Supporting Information for the paper:

Reactions of hydroperoxyl in ammonia oxidation

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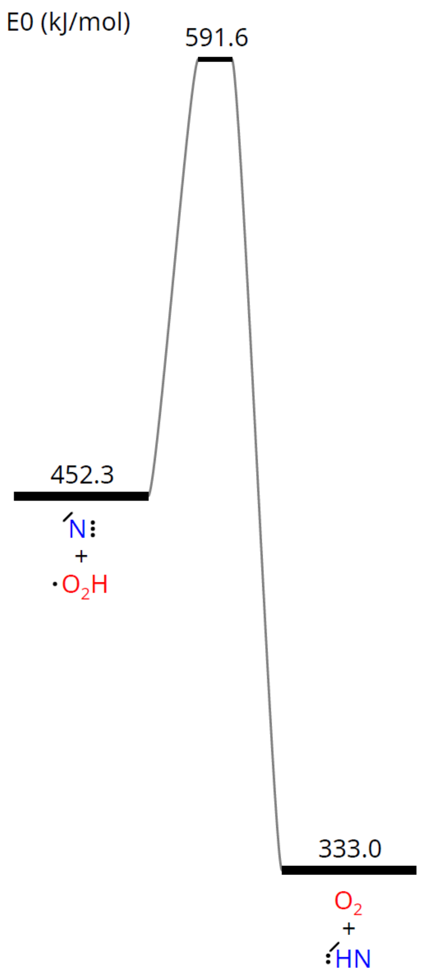
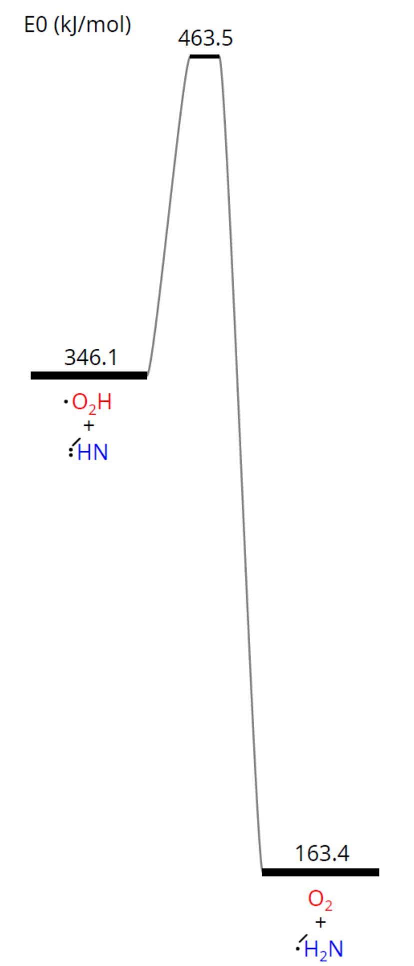
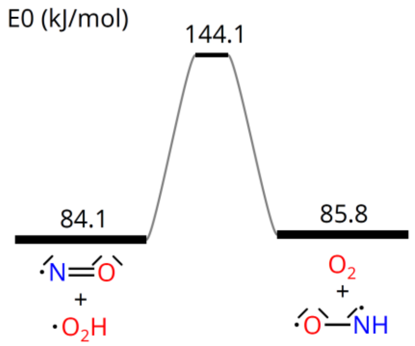
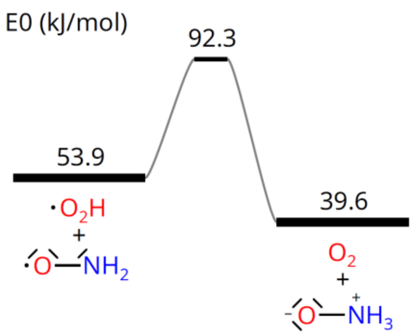
Table S1: Species SMILES representation and T1 diagnostic coefficient.

