}^{23} \\
7.9 \times 10^{-15} & \quad S \quad 298 & \quad \text{Tsang and Hampson}^{23}
\end{align*}
\]

\[
\text{OH} + \text{CH}_3 + \text{M} \rightarrow \text{CH}_3\text{OH} + \text{M}
\]

\[
\begin{align*}
\text{k}(\text{SF}_6) & = 7.2 \times 10^{-27} & \quad M \quad 298 & \quad 64-750 & \quad \text{Fagerström et al.}^{212} \\
\text{k}(\text{He}) & = 2.6 \times 10^{-27} & \quad M \quad 300 & \quad 0.5-2.5 & \quad \text{Humpfer et al.}^{176} \\
\text{k}(\text{SF}_6) & = 2.5 \times 10^{-27} & \quad M \quad 298 & \quad 64-750 & \quad \text{Fagerström et al.}^{126} \\
\text{k}(\text{He}) & = 2.0 \times 10^{-27} & \quad M \quad 300 & \quad 0.2-5 & \quad \text{Oser et al.}^{180} \\
\text{k}(\text{He}) & = 2.0 \times 10^{-27} & \quad M \quad 300 & \quad 1-7 & \quad \text{Oser et al.}^{181}
\end{align*}
\]

\[
\text{OH} + \text{CH}_3 \rightarrow \text{CH}_3\text{OH}
\]

\[
\begin{align*}
1.7 \times 10^{-10} & \quad M \quad 300 & \quad 0.5-2.5 & \quad \text{Humpfer et al.}^{176} \\
1.7 \times 10^{-10} & \quad M \quad 300 & \quad 1-7 & \quad \text{Oser et al.}^{181} \\
1.4 \times 10^{-10} & \quad M \quad 298 & \quad 64-750 & \quad \text{Fagerström et al.}^{126} \\
1.4 \times 10^{-10} & \quad M \quad 298 & \quad 64-750 & \quad \text{Fagerström et al.}^{126} \\
9.4 \times 10^{-11} & \quad M \quad 298 & \quad 750 & \quad \text{Anastasi et al.}^{122} \\
9.3 \times 10^{-11} & \quad M \quad 300 & \quad 0.2-5 & \quad \text{Oser et al.}^{180}
\end{align*}
\]

\[
\text{OH} + \text{CH}_3 \rightarrow ^3\text{O} + \text{CH}_4
\]

\[
\begin{align*}
1.8 \times 10^{-17} & \quad S \quad 298 & \quad \text{Cohen and Westberg}^{155} \\
3.0 \times 10^{-11} & \quad S \quad 298 & \quad \text{Tsang and Hampson}^{25} \\
5.0 \times 10^{-11} & \quad S \quad 298 & \quad \text{Tsang and Hampson}^{25}
\end{align*}
\]

\[
\text{OH} + ^2\text{CH}_2 \rightarrow \text{H}_2\text{CO} + \text{H}
\]

\[
\begin{align*}
8.5 \times 10^{-15} & \quad M \quad 298 & \quad 760 & \quad \text{Sworski et al.}^{153} \\
7.2 \times 10^{-15} & \quad M \quad 298 & \quad 10-20 & \quad \text{Smith and Zellner}^{154} \\
7.0 \times 10^{-15} & \quad M \quad 298 & \quad 15 & \quad \text{Atkinson et al.}^{155} \\
7.0 \times 10^{-15} & \quad M \quad 298 & \quad 15 & \quad \text{Atkinson et al.}^{155} \\
6.9 \times 10^{-15} & \quad M \quad 298 & \quad 50-300 & \quad \text{Tabukdar et al.}^{153} \\
6.7 \times 10^{-15} & \quad M \quad 298 & \quad 17-100 & \quad \text{Orkin et al.}^{185} \\
6.2 \times 10^{-15} & \quad M \quad 298 & \quad 100 & \quad \text{Ravishankara et al.}^{119} \\
6.1 \times 10^{-15} & \quad M \quad 298 & \quad 50 & \quad \text{Tully and Ravishankara}^{190} \\
5.8 \times 10^{-15} & \quad M \quad 298 & \quad 40-760 & \quad \text{Overend et al.}^{121} \\
5.3 \times 10^{-15} & \quad M \quad 298 & \quad 23 & \quad \text{Trainor and von Rosenberg Jr.}^{172} \\
6.4 \times 10^{-15} & \quad S \quad 298 & \quad \text{Tsang and Hampson}^{25} \\
6.2 \times 10^{-15} & \quad S \quad 300 & \quad \text{Baulch et al.}^{124}
\end{align*}
\]

\[
\text{OH} + \text{H} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}
\]

\[
\begin{align*}
\text{k}(\text{CO}_2) & = 9.0 \times 10^{-31} & \quad M \quad 300 & \quad 3-11 & \quad \text{Zellner et al.}^{123} \\
\text{k}(\text{N}_2) & = 4.8 \times 10^{-31} & \quad M \quad 300 & \quad 3-11 & \quad \text{Zellner et al.}^{123} \\
\text{k}(\text{Ar}) & = 2.3 \times 10^{-31} & \quad M \quad 300 & \quad 3-11 & \quad \text{Zellner et al.}^{123} \\
\text{k}(\text{He}) & = 1.5 \times 10^{-31} & \quad M \quad 300 & \quad 3-11 & \quad \text{Zellner et al.}^{123} \\
\text{k}(\text{H}_2\text{O}) & = 4.3 \times 10^{-30} & \quad S \quad 300 & \quad \text{Baulch et al.}^{24} \\
\text{k}(\text{N}_2) & = 6.8 \times 10^{-31} & \quad S \quad 300 & \quad \text{Baulch et al.}^{24} \\
\text{k}(\text{Ar}) & = 2.6 \times 10^{-31} & \quad S \quad 300 & \quad \text{Baulch et al.}^{24} \\
\text{k}(\text{H}_2\text{O}) & = 6.8 \times 10^{-31} & \quad S \quad 300 & \quad \text{Tsang and Hampson}^{25} \\
\text{OH} + \text{H} \rightarrow ^3\text{O} + \text{H}_2
\]

\[
\begin{align*}
5.6 \times 10^{-16} & \quad S \quad 300 & \quad \text{Kaufman and Del Greco}^{153} \\
9.9 \times 10^{-17} & \quad S \quad 298 & \quad \text{Cohen and Westberg}^{173} \\
1.1 \times 10^{-16} & \quad S \quad 300 & \quad \text{Tsang and Hampson}^{25} \\
3\times 10^{-11} & \quad S \quad 298 & \quad \text{Titatarchuk and Halpern}^{194} \\
2.1 \times 10^{-11} & \quad M \quad 298 & \quad \text{Schacke et al.}^{124} \\
2.7 \times 10^{-12} & \quad M \quad 298 & \quad 7 & \quad \text{Schmatjko and Wolfrum}^{157} \\
1.7 \times 10^{-11} & \quad S \quad 298 & \quad \text{Tsang}^{179} \\
7.6 \times 10^{-12} & \quad S \quad 298 & \quad \text{Baulch et al.}^{24} \\
3\times 10^{-11} & \quad S \quad 298 & \quad \text{Baulch et al.}^{24} \\
3\times 10^{-12} & \quad S \quad 298 & \quad \text{Tchen}^{200}
\end{align*}
\]

\[
3\times 10^{-11} \quad \text{M} \quad 298 & \quad 7 & \quad \text{Schmatjko and Wolfrum}^{157} \\
\text{O}_2 + \text{H} + \text{M} \rightarrow \text{O}_2 + \text{H} + \text{M}
\]

\[
\begin{align*}
\text{k}(\text{N}_2) & = 7.2 \times 10^{-32} - 1.0 \times 10^{-32} & \quad M \quad 300 & \quad 2-5 & \quad \text{Morgan et al.}^{199} \\
\text{k}(\text{O}_2) & = 1.0 \times 10^{-32} & \quad M \quad 298 & \quad 1-2 & \quad \text{Tchen}^{200}
\end{align*}
\]
$k_0(N_2) = 4.8 \times 10^{-33}$ M 298 2–15 Campbell and Gray

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$6.6 \times 10^{-16}$ M 300 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$1.2 \times 10^{-17}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$6.6 \times 10^{-19}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$5.0 \times 10^{-18}$ S 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$4.3 \times 10^{-18}$ S 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$1.9 \times 10^{-10}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$1.4 \times 10^{-10}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$1.4 \times 10^{-10}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$<2 \times 10^{-4}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$1.2 \times 10^{-10}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$1.1 \times 10^{-10}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$1.0 \times 10^{-10}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$9.4 \times 10^{-11}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$>3.0 \times 10^{-11}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$>3.0 \times 10^{-11}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$1.4 \times 10^{-10}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$1.3 \times 10^{-10}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$1.3 \times 10^{-10}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$1.3 \times 10^{-10}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$2.0 \times 10^{-10}$ S 298 2–15 Campbell and Thrush

