An experimental, theoretical and kinetic modeling study of the N2O-H2 system: Implications for N2O + H

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**SUPPLEMENTARY MATERIAL:**

Theoretical Kinetics for the HNNO + H Reaction

**Table S1**: Basis set convergence of CCSD(T) calculations for minima on H2N2O potential energy surface.a

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Species | CCSD(T)-F12 | | | CCSD(T) | | | | Delta |
|  | QZF | 5ZF | CBSF | AQZ | A5Z | A6Z | CBS | CBS |
| NH2 + NO | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| NH2NO | -50.99 | -51.07 | -51.15 | -49.60 | -50.42 | -50.74 | -51.11 | -0.04 |
| HNNOH  trans-cis | -51.89 | -51.92 | -51.96 | -50.71 | -51.41 | -51.67 | -51.98 | 0.02 |
| HNNOH  trans-trans | -51.10 | -51.14 | -51.18 | -49.98 | -50.65 | -50.89 | -51.19 | 0.01 |
| HNNOH  cis-trans | -51.09 | -51.13 | -51.16 | -49.95 | -50.63 | -50.88 | -51.17 | 0.01 |
| HNNOH  cis-cis | -44.79 | -44.83 | -44.86 | -43.62 | -44.32 | -44.58 | -44.83 | 0.02 |
| NHNHO  trans | -43.16 | -43.26 | -43.35 | -41.82 | -42.61 | -42.93 | -43.30 | -0.04 |
| NHNHO  cis | -37.89 | -38.01 | -38.13 | -36.51 | -37.33 | -37.67 | -38.07 | -0.05 |
| NNHOH  trans | -31.77 | -31.83 | -31.89 | -30.65 | -31.31 | -31.56 | -31.87 | -0.02 |
| NNHOH  cis | -26.46 | -26.53 | -26.61 | -25.31 | -25.99 | -26.26 | -26.59 | -0.01 |
| HNNO;t + H | 37.21 | 37.18 | 37.14 | 38.08 | 37.62 | 37.43 | 37.19 | -0.05 |
| HNNO;c + H | 43.64 | 43.61 | 43.57 | 44.52 | 44.04 | 43.85 | 43.61 | -0.04 |
| N2 + H2O | -125.86 | -125.88 | -125.89 | -125.27 | -125.62 | -125.74 | -125.88 | -0.01 |
| N2 + H + OH | -0.34 | -0.32 | -0.30 | -0.44 | -0.36 | -0.31 | -0.26 | -0.04 |
| NNH + OH | 3.39 | 3.39 | 3.40 | 3.42 | 3.40 | 3.40 | 3.41 | -0.02 |
| H2 + NNO | -44.32 | -44.36 | -44.41 | -43.38 | -43.87 | -44.11 | -44.40 | -0.01 |

a All energies are in kcal/mol relative to NH2 + NO.

**Table S2**: Basis set convergence of CCSD(T) calculations for saddle points on H2N2O potential energy surface.a

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Species | CCSD(T)-F12 | | | CCSD(T) | | | | Delta |
|  | QZF | 5ZF | CBSF | AQZ | A5Z | A6Z | CBS | CBS |
| NH2 + NO | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| NHNHO =  NNHOH | 3.52 | 3.44 | 3.35 | 4.84 | 4.07 | 3.76 | 3.39 | -0.04 |
| NHNHO =  NHNOH | 7.50 | 7.43 | 7.37 | 8.72 | 8.02 | 7.72 | 7.36 | 0.00 |
| NHNHO =  NHNOH;tau | 8.82 | 8.75 | 8.68 | 10.05 | 9.34 | 9.04 | 8.68 | 0.00 |
| NHNHO =  NH2NO | 12.26 | 12.19 | 12.11 | 13.58 | 12.81 | 12.51 | 12.15 | -0.04 |
| NNHOH=  N2 + H2O | -20.64 | -20.73 | -20.82 | -19.52 | 20.17 | -20.47 | -20.82 | 0.00 |
| H + HNNO;t =  H2 + 3NNO | 49.52 | 49.50 | 49.48 | 50.26 | 49.87 | 49.71 | 49.52 | -0.04 |
| H + HNNO;c =  H2 + 3NNO |  | 59.69 | 59.68 | 60.42 | 60.03 | 59.88 | 59.71 | -0.02 |
| NHNHOH;tc =  NHNHOH;tt | -41.91 | -41.94 | -41.96 | -40.78 | -41.46 | -41.69 | -41.97 | 0.01 |
| NHNHOH;ct =  NHNHOH;cc | -41.19 | -41.22 | -41.24 | -40.04 | -40.73 | -40.97 | -41.25 | 0.01 |
| ts2 | -17.48 | -17.55 | -17.62 | -16.13 | -16.92 | -17.24 | -17.62 | -0.01 |
| ts3 | -10.38 | -10.46 | -10.53 | -9.13 | -9.87 | -10.18 | -10.55 | 0.02 |
| ts4 | -13.07 | -13.14 | -13.21 | -11.90 | -12.59 | -12.87 | -13.21 | 0.01 |
| ts5;trans | -24.96 | -25.03 | -25.10 | -23.92 | -24.53 | -24.79 | -25.11 | 0.01 |
| ts5;cis | -5.96 | -6.05 | -6.15 | -4.52 | -5.39 | -5.73 | -6.13 | -0.01 |
|  |  |  |  |  |  |  |  |  |

a All energies are in kcal/mol relative to NH2 + NO.