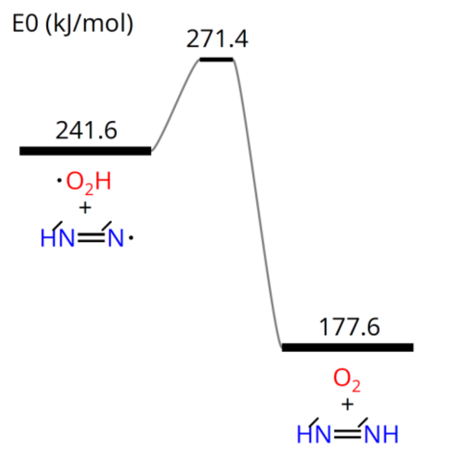
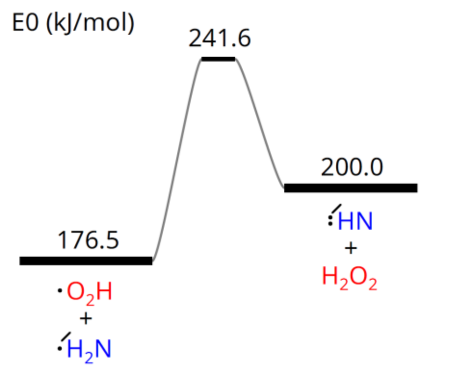
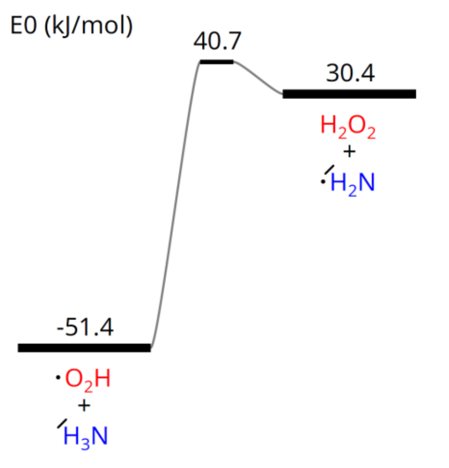
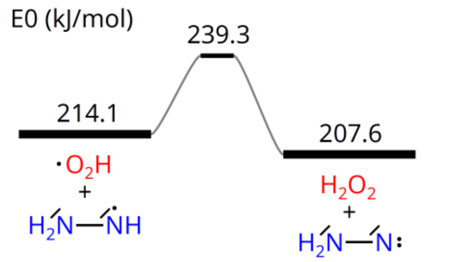
Species label [a]	SMILES representation	T1 diagnostic coefficient [b]
N(Q)	[N]	0.004
NH(T)	[NH]	0.007
NH2	[NH2]	0.008
NO	[N]=O	0.021
HNO	N=O	0.016
H2NO	N[O]	0.030
NH3O	[NH3+][O-]	0.013
NNH	[N]=N	0.028
N2H2	N=N	0.013
H2NN(T)	N[N]	0.025
N2H3	[NH]N	0.025
HNO	N=O	0.016
HNOH	[NH]O	0.025
NO2	[O-][N+]=O	0.025
HNO2	[O-][NH+]=O	0.020
O2(T)	[O][O]	0.008
HO2	O[O]	0.037
H2O2	OO	0.012

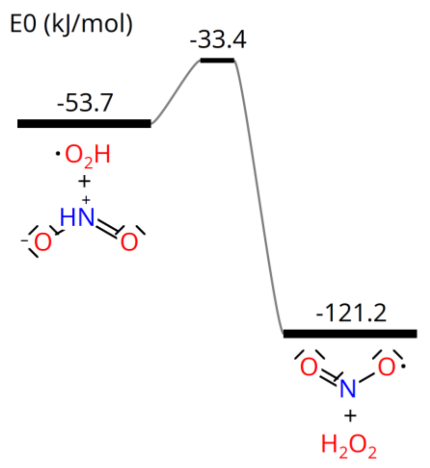
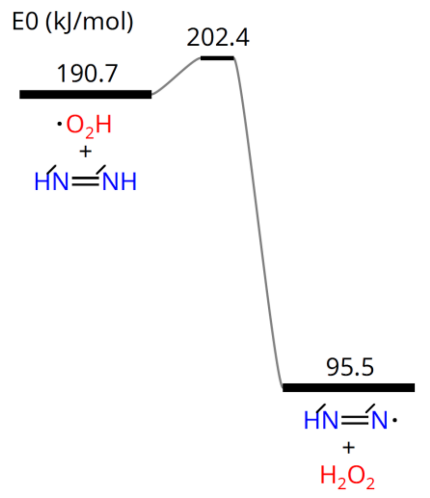
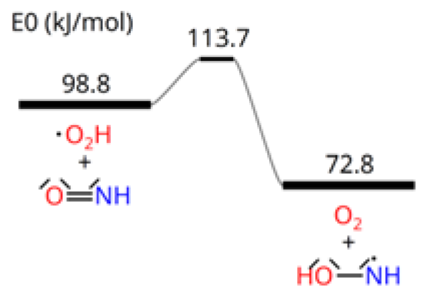
[a] The multiplicity is explicitly given in the species label (S, T, or Q in parenthesis stand for singlet, triplet, or quartet, respectively) where appropriate (i.e., ambiguous from the given structure or when the label is commonly used to describe another electronic state).
[b] The T1 diagnostic coefficient is based on the CCSD(T)-F12/aug-cc-pVTZ-F12 computation.