$\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}$

$1.9 \times 10^{-11}$ S 298 2–15 Campbell and Thrush

$\text{O} + \text{CH} \rightarrow \text{CO} + \text{H}$

$9.5 \times 10^{-11}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{CH} \rightarrow \text{CO} + \text{H}$

$9.4 \times 10^{-11}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{CH} \rightarrow \text{CO} + \text{H}$

$6.6 \times 10^{-11}$ S 298 2–15 Campbell and Thrush

$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$

$1.1 \times 10^{-17}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$

$1.0 \times 10^{-17}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$

$9.1 \times 10^{-18}$ M 298 2–15 Campbell and Thrush

$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$

$8.5 \times 10^{-18}$ S 298 2–15 Campbell and Thrush

$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$

$7.0 \times 10^{-18}$ S 298 2–15 Campbell and Thrush

$k_0(M) = 1.0 \times 10^{-33} - 8 \times 10^{-30}$
\[ k_0(M) = 4.4 \times 10^{-32} \]

\[ ^1O + CH_4 \rightarrow OH + CH_3 \]

\[ 3.8 \times 10^{-10} \quad M \quad 300 \quad 11 \quad Gauthier and Snelling \[28\] \]

\[ 2.2 \times 10^{-10} \quad M \quad 300 \quad 1-3 \quad Matsumi et al. \[24\] \]

\[ 1.9 \times 10^{-10} \quad M \quad 298 \quad 10 \quad Vranckx et al. \[23\] \]

\[ 1.7 \times 10^{-10} \quad M \quad 298 \quad 45 \quad Dillen et al. \[23\] \]

\[ 1.4 \times 10^{-10} \quad M \quad 295 \quad 25-250 \quad Blitz et al. \[22\] \]

\[ 4.0 \times 10^{-10} \quad S \quad 298 \quad \]

\[ ^1O + H_2 \rightarrow OH + H \]

\[ 3.0 \times 10^{-10} \quad M \quad 300 \quad 11 \quad Gauthier and Snelling \[28\] \]

\[ 2.7 \times 10^{-10} \quad M \quad 298 \quad 0.1 \quad Koppe et al. \[23\] \]

\[ 2.5 \times 10^{-10} \quad M \quad 298 \quad 7-21 \quad Stief et al. \[23\] \]

\[ 2.2 \times 10^{-10} \quad M \quad 298 \quad 1 \quad Matsumi et al. \[23\] \]

\[ 1.2 \times 10^{-10} \quad M \quad 298 \quad 1 \quad Matsumi et al. \[23\] \]

\[ 1.1 \times 10^{-10} \quad M \quad 298 \quad 100 \quad Ogren et al. \[23\] \]

M: Monitoring decay of reactants and/or production of products.
S: Suggested value based on experiments and/or evaluations at a range of temperatures.

Lennard-Jones Parameters

| Molecule       | \( \sigma \) (Å) | \( \epsilon/k_b \) (K) | Source                      |
|----------------|------------------|-------------------------|-----------------------------|
| CO             | 3.996            | ^a 190                  | Welty et al. \[45\]          |
| NCCO           | 4.38             | ^b 339                  | Welty et al. \[45\]          |
| CO\(_2\)       | 3.996            | 190                     | Welty et al. \[45\]          |
| CH\(_3\)CHO    | 3.97             | 436                     | Wang et al. \[46\]           |
| H\(_2\)CNOH    | 3.585            | ^c 507                  | Welty et al. \[45\]          |
| CH\(_3\)OH     | 3.585            | 507                     | Welty et al. \[45\]          |
| CH\(_2\)CO     | 3.97             | 436                     | Wang et al. \[46\]           |
| HCON           | 3.59             | ^e 498                  | Wang et al. \[46\]           |
| HOCN           | 3.59             | ^e 498                  | Wang et al. \[46\]           |
| HCNO           | 3.59             | ^e 498                  | Wang et al. \[46\]           |
| H\(_2\)CO      | 3.59             | 498                     | Wang et al. \[46\]           |
| HCCO           | 4.221            | ^d 185                  | Welty et al. \[45\]          |
| NCO            | 3.63             | ^g 569.1                | Reid et al. \[45\]           |
| H\(_2\)O\(_2\) | 4.196            | 289.3                   | Reid et al. \[45\]           |
| trans–HNOH     | 3.47             | ^f 119                  | Welty et al. \[45\]          |
| HCO            | 3.59             | 498                     | Wang et al. \[46\]           |
| HO\(_2\)       | 3.458            | 107.4                   | Wang et al. \[46\]           |
| N\(_2\)        | 3.681            | 91.5                    | Welty et al. \[45\]          |
| H\(_2\)O       | 2.649            | 356                     | Welty et al. \[46\]          |
| O\(_2\)        | 3.433            | 113                     | Welty et al. \[46\]          |
| NO             | 3.47             | 119                     | Welty et al. \[46\]          |
| OH             | 2.75             | 80                      | Wang et al. \[46\]           |
| H\(_2\)        | 2.968            | 33.3                    | Welty et al. \[45\]          |

^a L-J parameters based on those for CO\(_2\)
^b L-J parameters based on those for NCCN
^c L-J parameters based on those for H\(_2\)CO
^d L-J parameters based on those for C\(_2\)H\(_2\)
^e L-J parameters based on those for CH\(_3\)OH
^f L-J parameters based on those for NO
^g L-J parameters based on those for HCN

Theoretical Case Studies

The following case studies provide additional details for some of the non-standard reactions in this study. Examples include intersystem crossing reactions, reactions with vibrational intermediates or complex pathways, and reactions where BHHandHLYP/aug-cc-pVDZ misdiagnosed the barrier.
Case Study 1:

\[ CO_2 + ^1O \rightarrow ^1CO_2 \rightarrow ^3CO_3 \rightarrow CO_2 + ^3O \]

The deexcitation of \(^1O\) by CO\(_2\) has been studied extensively by both experimentally and theoretically.

Experiments confirm that the dominant quenching pathway leads to ground state oxygen atoms (\(^1O\)) \[24\]. RRKM and statistical models have been explored to quench the mechanism, but the dominant of which is to react \(^1O\) by CO\(_2\) to form singlet CO\(_3\), which then undergoes intersystem crossing to the triplet CO\(_3\) potential energy surface before decaying into \(^3O + CO_2\).

An experiment by Sedlacek et al. \[24\] measures the singlet PES quenching pathway, CO\(_2\) + \(^3O\) \rightarrow \(^1CO_3\), \rightarrow CO + O\(_2\), to be approximately 1000 times less efficient than the dominant mechanism.

Experimentally measured rate coefficients for the overall quenching of \(^1O\) by CO\(_2\) in the 295–300 K range from 1.0–2.3 × 10\(^{-10}\) cm\(^3\) s\(^{-1}\). Baulch et al. \[24\] reviewed the earliest of these experimental results and has suggested a \(k(298 \text{ K})\) value of 1.8 × 10\(^{-12}\) cm\(^3\) s\(^{-1}\). Mehlmann et al. \[56\] predict this reaction to have little or no activation barrier below 400 K.

We find no theoretical studies of this reaction.

We find the first step of this reaction to be the rate-limiting step. At the BHandHLYP/aug-cc-pVDZ level of theory, the first step of this reaction has a barrier; however, at the B3LYP/aug-cc-pVDZ level of theory, this reaction step is barrierless. We remove the barrier from our calculation to match expectation from experiment and obtain an overall rate coefficient of \(k(298 \text{ K}) = 3.1 \times 10^{-12}\) cm\(^3\) s\(^{-1}\) at the BHandHLYP/aug-cc-pVDZ level of theory. This is within a factor of 1.5 of the nearest experimental value.

Case Study 2:

\[ CO_2 + ^2N \rightarrow NCO_2 \rightarrow OCNO \rightarrow CO + NO \]

Experimental measurements of the rate coefficient for this reaction at 300 K are between 1.8–6.8 × 10\(^{-13}\) cm\(^3\) s\(^{-1}\). Herron \[24\] reviewed these experiments and suggested a value of 3.6 × 10\(^{-13}\) cm\(^3\) s\(^{-1}\).

There have been no theoretical studies performed on this reaction to date.

Husain et al. \[60\] suggest this reaction has a small energy barrier due to its fairly slow rate coefficient for a reaction of high exothermicity.

We do not find a barrier for this reaction at the BHandHLYP/aug-cc-pVDZ level of theory. We also do not find a barrier at the CCSD/aug-cc-pVDZ level of theory.

On the other hand, at the HF/aug-cc-pVDZ level of theory, we find a barrier of 34.3 kJ mol\(^{-1}\) at the transition state for a C-N bond distance of 1.89 Å.