**Table S3**: Energy components for minima on H2N2O potential energy surface.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Species | T(Q) | T(Q)b | TQ(P) | Core Val.c | Rel.d | DBOC | E0e | E0f | Totalg |
|  | DZ | TZ | DZ | CBS | Corr. |  | Har. | Anh. |  |
| NH2 + NO | 0 | 0 | 0 | 0 | 0 |  | 0 | 0 | 0 |
| NH2NO | -0.24 | -0.09 | 0.08 | -0.39 | 0.23 | -0.13 | 5.65 |  | -45.79 |
| HNNOH  trans-cis | -0.10 | 0.07 | 0.06 | -0.19 | 0.17 | -0.11 | 6.31 | -0.14 | -45.80 |
| HNNOH  trans-trans | -0.10 | 0.07 | 0.05 | -0.19 | 0.17 | -0.11 | 6.34 | -0.14 | -44.98 |
| HNNOH  cis-trans | -0.16 | 0.01 | 0.07 | -0.14 | 0.14 | -0.11 | 5.84 | -0.14 | -45.48 |
| HNNOH  cis-cis | -0.17 | 0.01 | 0.08 | -0.09 | 0.13 | -0.09 | 5.52 | -0.14 | -39.46 |
| NHNHO  trans | -0.45 | -0.28 | 0.15 | -0.34 | 0.25 | -0.11 | 7.09 | -0.13 | -36.72 |
| NHNHO  cis | -0.49 | -0.31 | 0.15 | -0.34 | 0.26 | -0.09 | 6.92 | -0.13 | -31.67 |
| NNHOH  trans | -0.66 | -0.50 | 0.18 | -0.28 | 0.17 | -0.10 | 4.96 | -0.14 | -27.61 |
| NNHOH  cis | -0.79 | -1.15 | 0.19 | -0.26 | 0.15 | -0.09 | 4.30 | -0.16 | -23.63 |
| HNNO;t + H | -1.21 | -1.06 | 0.27 | -0.30 | 0.17 | -0.05 | -1.37 | 0.04 | 34.84 |
| HNNO;c + H | -0.84 | -0.69 | 0.21 | -0.31 | 0.17 | -0.05 | -1.92 | 0.03 | 41.01 |
| N2 + H2O | 0.06 | 0.21 | 0.00 | -0.42 | 0.06 | -0.13 | 2.12 | -0.03 | -124.08 |
| N2 + H + OH | 0.17 | 0.16 | -0.02 | -0.20 | -0.09 | -0.03 | -6.01 | 0.14 | -6.35 |
| NNH + OH | -0.07 | 0.07 | -0.02 | -0.19 | 0.04 | 0.03 | -1.05 | -0.08 | 2.18 |
| H2 + NNO | -0.45 | -0.28 | 0.34 | -0.40 | 0.12 | -0.12 | -1.59 | 0.09 | -46.26 |

**Table S4**: Energy components for saddle points on H2N2O potential energy surface.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Species | T(Q) | T(Q)b | TQ(P) | Core Val.c | Rel.d | DBOC | E0e | E0f | Totalg |
|  | DZ | TZ | DZ | CBS | Corr. |  | Har. | Anh. |  |
| NH2 + NO | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| NHNHO =  NNHOH | -0.69 | -0.43 | 0.29 | -0.22 | 0.17 | -0.12 | 3.27 | -0.06 | 6.24 |
| NHNHO =  NHNOH | -0.90 | -0.61 | 0.36 | -0.20 | 0.15 | -0.10 | 2.37 | -0.04 | 9.29 |
| NHNHO =  NHNOH;tau | -0.95 | -0.66 | 0.35 | -0.21 | 0.16 | -0.10 | 2.57 | -0.04 | 10.75 |
| NHNHO =  NH2NO | -0.82 | -0.59 |  | -0.14 | 0.16 | -0.07 | 2.23 | -0.10 | 13.59 |
| NNHOH=  N2 + H2O | -1.56 | -1.17 |  | -0.36 | 0.12 | -0.09 | 1.87 | -0.16 | -20.61 |
| H + HNNO;t =  H2 + 3NNO | -1.40 |  |  | -0.04 | 0.06 | 0.13 | -3.42 | -0.03 | 46.20 |
| H + HNNO;c =  H2 + 3NNO | -1.09 |  |  | 0.00 | 0.05 | 0.25 | -3.91 | -0.03 | 56.11 |
| NHNHOH;tc =  NHNHOH;tt | 0.02 | 0.19 |  | -0.13 | 0.15 | -0.09 | 5.22 | -0.10 | -36.73 |
| NHNHOH;ct =  NHNHOH;cc | -0.09 | 0.08 |  | -0.07 | 0.11 | -0.10 | 4.82 | -0.10 | -36.49 |
| ts2 | -0.63 | -0.37 | 0.19 | -0.20 | 0.15 | -0.11 | 2.94 | -0.03 | -15.05 |
| ts3 | -0.52 | -0.31 | 0.14 | -0.36 | 0.20 | -0.13 | 3.32 | -0.09 | -7.76 |
| ts4 | -0.73 | -0.50 | 0.17 | -0.38 | 0.19 | -0.13 | 3.37 | -0.05 | -10.52 |
| ts5;trans | -0.81 | -0.67 | 0.18 | -0.05 | 0.01 | -0.10 | 1.75 |  | -23.98 |
| ts5;cis | -0.31 | -0.13 | 0.13 | -0.26 | 0.25 | -0.11 | 3.14 | -0.21 | -3.33 |