Table S2: Transition state geometries, frequencies, and reaction path zero-point energies

TS	Cartesian coordinates and active space	Vibrational frequencies (cm^{-1})	Energy diagram
TS1	N 0.00000000 1.69404400 0.89057200 O 0.00000000 -0.71670800 0.22994700 O 0.00000000 -0.72252700 -1.05242900 H 0.00000000 0.33134300 0.56740300 (18e, 13o)	2172.97 i 157.69 605.52 734.75 1354, 71 1414.72	

TS2 **m=2**	N -0.40131100 1.64071300 0.60882400 H 0.36207000 2.29684100 0.37964900 O -0.34915100 -1.06744400 -0.89027700 O 0.37933600 -0.68896700 0.11302300 H 0.00905700 0.27548400 0.40183600 (19e, 14o)	1623.94 i 75.68 156.10 453.06 636.95 1049.35 1366.72 1498.26 3359.58	
TS3	N -0.00000000 -1.36720300 0.15499300 O -0.00000000 -1.10333100 -0.98685800 H -0.00000000 -0.28110100 0.76732400 O 0.00000000 0.97476200 0.91364300 O 0.00000000 1.44007500 -0.27062400 (24e, 15o)	1880.22 i 91.78 179.31 430.24 513.27 638.25 1356.30 1680.82 1752.81	
TS4	O 0.00000000 -1.38863500 0.17427700 O 0.00000000 -0.95108900 -1.03197800 H 0.00000000 -0.39177700 0.77372600 N -0.00000000 0.93429900 0.92886100 O -0.00000000 1.38114400 -0.31935600 H 0.84302700 1.18576200 1.44701800 H -0.84302700 1.18576200 1.44701800 (26e, 14o)	1948.51 i 158.75 206.22 402.18 502.92 639.14 1106.65 1206.62 1256.96 1301.54 1383.21 1647.72 1697.62 3363.85 3458.05	

TS5	O -0.00000000 -0.99700800 -1.03519000 O -0.00000000 -1.26645600 0.21802800 H 0.00000000 -0.22934600 0.76889100 N 0.00000000 1.55739400 -0.07974700 N 0.00000000 1.06016900 1.00187400 H 0.00000000 2.59759500 -0.09935400 (24e, 13o)	2089.99 i 121.51 165.26 408.14 439.84 619.66 1176.15 1215.89 1321.86 1680.53 1808.61 3106.35	
TS6	N 0.39567400 1.63454200 0.53513100 H -0.48943100 2.14237900 0.39371400 O 0.12870400 -0.88723000 -1.13921400 O -0.36488000 -0.61179000 0.14681300 H 0.98970200 -1.29142000 -0.95428400 H 0.10522800 0.42446600 0.41221100 (20e, 11o)	1960.66 i 69.23 174.98 373.69 500.21 733.93 988.71 1160.60 1346.64 1397.52 3382.81 3718.04	
TS7	O -1.07712700 0.74985600 0.50000500 O 0.18725500 0.67560900 -0.15177900 H -0.82110400 0.79350000 1.43206900 N 0.42155600 -1.68505200 -0.43860900 H 0.42105200 -0.41787000 -0.10670200 H -0.53220100 -1.87662300 -0.74727100 H 0.99800600 -1.79030600 -1.27422700 (21e, 11o)	1935.56 i 133.11 168.90 342.32 493.91 618.82 749.40 650.90 1226.73 1382.41 1552.62 1579.14 3439.38 3531.48 3738.62	
TS8	O 0.08555600 1.44420800 -0.37093000 O 0.07764300 0.92638300 0.93781400 H -0.83812000 1.71190200 -0.49277100 N -0.06914300 -1.27302200 -0.94214500 N -0.02631900 -1.41836800 0.37864500 H 0.27712800 -2.06540300 -1.46683600 H 0.21724500 -0.35336000 -1.28838400 H 0.00571800 -0.32857600 0.82614800 (26e, 14o)	1299.83 i 122.09 226.43 308.98 371.93 497.68 649.00 699.66 856.86 996.79 1219.08 1279.92 1368.97 1576.12 1657.76 3340.12 3572.29 3711.77	