In a computational methods comparison study on the reaction of CH\(_4\) + H \rightarrow CH\(_2\) + H\(_2\), we found the variational transition state barrier at the HF/aug-cc-pVDZ level of theory to be approximately twice the size of the barrier calculated at the BHandHLYP/aug-cc-pVDZ level of theory. We insert an artificial barrier of half the HF value (17.15 kJ mol\(^{-1}\)) into the calculation for \(k(298 \text{ K})\) at the BHandHLYP/aug-cc-pVDZ level of theory, and obtain a rate coefficient of 3.2 × 10\(^{-14}\) cm\(^3\) s\(^{-1}\). This value is ~6 times smaller than the nearest experimental value.

Case Study 3:

\[ CO_2 + CH \rightarrow CHCO_2 \rightarrow HCOCO \rightarrow HCO + CO \]

The rate coefficients for this reaction have been measured experimentally at 298 K and range from 1.8–2.1 × 10\(^{-12}\) cm\(^3\) s\(^{-1}\). Baulch et al. \[24\] reviewed the earliest of these experimental results and has suggested a \(k(298 \text{ K})\) value of 1.8 × 10\(^{-12}\) cm\(^3\) s\(^{-1}\). Mehlmann et al. \[56\] predict this reaction to have little or no activation barrier below 400 K.

We find no theoretical studies of this reaction.

We find the first step of this reaction to be the rate-limiting step. At the BHandHLYP/aug-cc-pVDZ level of theory, the first step of this reaction has a barrier; however, at the B3LYP/aug-cc-pVDZ level of theory, this reaction step is barrierless. We remove the barrier from our calculation to match expectation from experiments and obtain an overall rate coefficient of \(k(298 \text{ K}) = 3.1 \times 10^{-12}\) cm\(^3\) s\(^{-1}\) at the BHandHLYP/aug-cc-pVDZ level of theory. This is within a factor of 1.5 of the nearest experimental value.

Case Study 4: \[ CO_2 + ^3CH_2 \rightarrow H_2CO + CO \]

Laufer and Bass \[24\] experimentally measured the rate coefficient for this reaction at 298 K to be 3.9 × 10\(^{-14}\) cm\(^3\) s\(^{-1}\). Darwin and Moore \[24\] performed upper bound experiments on this reaction and found \(k(298)\) to be no greater than 1.4 × 10\(^{-14}\) cm\(^3\) s\(^{-1}\).

Kovacs and Jackson \[24\] studied this reaction theoretically, and found the lowest energy path to be the \(^3\)CH\(_2\)···CO\(_2\) complex, followed by the subsequent reaction into \(^3\)CH\(_2CO_2\) over a 19.3 kcal mol\(^{-1}\) barrier (at the G2 level of theory). They found that the lowest energy path from the \(^3\)CH\(_2\)···CO\(_2\) complex is to fragment back into \(^3\)CH\(_2\) and CO\(_2\) over a 1.1 kcal mol\(^{-1}\) barrier. They also suggest an intersystem crossing reaction from this complex to the singlet surface is unlikely, and that \(^3\)CH\(_2\) would may require collisional reaction to the singlet state in order for this reaction to proceed.

We find similar results to Kovacs and Jackson \[24\] at the BHandHLYP/aug-cc-pVDZ and CCSD/aug-cc-pVDZ levels of theory. CO\(_2\) + \(^3\)CH\(_2\) proceeds via a barrierless reaction to form the \(^3\)CH\(_2\)···CO\(_2\) complex with a C-C bond distance of 3.25 (3.23) Å at the BHandHLYP/aug-cc-pVDZ (CCSD/aug-cc-pVDZ) level of theory. This reaction efficiently decays back into CO\(_2\) + \(^3\)CH\(_2\), and the barrier to \(^3\)CH\(_2CO_2\) is 15.7 (19.3) kcal mol\(^{-1}\) at the BHandHLYP/aug-cc-pVDZ (CCSD/aug-cc-pVDZ) level of theory. We find the rate coefficient for the reaction CO\(_2\) + \(^3\)CH\(_2\) →
For $\text{HCO} + \text{HCO} \rightarrow \text{H}_2\text{CO} + \text{CO}$, we find an inefficient abstraction reaction $\text{HCO} \rightarrow \text{H}_2\text{CO} + \text{CO}$. We do however find an inefficient abstraction reaction for $\text{HCO} + \text{HCO} \rightarrow \text{H}_2\text{CO} + \text{CO}$, with a $k(298\ \text{K})$ rate coefficient of $3.4\times10^{-24}\ \text{cm}^3\text{s}^{-1}$ at the BHandHLYP/aug-cc-pVDZ level of theory.

We find the reaction $\text{HCO} + \text{HCO} \rightarrow \text{trans-C}_2\text{H}_2\text{O}_2$ to have a barrierless rate coefficient of $4.1\times10^{-13}\ \text{cm}^3\text{s}^{-1}$ at 298 K at the BHandHLYP/aug-cc-pVDZ level of theory. At the same level of theory, we calculate the rate coefficient for $\text{HCO} + \text{HCO} \rightarrow \text{anti-HCOH} + \text{CO}$ ($k(298\ \text{K}) = 7.1\times10^{-34}\ \text{s}^{-1}$) to be slightly smaller than the decay back into $\text{HCO} + \text{HCO}$ ($k(298\ \text{K}) = 1.7\times10^{-33}\ \text{s}^{-1}$). Finally, we find $\text{HCOH} + \text{CO}$ to have a rate coefficient of $1.2\times10^{-13}\ \text{s}^{-1}$, which is slightly reduced from the barrierless value due to the slight preference in the decay back to $\text{HCO} + \text{HCO}$ over $\text{HCOH} + \text{CO}$. This is only a factor of 2 smaller than the nearest experimental value for $\text{HCO} + \text{HCO} \rightarrow \text{trans-C}_2\text{H}_2\text{O}_2$.

We calculate the reaction $\text{HCO} + \text{HCO} \rightarrow \text{cis-C}_2\text{H}_2\text{O}_2 \rightarrow \text{CO} + \text{CO} + \text{H}_2$ to have a rate coefficient of $k(298\ \text{K}) = 7.4\times10^{-11}\ \text{cm}^3\text{s}^{-1}$ at the BHandHLYP/aug-cc-pVDZ level of theory. This is only a factor of 2 larger than the only experimental value.

Experimental measurements of the rate coefficient for this reaction at 296–300 K range from $8.5\times10^{-14}$ to $9.7\times10^{-13}\ \text{cm}^3\text{s}^{-1}$.

Baulch et al. review the kinetic data from experiments and suggest a very slight temperature dependence, suggesting this reaction proceeds with little or no reaction barrier.

There are multiple reaction pathways for this reaction, but the fastest is that which proceeds through the $\text{OH} \cdot \cdot \cdot \text{CO} \cdot \cdot \cdot \text{cis-HOCO} \cdot \cdot \cdot \text{intermediate}$. At the BHandHLYP/aug-cc-pVDZ level of theory, we calculate $k(298\ \text{K})$ for the barrierless first step, $\text{CO} + \text{OH} \rightarrow \text{OH} \cdot \cdot \cdot \text{CO} \cdot \cdot \cdot$, to be $9.7\times10^{-12}\ \text{cm}^3\text{s}^{-1}$. However, we find intermediate barriers at the second and third steps of this calculation at the BHandHLYP/aug-cc-pVDZ level of theory, making the overall rate coefficient for $\text{CO} + \text{OH} \rightarrow \text{OH} \cdot \cdot \cdot \text{CO} \cdot \cdot \cdot \text{cis-HOCO} \cdot \cdot \cdot \text{CO}_2 + \text{H}, 5.7\times10^{-19}\ \text{cm}^3\text{s}^{-1}$. This is several orders of magnitude smaller than the range of experimental values. At the B3LYP/aug-cc-pVDZ level of theory, these barriers are more comparable, resulting in only a factor of 3.4 reduction between the barrierless first step and the overall rate coefficient. Ab initio calculations show similar barrier heights to our the B3LYP/aug-cc-pVDZ calculation.

We reduce the calculated rate coefficient for the barrierless first step at the BHandHLYP/aug-cc-pVDZ level of theory by a factor of 3.4 to match the barrier effects at the B3LYP/aug-cc-pVDZ level of theory. This gives us a rate coefficient of $k(298) = 2.9\times10^{-12}\ \text{cm}^3\text{s}^{-1}$, which is a factor of 3 higher than the nearest experimental value.
Experimental measurements for this reaction at 298–300 K range from 2.3–4.3×10⁻¹¹ cm³s⁻¹ [157][160].