TS9	O 0.47679400 -1.60702800 0.41126000 N -0.63062100 -1.81884300 -0.03582200 O -0.97512000 -2.58771200 -0.91453500 H -1.54141400 -1.20036400 0.42495200 O -3.56993100 -1.56625200 0.17492200 H -3.73947700 -1.24058900 -0.72644800 O -2.66641200 -0.67439600 0.68269300 (31e, 16o)	2033.47 i 70.24 90.79 262.35 322.09 383.87 498.09 818.32 1096.02 1120.02 1360.98 1409.96 1610.77 1643.16 3660.69	
TS10	O 0.11666500 1.53489300 -0.23531100 O -0.05359800 1.02990900 1.02510700 H -0.76762700 1.47512400 -0.63386900 N -0.15179100 -1.14044800 -0.84003800 N 0.13997200 -1.35068900 0.32038300 H -0.12482300 -2.02010100 -1.38182100 H 0.11141400 -0.36458900 0.84294400 (25e, 13o)	1091.83 i 128.12 160.65 327.24 390.22 530.00 781.05 117.05 1286.41 1400.56 1496.94 1628.76 1796.55 3238.83 3672.19	
TS11	H -0.14138700 0.22431900 0.78909500 O -0.97133400 0.34191200 -0.03137700 O -0.29348500 0.02662500 -1.06715700 H 1.78409300 0.37930200 -0.70027600 N 1.35575800 -0.44601100 -0.23661100 O 1.03924000 -0.10453100 0.96041200 (25e, 13o)	524.98 i 215.24 529.61 710.53 735.46 906.76 932.29 1273.47 1395.17 1476.06 1870.35 3166.51	

Details on rate coefficient kinetic computations and statistical mechanics

Rate coefficients were calculated using traditional transition state theory (TST, Eq. S1).

$$k_{\mathrm{TST}}(T) = \sigma \frac{k_b T}{h} \frac{Q_{\mathrm{TS}}(T)}{Q_{\mathrm{R}}(T)} e^{-\frac{\Delta V^{\ddagger}}{k_b T}},$$

(Eq. S1)

The Eckart function was applied to obtain more accurate rate coefficients and describe quantum chemical tunneling.

For more details, see reference [1].

Rate coefficient comparisons

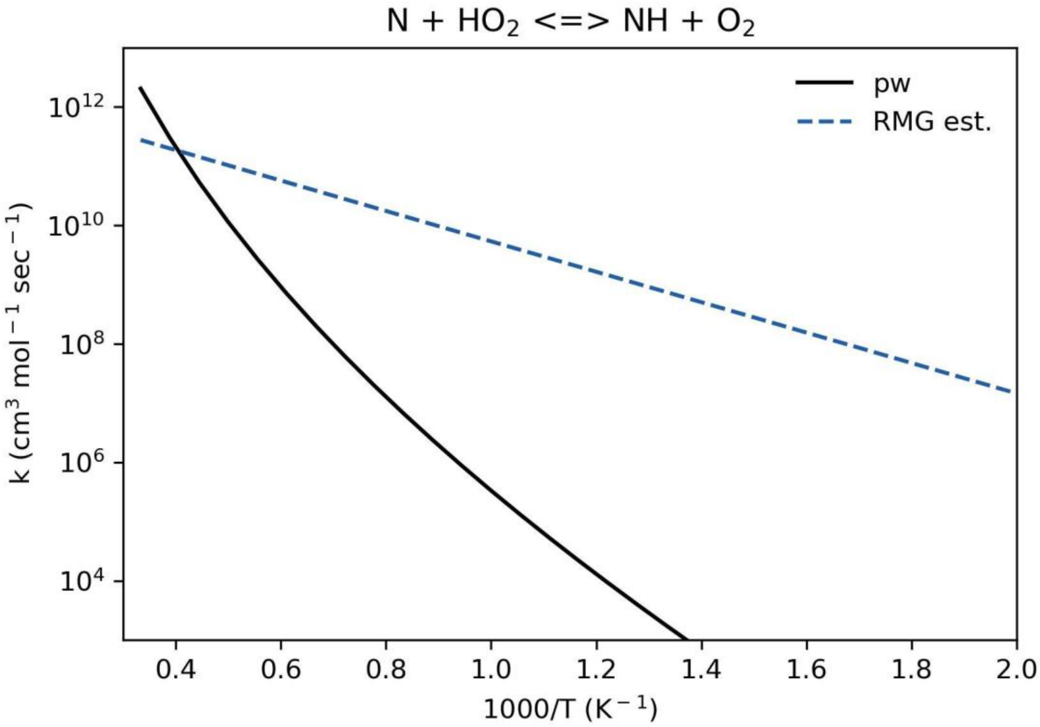


Fig. S1: The rate coefficients for $N + HO_2 \Leftrightarrow NH + O_2$ (Reaction R1) computed here (pw) and estimated by RMG.

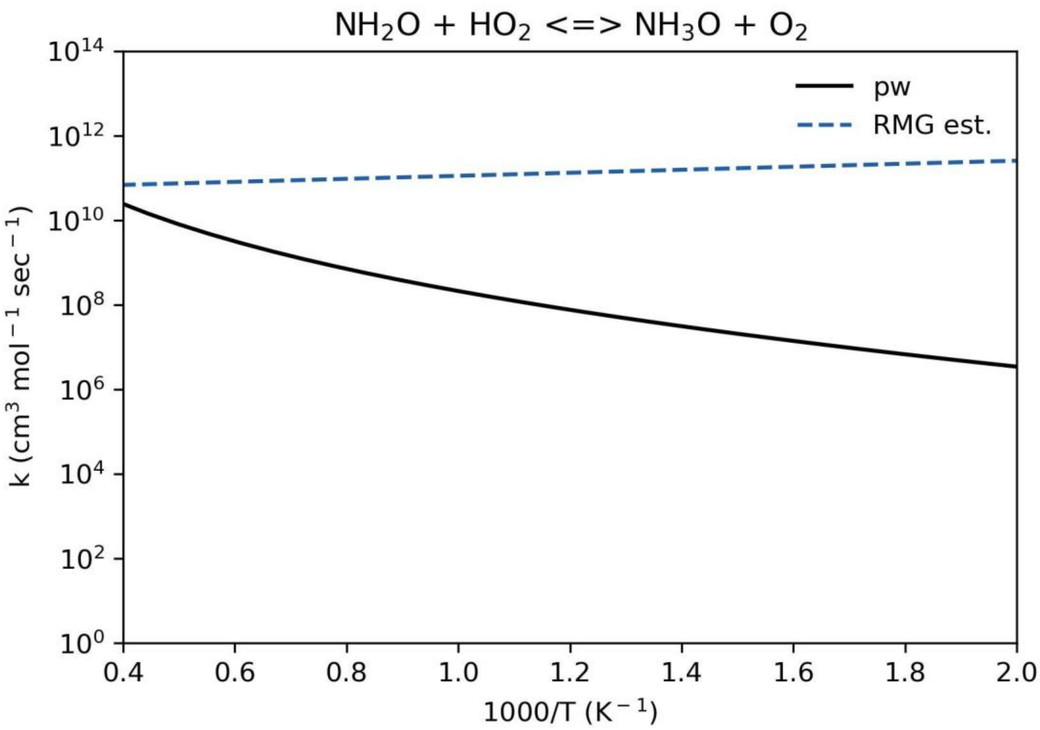


Fig. S2: The rate coefficients for $NH_2O + HO_2 \Leftrightarrow NH_3O + O_2$ (Reaction R4) computed here (pw) and estimated by RMG.