This reaction proceeds through HO₂, which, in its ground vibrational state has been noted to be long-lived [157][158][159]. Our calculations confirm that the decay of HO₂ into O₂ + H is slow (<10⁻⁴⁷ s⁻¹). This suggests this reaction proceeds through an excited vibrational state, as is to be expected when two reactants combine to form a single product [160].

We calculate the rate coefficient of OH + ³O → HO₂ at 298 K at the BHandHLYP/aug-cc-pVDZ level of theory to be 7.4×10⁻¹¹ cm³s⁻¹, and assume the subsequent vibrational decay into O₂ + H. Our calculated rate coefficient is within a factor of 2 of the experimental range.

There are currently no experimental measurements for the rate coefficient of OH + ³O → O₂ + H, which we find also proceeds through HO₂. We calculate the rate coefficient of OH + ¹O → HO₂ at 298 K at the BHandHLYP/aug-cc-pVDZ level of theory to be 1.0×10⁻⁹ cm³s⁻¹, and similarly assume the vibrational decay into O₂ + H.

Case Study 8: OH + NH → products

No experiments have been performed to date on the reaction of OH + NH. Cohen and Westberg [25] use analogous reactions to suggest rate coefficients of k(298 K) = 3.3×10⁻¹¹ cm³s⁻¹ and 5.1×10⁻¹² cm³s⁻¹ for OH + NH → HNO + H and OH + NH → H₂O + ⁴N, respectively. They suggest little or no barrier exists for either pathway.

Grado n performed theoretical transition state theory calculations for this reaction using a range of computational quantum methods. They calculated 298 K reaction rate coefficients of 6.8×10⁻¹¹ cm³s⁻¹ and 1.4×10⁻¹² cm³s⁻¹ for OH + NH → HNO + H and OH + NH → H₂O + ⁴N, respectively.

We find the OH + NH → HNO + H reaction to proceed through multiple intermediates, including OH··NH·, trans-HNOH·, and H₂NO·. We calculate the barrierless first step of this reaction OH + NH → OH··NH· at 298 K at the BHandHLYP/aug-cc-pVDZ level of theory to be 7.0×10⁻¹² cm³s⁻¹. However, at this level of theory, we find a large forward barrier at the third reaction step (i.e., trans-HNOH· → HNO + H), which reduces the overall rate coefficient to 2.6×10⁻¹⁴ cm³s⁻¹. This is over three orders of magnitude smaller than the recommended and theoretical values. Conversely, at the B3LYP/aug-cc-pVDZ level of theory, the third forward reaction step barrier is smaller than the reverse barrier, which makes the barrierless first step the rate limiting step.

We remove the barrier at the third reaction step from our calculation to match the kinetic data and theoretical studies, and obtain an overall rate coefficient for OH + NH → HNO + H of k(298 K) = 7.0×10⁻¹² cm³s⁻¹ at the BHandHLYP/aug-cc-pVDZ level of theory. This value is a factor of 5 smaller than the suggested value [25].

We calculate the rate coefficient for OH + NH → H₂O + NH at 298 K at the BHandHLYP/aug-cc-pVDZ level of theory to be 6.8×10⁻¹³ cm³s⁻¹. This is a factor of 5 smaller than the suggested value by Cohen and Westberg [25].

Case Study 9: O + H₂CN → CH₃NO· → products

No experiments to date have measured the rate coefficient of ³O + H₂CN → HCN + OH. Tomeczek and Grado n suggested a temperature-independent rate of 8.5×10⁻¹¹ cm³s⁻¹ based on calculations using published chemical compositions of the flames of methane, nitrogen and oxygen at >1850 K. They note that this calculation does not include the effects of an energy barrier, and thus this value is not reliable at 298 K. Tomeczek and Grado n also suggested this same rate coefficient for the reaction H + H₂CN → HCN + H₂.

No previous theoretical studies regarding this reaction have been performed.

Unlike H + H₂CN → HCN + H₂, which we found in previous work to proceed efficiently through a barrierless abstraction mechanism [19], we find no abstraction pathway for ³O + H₂CN → HCN + OH. Instead, we find that ³O and H₂CN efficiently react to form CH₃NO· with a rate coefficient of 3.1×10⁻¹¹ cm³s⁻¹. This product most commonly decays back into the original reactants; however, there are two other favorable pathways. The mechanistic model for these reactions is shown in Figure S1.

FIG. S1. Mechanistic model for the reaction of ³O + H₂CN. Two efficient product channels on the doublet surface exist: (A) HCN + OH and (B) HCNO + H.

Using the mechanistic model above, we use the steady-state solutions to the kinetic rate equations to calculate the overall rate coefficients for paths A and B. This is done by equating the kinetic rate equations for each species in the mechanistic model to zero (e.g. \( \frac{d[CH₂NO]}{dt} = 0 = k₁[³O + H₂CN] + k₂[HCNOH] - (k₋₁ + k₂)[CH₂NO] \)), and substituting these equations...
into the overall kinetic rate equations for products A and B from the initial reactants. This gives us the following rate coefficients for paths A and B:

\[ k_A = \frac{k_1k_3}{\alpha}, \quad (S6) \]

\[ \alpha = \frac{(k_{-1} + k_2 + k_4)(k_{-2} + k_3)}{k_2} - k_{-2}. \quad (S7) \]

\[ k_B = \frac{k_1k_4}{\beta}, \quad (S8) \]

\[ \beta = k_{-1} + k_2 + k_4 - \frac{k_{-2}k_2}{k_{-2} + k_3}. \quad (S9) \]

We calculate these rate coefficients at the BHandHLYP/aug-cc-pVDZ level of theory to be \( k_A = 4.0 \times 10^{-14} \) and \( k_B = 8.3 \times 10^{-15} \) cm\(^3\)s\(^{-1}\) at 298 K, respectively.

We propose that the suggested barrierless rate coefficient for \( ^3\)O + H\(_2\)CN → HCN + OH by Tomeczek and Grado´n \(^{252}\) is not an accurate estimate for this overall reaction at 298 K. In fact, the large barrier for CH\(_2\)NO · → HCNOH · isomerization at 298 K plays a key role in decreasing this overall rate coefficient. We find the isomerization barrier to also have similar heights when using the B3LYP and CCSD computational methods.

We use similar mechanistic modeling to calculate the rate coefficients for the reactions of \(^1\)O + H\(_2\)CN → CH\(_2\)NO · → products. However, along with the two decay pathways above, there is an additional decay pathway to \(^3\)O + H\(_2\)CN. We are the first to calculate these three \(^1\)O + H\(_2\)CN reaction rate coefficients.

At the BHandHLYP/aug-cc-pVDZ level of theory, we calculate the rate coefficients for the reaction of \(^1\)O + H\(_2\)CN to products (A) HCN + OH, (B) HCNO + H, and (C) \(^3\)O + H\(_2\)CN, to be \(1.2 \times 10^{-13}, 6.0 \times 10^{-13}, \) and \(4.5 \times 10^{-10} \) cm\(^3\)s\(^{-1}\), respectively.

Given the potential importance of \(^1\)O + H\(_2\)CN → HCN + OH to produce HCN in atmospheres, and the similar barrier heights to the three product channels, we also calculated these rate coefficients at the \(\omega\)B97XD/aug-cc-pVDZ and CCSD/aug-cc-pVDZ levels of theory.

At the \(\omega\)B97XD/aug-cc-pVDZ level of theory, we calculate the rate coefficients for the reaction of \(^1\)O + H\(_2\)CN to products (A) (B), and (C), to be \(5.3 \times 10^{-11}, 2.8 \times 10^{-10}, \) and \(6.6 \times 10^{-23} \) cm\(^3\)s\(^{-1}\), respectively.

At the CCSD/aug-cc-pVDZ level of theory, we calculate the rate coefficients for the reaction of \(^1\)O + H\(_2\)CN to products (A), (B), and (C), to be \(8.8 \times 10^{-11}, 1.9 \times 10^{-11}, \) and \(2.2 \times 10^{-10} \) cm\(^3\)s\(^{-1}\), respectively.

In the case of BHandHLYP and CCSD, the dominant channel for the reaction of \(^1\)O + H\(_2\)CN is (C). This is not the case for \(\omega\)B97XD, where channel (C) is negligible, and the dominant channel is (B). The rate coefficient for the potentially important HCN source, channel (A), varies by a factor of 733 across the three levels of theory. Given these discrepancies, we recommend these reactions be followed up with an experimental study.

**Case Study 10: \(^3\)O + CH\(_2\) → products**

\(^3\)O + \(^3\)CH\(_2\) combine to form a vibrationally excited H\(_2\)CO molecule\(^{259}\). In high atmospheric pressures, this molecule can be collisionally deexcited in the reaction

\(^3\)O + \(^3\)CH\(_2\) + M → H\(_2\)CO + M.