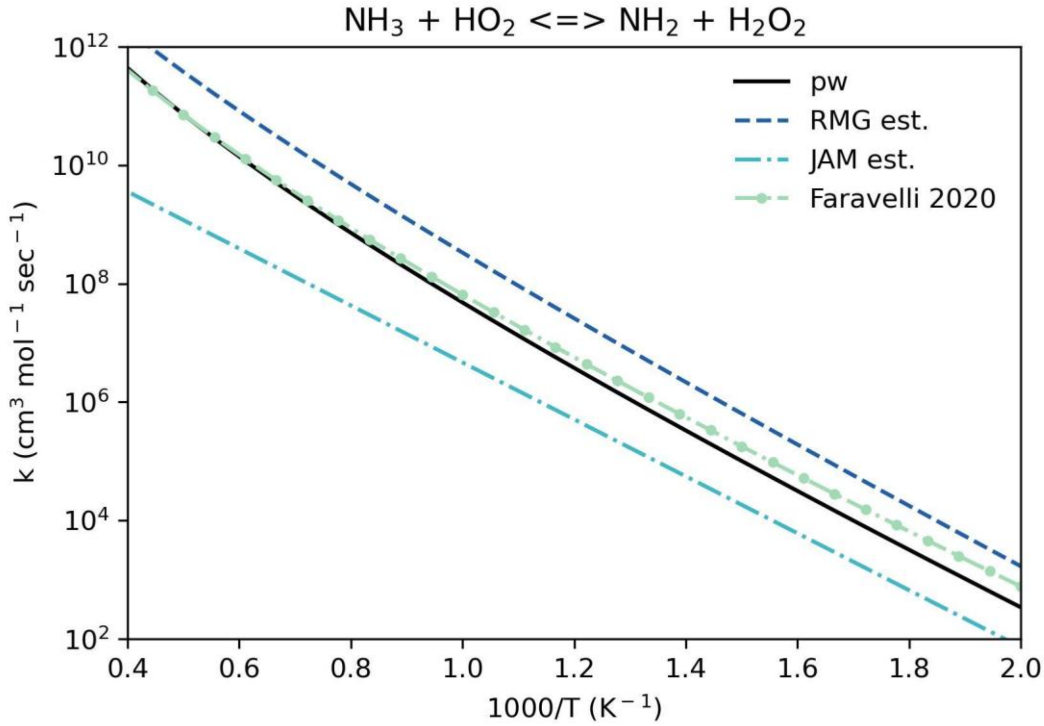


Fig. S3: Comparison of rate coefficients for $NH_3 + HO_2 \Leftrightarrow NH_2 + H_2O_2$ (Reaction R7). pw: present work. RMG est.: RMG estimation. JAM est.: James A. Miller estimation.[2] Faravelli 2020 [3].