However, in upper atmospheres, where collisions are less frequent, the vibrationally excited H\(_2\)CO will dissociate via 2 equally favourable pathways:

\(^3\)O + \(^3\)CH\(_2\) → H\(_2\)CO\((\nu)\) · → CO + H + H

\(^3\)O + \(^3\)CH\(_2\) → H\(_2\)CO\((\nu)\) · → CO + H\(_2\)

Experimental measurements of the rate coefficient of \(^3\)O + \(^3\)CH\(_2\) → products at 295–296 K are \(1.3 \times 10^{-10} \) cm\(^3\)s\(^{-1}\) \(^{222,223}\). Reviews of this reaction over a range of temperatures and pressures suggest a wider range of \(1.9 \times 10^{-11}–2.0 \times 10^{-10} \) cm\(^3\)s\(^{-1}\) \(^{27,28}\).

We calculate the rate coefficient of \(^3\)O + \(^3\)CH\(_2\) → H\(_2\)CO at the BHandHLYP/aug-cc-pVDZ level of theory to be \(k(298 \text{ K}) = 6.7 \times 10^{-11} \) cm\(^3\)s\(^{-1}\), which is within the range of suggested values, and only a factor of 2 lower than the two experimental measurements. We allow this reaction to proceed along the two equally favourable dissociation channels, each with a calculated rate coefficient of \(3.4 \times 10^{-11} \) cm\(^3\)s\(^{-1}\).

Excited oxygen \((^1\)O) and methylene \((^1\)CH\(_2\)) also react to produce vibrationally excited H\(_2\)CO.

We calculate the rate coefficient of \(^1\)O + \(^1\)CH\(_2\) → H\(_2\)CO at the BHandHLYP/aug-cc-pVDZ level of theory to be \(k(298 \text{ K}) = 3.3 \times 10^{-10} \) cm\(^3\)s\(^{-1}\)\(^\pm 3\). We assume that the two dissociation pathways for vibrationally excited H\(_2\)CO are equally favourable for this reaction, and allow this reaction to proceed to form CO + H + H and CO + H\(_2\) with equal rate coefficients of \(1.7 \times 10^{-10} \) cm\(^3\)s\(^{-1}\).

**Case Study 11: \(^1\)O + CH\(_4\) → CH\(_3\)OH\((\nu)\) → OH + CH\(_3\)**

\(^1\)O and CH\(_4\) mainly react to form vibrationally excited CH\(_3\)OH, the dominant subsequent pathway of which is to produce OH + CH\(_3\) \(^{291,292,293}\).

Experimental measurements of \(^1\)O + CH\(_4\) → OH + CH\(_3\) from 295–300 K range from \(1.4–3.8 \times 10^{-10}\) \(^{252,253,254,255}\).
We calculate the rate coefficient of $^1$O + CH$_4$ $\rightarrow$ CH$_3$OH at 298 K with the BHandHLYP/aug-cc-pVDZ level of theory to be $5.8 \times 10^{-9}$ cm$^3$s$^{-1}$, and assume the vibrational decay into OH + CH$_3$ as suggested. Our calculated rate coefficient is a factor of 15 larger than the nearest experimental value.

**Case Study 12:** $^1$O + H$_2$ $\rightarrow$ H$_2$O($\nu$) $\rightarrow$ OH + H

Experimental measurements of the rate coefficient for $^1$O + H$_2$ $\rightarrow$ OH + H at 298–300 K are between $1.1 \times 10^{-10}$ and $3.0 \times 10^{-10}$ cm$^3$s$^{-1}$.

This reaction is known to proceed through vibrationally excited H$_2$O in its ground electronic state.

We calculate the rate coefficient for $^1$O + H$_2$ $\rightarrow$ H$_2$O at 298 K at the BHandHLYP/aug-cc-pVDZ level of theory to be $7.1 \times 10^{-10}$ cm$^3$s$^{-1}$, and assume vibrational decay into OH + H, as suggested. This calculated value is a factor of 2 larger than the nearest experimental value.

### Quantum Chemistry Data

**TABLE S5:** Quantum Chemistry Simulation Data at the BHandHLYP/aug-cc-pVDZ level of theory. Cartesian coordinates are in angstroms. Energies are in kJ mol$^{-1}$. $E_e$ is the electronic energy, ZPE is the zero point energy, and $q_{vt}$ are the partition functions (t: translational, e: electronic, v:vibrational, r:rotational).

| Reac. Species | Geometry (Atom, X, Y, Z) | $E_e + ZPE$ | q/$V$ (m$^{-3}$) | q$_{e}$ | q$_{v}$ | q$_{r}$ |
|---------------|--------------------------|-------------|-----------------|--------|--------|--------|
| 1/33 CO$_2$   | O, 0.00000, 0.00000, 1.15274 | -494197.399028 | 2.82E+32 | 1.07E+00 | 5.23E+02 |
|               | O, 0.00000, 0.00000, -1.15274 | -196788.921964 | 6.19E+31 | 1.00E+00 | 1.00E+00 |
|               | C, 0.00000, 0.00000, 0.00000 | -691707.204162 | 4.49E+32 | 1.07E+00 | 1.26E+05 |
| 1/33 O        | O, 0.00000, 0.00000, 0.00000 | -196788.921964 | 6.19E+31 | 1.00E+00 | 1.00E+00 |
| 1/33 TS       | O, 1.15275, 1.18505, 0.00000 | -691904.373961 | 4.49E+32 | 1.14E+00 | 2.10E+04 |
| 1/33 CO$_3$   | O, 0.77156, -0.80876, 0.00000 | -298768.200141 | 1.51E+32 | 1.00E+00 | 7.26E+02 |

**Table Continued...**
H, 0.60545, 0.13501, 0.00000
O, -1.43123, -0.39780, 0.00000
O, 1.89813, -0.12784, 0.00000

42 H₂CO
C, 0.00000, -0.52451, 0.00000
H, 0.00000, -1.10548, -0.93804
H, 0.00000, -1.10548, 0.93804
O, 0.00000, 0.66975, 0.00000

¹O
O, 0.00000, 0.00000, 0.00000
TS
C, -1.77953, 0.34320, 0.00000
H, -1.48268, 1.40545, 0.00000
H, -2.86259, 0.13442, -0.00000
O, -0.97089, -0.53624, 0.00000
O, 2.84870, 0.08636, 0.00000

43 H₂CO
C, 0.00000, -0.52451, 0.00000
H, 0.00000, -1.10548, -0.93804
H, 0.00000, -1.10548, 0.93804
O, 0.00000, 0.66975, 0.00000
CH₃
C, 0.00000, -0.00018, 0.00042
H, -0.93570, -0.53955, -0.00085
H, 0.93580, -0.53939, -0.00085
O, 0.00000, 0.66975, 0.00000
TS
C, 0.78646, 0.45348, 0.00000
H, 1.07291, 1.52901, 0.00000
H, -0.51355, 0.21771, 0.00000
O, 1.57243, -0.42799, 0.00000
C, -1.89866, -0.09510, 0.00000
H, -1.90272, -1.18086, -0.00001
H, -2.28144, 0.35391, -0.91204
H, -2.28144, 0.35392, 0.91204

44 H₂CO
C, 0.00000, -0.52451, 0.00000
H, 0.00000, -1.10548, -0.93804
H, 0.00000, -1.10548, 0.93804
O, 0.00000, 0.66975, 0.00000
³CH₂
C, 0.00000, 0.00000, 0.10395
H, 0.00000, -0.99689, -0.31186
H, 0.00000, 0.99689, -0.31186
TS
C, 0.14050, 0.09150, 0.05065
O, 0.06828, -0.07800, 1.21819
H, 0.89195, -0.40846, -0.59523
C, -1.56816, 1.76660, -1.21646
H, -0.63273, 0.85440, -0.54742
H, -2.29851, 2.25059, -0.58010
H, -1.47869, 1.90289, -2.28736

45 H₂CO
C, 0.00000, -0.52451, 0.00000
H, 0.00000, -1.10548, -0.93804
H, 0.00000, -1.10548, 0.93804
O, 0.00000, 0.66975, 0.00000
³CH₂
C, 0.00000, 0.17399, 0.00000
H, 0.86403, -0.52196, 0.00000
H, -0.86403, -0.52196, 0.00000
TS
C, -0.68910, 0.48572, -0.08639
O, -1.38273, -0.46949, 0.05703
H, -0.94950, 1.48003, 0.31230
C, 2.03635, -0.06055, -0.09460
H, 0.26632, 0.44354, -0.67581
H, 1.72584, -1.10952, 0.07940
H, 1.93572, 0.39090, 0.91387