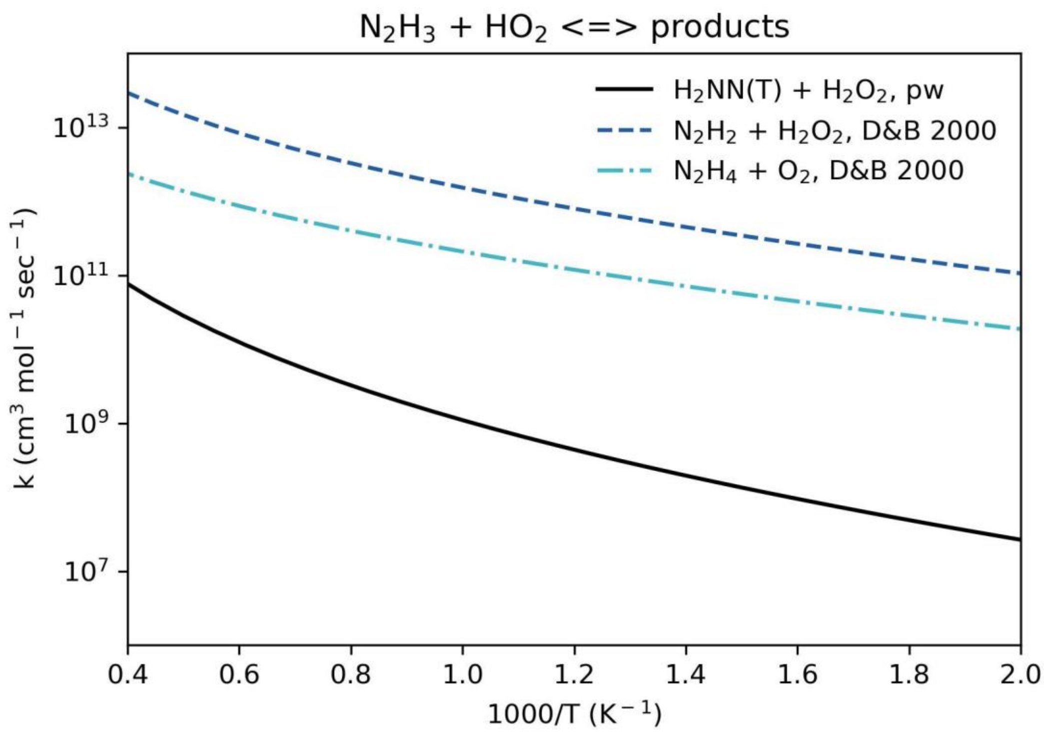


Fig. S4: Comparison of rate coefficients for $N_2H_3 + HO_2$ giving $H_2NN(T) + H_2O_2$ (Reaction R8) computed here (pw), $N_2H_2 + H_2O_2$,[4] and $N_2H_4 + O_2$.[4]

Table S3: Chemkin format thermodynamic NASA polynomials for NH_3O and $H_2NN(T)$ and kinetic rate coefficients for the reactions reported in the manuscript.

```
NH3O                   H   3N   1O   1     G   298.000  2500.000  807.49       1
 3.01462987E-01 1.48245827E-02-8.01027541E-06 2.14844634E-09-2.28543657E-13    2
 7.18715445E+03 2.09658807E+01 3.72114996E+00-2.11592088E-03 2.34597828E-05    3
-2.38343720E-08 7.81608932E-12 6.63490361E+03 5.19921590E+00                   4

H2NN(T)                H   2N   2          G   298.000  2500.000  838.09       1
 2.59199177E+00 8.45900947E-03-4.70219807E-06 1.34562577E-09-1.55636787E-13    2
 4.28488836E+04 1.11873116E+01 3.04503833E+00 4.70395525E-03 4.86926551E-06    3
-8.53573134E-09 3.46838004E-12 4.28288824E+04 9.41536664E+00                   4


! R1
 N+HO2=NH+O2                              1.82E-27   9.81   14460

! R2
! NH+HO2=NH2+O2, no rate provided

! R3
 NO+HO2=HNO+O2                            1.19E-5   5.06   7146

! R4
 H2NO+HO2=NH3O+O2                         1.40E-05   4.53   1936

! R5
 NNH+HO2=N2H2+O2                          6.25E-05   4.57   526

! R6
 NH2+HO2=NH+H2O2                          1.97E-05   5.23   8174

! R7
 NH3+HO2=NH2+H2O2                         4.44E-01   4.00   18054

! R8
 N2H3+HO2=H2NN(T)+H2O2                    2.79E-03   4.00   1888

! R9
 HNO2+HO2=NO2+H2O2                        2.49E-03   4.52   50

! R10
 N2H2+HO2=NNH+H2O2                        7.79E-01   3.96   -143

! R11
 HNO+HO2=HNOH+O2                          3.08E+00   2.98   574
```