46 H₂CO
C, 0.00000, -0.52451, 0.00000
H, 0.00000, -1.10548, -0.93804
H, 0.00000, -1.10548, 0.93804
O, 0.00000, 0.66975, 0.00000
CH
C, 0.00000, 0.00000, 0.16040
H, 0.00000, 0.00000, -0.96239

-300426.644475 1.59E+32 1 1.00E+00 1.39E+03
-300426.644475 1.59E+32 1 1.00E+00 1.39E+03
-300426.644475 1.59E+32 1 1.00E+00 1.39E+03
-300426.644475 1.59E+32 1 1.00E+00 1.39E+03
-300426.644475 1.59E+32 1 1.00E+00 1.39E+03
| Reaction | C       | O       | H       | N       | H       | E    | Z   |
|----------|---------|---------|---------|---------|---------|-----|-----|
| TS(CO + NH₂) | 1.00716 | -0.60363 | 0.00000 | 1.00000 | -0.58725 | 5.63E+31 | 1.00E+00 | 1.24E+01 |
| TS(HNHCO) C | 0.79683 | 0.38808 | -0.00001 | -0.85649 | 1.22238 | 2.83E+32 | 2.37E+01 | 3.02E+04 |
| TS C | -0.73136 | 0.43137 | -0.00000 | -0.72905 | 0.41200 | -0.21E-01 | 0.00E+00 | 2.37E+04 |
| TS C | -0.96022 | 0.53343 | -0.00000 | -0.72905 | 0.41200 | -0.21E-01 | 0.00E+00 | 2.37E+04 |
| TS C | -1.02091 | 0.53057 | -0.00000 | -0.72905 | 0.41200 | -0.21E-01 | 0.00E+00 | 2.37E+04 |
| TS C | -1.18076 | 0.58286 | -0.00000 | -0.93570 | 0.53955 | -0.15E+01 | 0.00E+00 | 2.37E+04 |
| TS C | -1.18076 | 0.58286 | -0.00000 | -1.80285 | 0.60268 | -0.15E+01 | 0.00E+00 | 2.37E+04 |
| HCO C | 0.06118 | 0.57927 | 0.00000 | -0.93570 | 0.53955 | -0.15E+01 | 0.00E+00 | 2.37E+04 |
| HCO C | 0.06118 | 0.57927 | 0.00000 | -1.80285 | 0.60268 | -0.15E+01 | 0.00E+00 | 2.37E+04 |
\[ CH_2 \]

C, 0.00000, 0.00000, 0.10395
H, 0.00000, -0.99689, -0.31186
H, 0.00000, 0.99689, -0.31186

TS(CH_3 + CO)
C, 1.18089, -0.58830, 0.00000
O, 1.76377, 0.42079, -0.00000
H, 0.06058, -0.69428, -0.00001
H, -2.39692, -0.07616, 0.00000
H, -2.55762, 1.15053, 0.00001

TS(CH_2HCO)
C, 0.88495, 0.42556, -0.00000
O, 1.70057, -0.40713, 0.00000
H, 1.07614, 1.52704, -0.00000
H, -2.55118, -1.14473, -0.00000
H, -3.05762, 0.77835, 0.00001

65
HCO
C, 0.06118, 0.57927, 0.00000
O, 0.06118, -0.58725, 0.00000
H, -0.85649, 1.22238, 0.00000

\[ CH \]

C, 0.00000, 0.00000, 0.16040
H, 0.00000, 0.00000, -0.96239

TS
C, -1.00243, 0.52281, 0.00000
O, -1.75206, -0.37324, 0.00000
H, 0.11410, 0.43659, -0.00000
H, -3.54630, -0.03468, 0.08692
H, -7.34349, 0.94753, -0.41695

66
HCO
C, 0.06118, 0.57927, 0.00000
O, 0.06118, -0.58725, 0.00000
H, -0.85649, 1.22238, 0.00000

CH
C, 0.00000, 0.00000, 0.16040
H, 0.00000, 0.00000, -0.96239

TS
C, 0.95316, -0.57236, -0.06467
O, 1.55803, 0.41893, 0.04383
H, -0.17127, -0.65680, -0.06725
H, -2.54630, -0.03468, 0.08692
H, -7.34349, 0.94753, -0.41695

68/69
HCO
C, 0.06118, 0.57927, 0.00000
O, 0.06118, -0.58725, 0.00000
H, -0.85649, 1.22238, 0.00000

H
C, 0.00000, 0.00000, -0.64038

TS(CO + H_2)
C, 0.10339, -0.52516, -0.00000
O, -0.66721, 0.34873, 0.00000
H, 1.22122, -0.40563, 0.00005
H, 3.49608, 0.76762, -0.00001

TS(H_2CO)
C, -0.28186, 0.33762, 0.00000
O, 0.67158, -0.33299, -0.00000
H, -0.28760, 1.45702, -0.00001
H, -3.39303, -0.81883, -0.00000