Table S4: Cantera format thermodynamic NASA polynomials for NH_3O and $H_2NN(T)$ and kinetic rate coefficients for the reactions reported in the manuscript.


```
species:
- name: H2NN(T)
  composition: {H: 2, N: 2}
  thermo:
    model: NASA7
    temperature-ranges: [298.0, 838.09, 2500.0]
    data:
    - [3.04503833, 4.70395525e-03, 4.86926551e-06, -8.53573134e-09, 3.46838004e-12,
      4.28288824e+04, 9.41536664]
    - [2.59199177, 8.45900947e-03, -4.70219807e-06, 1.34562577e-09, -1.55636787e-13,
      4.28488836e+04, 11.1873116]
    note: 'N[N]'
- name: NH3O
  composition: {H: 3, N: 1, O: 1}
  thermo:
    model: NASA7
    temperature-ranges: [298.0, 807.49, 2500.0]
    data:
    - [3.72114996, -2.11592088e-03, 2.34597828e-05, -2.3834372e-08, 7.81608932e-12,
      6634.90361, 5.1992159]
    - [0.301462987, 0.0148245827, -8.01027541e-06, 2.14844634e-09, -2.28543657e-13,
      7187.15445, 20.9658807]
    note: '[NH3+][O-]'

reactions:
- equation: N + HO2 <=> NH + O2
  rate-constant: {A: 1.82e-27, b: 9.81, Ea: 14460}
  note: R1
- equation: NO + HO2 <=> HNO + O2
  rate-constant: {A: 1.19e-05, b: 5.06, Ea: 7146}
  note: R3
- equation: H2NO + HO2 <=> NH3O + O2
  rate-constant: {A: 1.40e-05, b: 4.53, Ea: 1936}
  note: R4
- equation: NNH + HO2 <=> N2H2 + O2
  rate-constant: {A: 6.25e-05, b: 4.57, Ea: 526}
  note: R5
- equation: NH2 + HO2 <=> NH + H2O2
  rate-constant: {A: 1.97e-05, b: 5.23, Ea: 8174}
  note: R6
- equation: NH3 + HO2 <=> NH2 + H2O2
  rate-constant: {A: 0.444, b: 4.00, Ea: 18054}
  note: R7
- equation: N2H3 + HO2 <=> H2NN(T) + H2O2
  rate-constant: {A: 2.79e-03, b: 4.00, Ea: 1888}
  note: R8
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- equation: HNO2 + HO2 <=> NO2 + H2O2
  rate-constant: {A: 2.49e-03, b: 4.52, Ea: 50}
  note: R9
- equation: N2H2 + HO2 <=> NNH + H2O2
  rate-constant: {A: 0.779, b: 3.96, Ea: -143}
  note: R10
- equation: HNO + HO2 <=> HNOH + O2
  rate-constant: {A: 3.08, b: 2.98, Ea: 574}
  note: R11
```

Table S5: The main reference determinants of the CASSCF calculation for each TS, only showing CI expansion coefficients above 0.05.

TS label	**CI expansion coefficients**	**Active orbital occupation**
TS1	0.93090	22222221111
TS2, m=2	0.41683 0.27965 0.24746	22222222210 22222222012 22222222111
TS2, m=4	0.92390	222222221110
TS3	0.88961	2222222222211
TS4	0.99697	22222222222211
TS5	0.99550	2222222222211
TS6	0.99997	22222222211
TS7	1.00000	22222222221
TS8	0.99685	22222222222211
TS9	1.00000	2222222222222221
TS10	1.00000	2222222222221
TS11	1.00000	2222222222221

References:

1. A. Grinberg Dana, et al. "Automated reaction kinetics and network exploration (Arkane): A statistical mechanics, thermodynamics, transition state theory, and master equation software." *International Journal of Chemical Kinetics* **2023**, 55(6), 300–323, doi: 10.1002/kin.21637

2. P. Glarborg, J.A. Miller, B. Ruscic, S.J. Klippenstein, Modeling nitrogen chemistry in combustion, *Prog. Energy Comb. Sci.* **2018**, 67, 31–68. doi: 10.1016/j.pecs.2018.01.002

3. A. Stagni, C. Cavallotti, S. Arunthanayothin, Y. Song, O. Herbinet, F. Battin-Leclerc, T. Faravelli, *React. Chem. Eng*. **2020**, 5, 696–711. doi: 10.1039/C9RE00429G

4. A.M. Dean, J.W. Bozzelli, Combustion Chemistry of Nitrogen. In Gas-Phase Combustion Chemistry, Gardiner, W. C., Ed.; Springer New York: New York, NY, 2000, pp 125–341.