71
CO
C, 0.00000, 0.00000, -0.64038
O, 0.00000, 0.00000, 0.48029

OH
O, 0.00000, 0.00000, 0.10734
H, 0.00000, 0.00000, -0.85876

TS
O, 0.00000, 0.00000, 2.70789

-102701.224038  5.08E+31  3  1.01E+00  8.96E+01

-401475.384064  2.73E+32  2  1.46E+02  3.90E+04

-401473.748377  2.73E+32  2  1.12E+02  3.36E+04

-102649.483309  5.08E+31  1  1.00E+00  1.31E+02

-401422.503868  2.73E+32  2  8.57E+01  3.13E+04

-298768.200141  1.51E+32  2  1.00E+00  7.26E+02

-100985.100094  4.54E+31  2  1.00E+00  1.44E+01

-399758.934558  2.63E+32  3  2.76E+01  3.09E+04

-298768.200141  1.51E+32  2  1.00E+00  7.26E+02

-100985.100094  4.54E+31  2  1.00E+00  1.44E+01

-399761.111098  2.63E+32  1  2.66E+01  3.08E+04

-298768.200141  1.51E+32  2  1.00E+00  7.26E+02

-1307.704984  9.79E+29  2  1.00E+00  1.00E+00

-300077.962322  1.59E+03  1  4.64E+02  4.25E+03

-300077.773286  1.59E+03  1  5.26E+00  4.04E+03

-297385.023729  1.43E+02  1  1.00E+00  1.06E+02

-198772.724511  6.78E+31  2  1.00E+00  1.09E+01

-496160.381617  2.92E+32  2  2.35E+01  2.55E+03
| Entry | Formula | Coordinates | Energy | ZPE | Enthalpy | Entropy | G | B | T | A |
|-------|---------|-------------|--------|-----|----------|---------|----|---|---|---|
| 72    | H₂O     | H, 0.0000, 0.0000, 1.73998 C, 0.0000, 0.0000, -1.03211 O, 0.0000, 0.0000, -2.15130 | -200534.424509 | 7.40E+31 | 1.00E+00 | 8.42E+01 |    |   |   |   |
| 73    | H₂O     | H, 0.0000, 0.0000, 0.11552 O, 0.0000, 0.75819, -1.46207 O, 0.0000, -0.75819, -1.46207 | -200534.424509 | 7.40E+31 | 1.00E+00 | 8.42E+01 |    |   |   |   |
| TS    | O       | H, -1.88602, 0.75858, 0.39238 O, -1.58903, -0.0000, -0.10594 H, -1.88608, -0.75855, 0.39240 O, 2.05919, -0.0000, 0.00784 | -197688.921964 | 6.19E+31 | 1.00E+00 | 1.00E+00 |    |   |   |   |
| TS(H₂OCN) | O | C, 0.0000, -1.88062, 0.75858, 0.39238 O, -1.58903, -0.0000, -0.10594 H, -1.88608, -0.75855, 0.39240 O, 2.05919, -0.0000, 0.00784 | -196788.921964 | 6.19E+31 | 1.00E+00 | 1.00E+00 |    |   |   |   |
| TS(OH + HCN) | O | H, -1.88068, -0.75855, 0.39240 O, 2.05919, -0.0000, 0.00784 C, 0.0000, 0.0000, -0.16237 | -196788.921964 | 6.19E+31 | 1.00E+00 | 1.00E+00 |    |   |   |   |
| 74    | H₂O     | H, 0.0000, 0.0000, 1.1552 O, 0.0000, 0.75819, -1.46207 O, 0.0000, -0.75819, -1.46207 | -200534.424509 | 7.40E+31 | 1.00E+00 | 8.42E+01 |    |   |   |   |
| 2N    | N       | C, 0.0000, -1.88062, 0.75858, 0.39238 O, -1.58903, -0.0000, -0.10594 H, -1.88608, -0.75855, 0.39240 O, 2.05919, -0.0000, 0.00784 | -196788.921964 | 6.19E+31 | 1.00E+00 | 1.00E+00 |    |   |   |   |
| TS    | O       | H, -1.88068, -0.75855, 0.39240 O, 2.05919, -0.0000, 0.00784 C, 0.0000, 0.0000, -0.16237 | -196788.921964 | 6.19E+31 | 1.00E+00 | 1.00E+00 |    |   |   |   |
| 75    | H₂O     | H, 0.0000, 0.0000, 1.1552 O, 0.0000, 0.75819, -1.46207 O, 0.0000, -0.75819, -1.46207 | -200534.424509 | 7.40E+31 | 1.00E+00 | 8.42E+01 |    |   |   |   |
| CH    | C       | C, 0.0000, -1.88062, 0.75858, 0.39238 O, -1.58903, -0.0000, -0.10594 H, -1.88608, -0.75855, 0.39240 O, 2.05919, -0.0000, 0.00784 | -196788.921964 | 6.19E+31 | 1.00E+00 | 1.00E+00 |    |   |   |   |
| TS    | O       | H, -1.88068, -0.75855, 0.39240 O, 2.05919, -0.0000, 0.00784 C, 0.0000, 0.0000, -0.16237 | -196788.921964 | 6.19E+31 | 1.00E+00 | 1.00E+00 |    |   |   |   |
| 76/92 | H₂O     | H, 0.0000, 0.0000, 1.1552 O, 0.0000, 0.75819, -1.46207 O, 0.0000, -0.75819, -1.46207 | -200534.424509 | 7.40E+31 | 1.00E+00 | 8.42E+01 |    |   |   |   |
| CH    | C       | C, 0.0000, -1.88062, 0.75858, 0.39238 O, -1.58903, -0.0000, -0.10594 H, -1.88608, -0.75855, 0.39240 O, 2.05919, -0.0000, 0.00784 | -196788.921964 | 6.19E+31 | 1.00E+00 | 1.00E+00 |    |   |   |   |
| TS    | O       | H, -1.88068, -0.75855, 0.39240 O, 2.05919, -0.0000, 0.00784 C, 0.0000, 0.0000, -0.16237 | -196788.921964 | 6.19E+31 | 1.00E+00 | 1.00E+00 |    |   |   |   |
| OH    | O       | H, 0.0000, 0.0000, 1.1552 O, 0.0000, 0.75819, -1.46207 O, 0.0000, -0.75819, -1.46207 | -196788.921964 | 6.19E+31 | 1.00E+00 | 1.00E+00 |    |   |   |   |
| 3CH₂  | C       | C, 0.0000, -1.88062, 0.75858, 0.39238 O, -1.58903, -0.0000, -0.10594 H, -1.88608, -0.75855, 0.39240 O, 2.05919, -0.0000, 0.00784 | -196788.921964 | 6.19E+31 | 1.00E+00 | 1.00E+00 |    |   |   |   |
77  OH  
H, 0.00000, 0.99689, -0.31186  
O, 0.00000, 0.00000, 0.10734  
-198772.724511 6.78E+31 2 1.00E+00 1.09E+01
H, 0.00000, 0.00000, -0.85876
HCN  
N, 0.00000, 0.00000, 0.64811  
C, 0.00000, 0.00000, -0.49567  
H, 0.00000, 0.00000, -1.56273 
-245122.398339 1.36E+32 1 1.05E+00 1.38E+02
TS  
N, 1.18289, -0.45813, 0.00000  
C, 0.53038, 0.50741, 0.00000  
H, 0.29374, 1.55076, 0.00000
-443875.717780 2.83E+32 2 1.07E+00 1.34E+04

78  OH  
H, 0.00000, 0.00000, 0.10734  
O, 0.00000, 0.00000, 0.85876
CN  
N, 0.00000, 0.00000, 0.53334  
C, 0.00000, 0.00000, 0.62339
-243282.319290 1.28E+32 2 1.00E+00 1.06E+02

TS(HO···CN)  
C, -2.32702, -0.06687, 0.00000  
O, 1.05860, -0.06687, 0.00000
-442060.005996 2.73E+32 3 6.27E+01 1.16E+04

3HOCN  
O, 1.31726, -0.06057, -0.11557  
C, -0.15295, 0.51436, -0.07208
H, 0.93798, 0.53268, 0.00000
-442054.894147 2.73E+32 3 1.38E+00 6.50E+03

TS(HO···CN)  
C, -0.57866, -0.37506, 0.00000  
O, 1.06580, -0.23905, -0.00000
H, 2.14288, 0.16576, 0.00000
-442071.736730 2.73E+32 3 3.19E+01 1.16E+04

TS(3HOCN)  
O, 1.07076, -0.23701, 0.00000  
H, 1.04987, 0.95445, -0.00000
C, -0.10294, 0.31551, 0.00000
-442054.894147 2.73E+32 3 1.47E+00 6.08E+03

79  OH  
H, 0.00000, 0.00000, 0.10734  
O, 0.00000, 0.00000, 0.85876
CN  
N, 0.00000, 0.00000, 0.53334  
C, 0.00000, 0.00000, 0.62339
-243282.319290 1.28E+32 2 1.00E+00 1.06E+02
TS  
O, 1.77507, -0.07477, 0.00000  
H, 0.93798, 0.53268, 0.00000
C, -0.54988, 0.09824, 0.00000
-442050.029096 2.73E+32 3 5.20E+00 1.32E+04

3HOCN  
O, 1.00788, -0.18867, -0.07300  
H, 1.50896, 0.17125, 0.59267
C, -0.15259, 0.44358, -0.05620
-442021.236892 2.73E+32 3 1.38E+00 6.50E+03

TS(3HOCN)  
O, 0.86057, -0.06057, -0.11557  
C, -0.15295, 0.51436, -0.07208
H, 0.93798, 0.53268, 0.00000
-442054.894147 2.73E+32 3 1.47E+00 6.08E+03

80  OH  
H, 0.00000, 0.00000, 0.10734  
O, 0.00000, 0.00000, 0.85876
CN  
N, 0.00000, 0.00000, 0.53334  
C, 0.00000, 0.00000, 0.62339
-243282.319290 1.28E+32 2 1.00E+00 1.06E+02
TS  
O, -1.47228, -0.16710, 0.00000  
H, -0.76057, 0.69068, 0.00000
C, 1.34908, -0.45881, 0.00000
-442023.178107 2.73E+32 3 5.20E+00 1.32E+04

81  OH  
H, 0.00000, 0.00000, 0.10734  
O, 0.00000, 0.00000, 0.85876
CN  
N, 0.00000, 0.00000, 0.53334  
C, 0.00000, 0.00000, 0.62339
-243282.319290 1.28E+32 2 1.00E+00 1.06E+02
TS  
H, 1.14564, -0.83725, -0.00000  
O, 1.44781, 0.08292, 0.00000
-397324.930652 1.92E+32 3 2.29E+00 6.78E+03

85  OH  
H, 0.00000, 0.00000, 0.10734  
O, 0.00000, 0.00000, 0.85876
NH  
N, 0.00000, 0.00000, -0.03255  
H, 0.00000, 0.00000, 1.03180
-144933.050538 5.63E+31 3 1.00E+00 1.24E+01
TS  
O, 0.05070, -1.15122, 0.00000
H, -0.90707, -1.27429, 0.00000
-343699.917559 1.75E+32 4 1.36E+00 3.77E+03
| Reaction | Coordinates | Energy | Frequency | Intensity |
|----------|-------------|--------|-----------|-----------|
| TS(HCNO + H) | C, -1.01152, 0.43493, 0.00000 | -443628.579465 | 2.83E+32 | 2 1.99E+00 7.86E+03 |
| | N, 0.00000, -0.12833, 0.00000 | | | |
| | H, -2.06888, 0.55214, 0.00000 | | | |
| | O, 1.09251, -0.60621, 0.00000 | | | |
| HCNO | N, 0.01434, -0.00045, 0.00000 | -443625.880451 | 2.83E+32 | 2 1.16E+00 8.32E+03 |
| | C, 1.16967, -0.00244, 0.00000 | | | |
| | H, 2.23036, 0.01076, 0.00000 | | | |
| | O, -1.17517, 1.00421, 0.00000 | | | |
| H | N, 1.13711, 0.29236, 0.00000 | -443791.239692 | 2.83E+32 | 2 1.32E+00 7.41E+03 |
| | C, 1.13197, -0.37849, 0.00000 | | | |
| | H, 2.17962, -0.01488, 0.00000 | | | |
| | O, -1.07487, 1.00421, 0.00000 | | | |
| TS(HCNOH) | C, 0.00000, 0.00000, -0.62339 | -197065.919094 | 6.19E+31 | 3 1.00E+00 1.00E+00 |
| | N, 0.00000, 0.00000, 1.12869 | | | |
| | H, -2.05048, 0.00059, 1.10631 | | | |
| 102/103 | 102 | O, 0.00000, 0.00000, 0.00000 | -197065.919094 | 6.19E+31 | 3 1.00E+00 1.00E+00 |
| | H, 0.00000, 0.00000, 0.00000 | | | |
| | O, 0.00000, 0.00000, 0.00000 | | | |
| 104 | 104 | O, 0.00000, 0.00000, 0.00000 | -197065.919094 | 6.19E+31 | 3 1.00E+00 1.00E+00 |
| | H, 0.00000, 0.00000, 0.00000 | | | |
| | O, 0.00000, 0.00000, 0.00000 | | | |
| 106 | 106 | O, 0.00000, 0.00000, 0.00000 | -197065.919094 | 6.19E+31 | 3 1.00E+00 1.00E+00 |
| | H, 0.00000, 0.00000, 0.00000 | | | |
| | O, 0.00000, 0.00000, 0.00000 | | | |
| 107 | 107 | O, 0.00000, 0.00000, 0.00000 | -197065.919094 | 6.19E+31 | 3 1.00E+00 1.00E+00 |
| | H, 0.00000, 0.00000, 0.00000 | | | |
| | O, 0.00000, 0.00000, 0.00000 | | | |
| 109 | $^3$O | O, 0.00000, 0.00000, 0.00000 -197065.919094 6.19E+31 3 1.00E+00 1.00E+00 |
| CH$_3$ | C, 0.00000, -0.00018, 0.00042 -10455.380974 5.63E+31 2 1.08E+00 2.53E+02 |
| H, -0.93570, -0.53955, -0.00085 |
| H, 0.93580, -0.53939, -0.00085 |
| TS | C, -1.66894, -0.00071, 0.00146 -301523.504861 1.67E+32 2 9.00E+00 1.43E+04 |
| H, -1.70388, -0.20404, -1.05871 |
| O, 1.88105, 0.00081, -0.00165 |
| H, -1.68219, 1.01954, 0.35561 |
| 112 | $^3$O | O, 0.00000, 0.00000, 0.00000 -197065.919094 6.19E+31 3 1.00E+00 1.00E+00 |
| CH$_2$ | C, 0.00000, 0.17399, 0.00000 -102649.483309 5.08E+31 1 1.00E+00 1.31E+02 |
| H, 0.86403, -0.52196, 0.00000 |
| H, 0.00000, 0.00000, -0.96239 |
| TS | C, 1.72138, 0.00000, -0.16790 -299717.767352 1.59E+32 3 4.38E+00 1.02E+04 |
| H, 1.61465, 0.86374, 0.51996 |
| H, 1.61465, -0.86374, 0.51996 |
| O, 3.25815, 0.00000, 1.32701 |
| 114 | $^3$O | O, 0.00000, 0.00000, 0.00000 -197065.919094 6.19E+31 3 1.00E+00 1.00E+00 |
| CH | C, 0.00000, 0.00000, 0.16040 -100985.100094 4.54E+31 2 1.00E+00 1.44E+01 |
| H, 0.00000, 0.00000, -0.96239 |
| TS | C, -0.03805, 0.00000, -0.00739 -298053.609930 1.59E+32 4 2.20E+00 6.90E+03 |
| H, -0.08343, 0.00000, 1.12287 |
| O, 3.25815, 0.00000, 1.32701 |
| 116/117/ | $^3$O | O, 0.00000, 0.00000, 0.00000 -196788.921964 6.19E+31 1 1.00E+00 1.00E+00 |
| H$_2$CN | C, -0.50346, 0.00000, 0.00005 -246571.579821 1.43E+32 2 1.02E+00 1.39E+03 |
| N, 0.73653, 0.00000, -0.00006 |
| H, -1.06749, 0.93849, 0.00008 |
| TS(CH$_2$NO) | C, -0.00026, -2.06042, 0.00000 -443634.228372 2.83E+32 2 7.58E+01 2.15E+04 |
| N, 0.00000, -0.82063, 0.00000 |
| H, -0.00039, -2.62401, -0.93865 |
| O, 0.00030, 2.91937, 0.00000 |
| CH$_2$NO | C, -1.1068, 0.12008, 0.00000 -443897.716844 2.83E+32 2 1.18E+00 6.75E+03 |
| N, 0.06743, -0.35642, 0.00000 |
| H, -1.92868, -0.58030, 0.00000 |
| H, -1.27043, 1.19243, 0.00000 |
| O, 1.17239, 0.14529, 0.00000 |
| TS($^3$O + H$_2$CN) | C, -1.17076, 0.51441, 0.00000 -443639.120847 2.83E+32 2 8.34E+00 3.93E+04 |
| N, -1.43659, -0.69718, 0.00000 |
| H, -1.96887, 1.26430, 0.00004 |
| H, -0.13238, 0.86080, 0.00004 |
| O, 2.39774, -0.04141, -0.00000 |
| TS(HCNO + H) | C, -1.01152, 0.43493, 0.00000 -443628.579465 2.83E+32 2 1.99E+00 7.86E+03 |
| N, 0.00000, -0.12833, 0.00000 |
| H, -0.60205, 2.58631, 0.00000 |
| O, 1.09251, -0.60621, 0.00000 |
| TS(HCNOH) | C, 0.01434, -0.00045, 0.00190 -443625.880451 2.83E+32 2 1.16E+00 8.32E+03 |
| N, 0.00003, 0.00007, 1.24192 |
| H, 1.35095, 0.00005, 0.03246 |
| H, -0.76839, -0.00108, -0.74539 |
| O, 1.46065, 0.00063, 1.28767 |
| HCNOH | C, 1.13711, 0.29236, 0.00000 -443791.239692 2.83E+32 2 1.32E+00 7.41E+03 |
| N, 0.15491, -0.44299, 0.00000 |
| H, 2.17692, -0.01488, 0.00000 |
| H, -1.07487, 1.00421, -0.00000 |
| O, -1.12614, 0.0468, 0.00000 |
| TS(HCN + OH) | C, 0.03282, 0.00008, 0.03546 -443764.756273 2.83E+32 2 1.82E+00 9.57E+03 |
| N, 0.00597, 0.00012, 1.22817 |
| H, 0.70873, -0.00010, -0.80034 |
| O, -1.48608, 0.00048, 1.88445 |
H, -2.05048, 0.00059, 1.10631

\[ \begin{array}{llllll}
121 & ^1\text{O} & \text{O}, & 0.00000, & 0.00000, & 0.00000 \quad -196788.921964 \quad 6.19\text{E}+31 \quad 1 \quad 1.00\text{E}+00 \quad 1.00\text{E}+00 \\
& \text{CH}_3 & \text{C}, & 0.00000, & -0.00018, & 0.00042 \quad -104455.380974 \quad 5.63\text{E}+31 \quad 2 \quad 1.08\text{E}+00 \quad 2.53\text{E}+02 \\
& & \text{H}, & -0.93570, & -0.53955, & -0.00085 \\
& & \text{H}, & 0.93580, & -0.53939, & -0.00085 \\
& & \text{H}, & -0.00010, & 1.08002, & -0.00085 \\
& \text{TS} & \text{C}, & -1.93246, & -0.00001, & 0.00003 \quad -301245.952754 \quad 1.67\text{E}+32 \quad 2 \quad 1.03\text{E}+01 \quad 1.90\text{E}+04 \\
& & \text{H}, & -1.94189, & -0.95530, & -0.50390 \\
& & \text{O}, & 2.17754, & 0.00002, & -0.00003 \\
& & \text{H}, & -1.94115, & 0.04121, & 1.07930 \\
& & \text{H}, & -1.94251, & 0.91405, & -0.57530 \\
122 & ^1\text{O} & \text{O}, & 0.00000, & 0.00000, & 0.00000 \quad -196788.921964 \quad 6.19\text{E}+31 \quad 1 \quad 1.00\text{E}+00 \quad 1.00\text{E}+00 \\
& ^3\text{CH}_2 & \text{C}, & 0.00000, & 0.00000, & 0.10395 \quad -102701.224038 \quad 5.08\text{E}+31 \quad 3 \quad 1.01\text{E}+00 \quad 8.96\text{E}+01 \\
& & \text{H}, & 0.00000, & -0.99689, & -0.31186 \\
& & \text{H}, & 0.00000, & 0.99689, & -0.31186 \\
& \text{TS} & \text{C}, & -2.00426, & -0.00000, & -0.10318 \quad -299491.422997 \quad 1.59\text{E}+32 \quad 3 \quad 7.05\text{E}+00 \quad 1.42\text{E}+04 \\
& & \text{H}, & -2.08479, & 0.99757, & 0.30347 \\
& & \text{H}, & -2.08468, & -0.99758, & 0.30347 \\
& & \text{O}, & 2.02438, & 0.00000, & 0.00152
\end{array} \]