**The HO4H → O3 + H2O Reaction Catalyzed by Acidic, Neutral and Basic Catalysts in the Troposphere**

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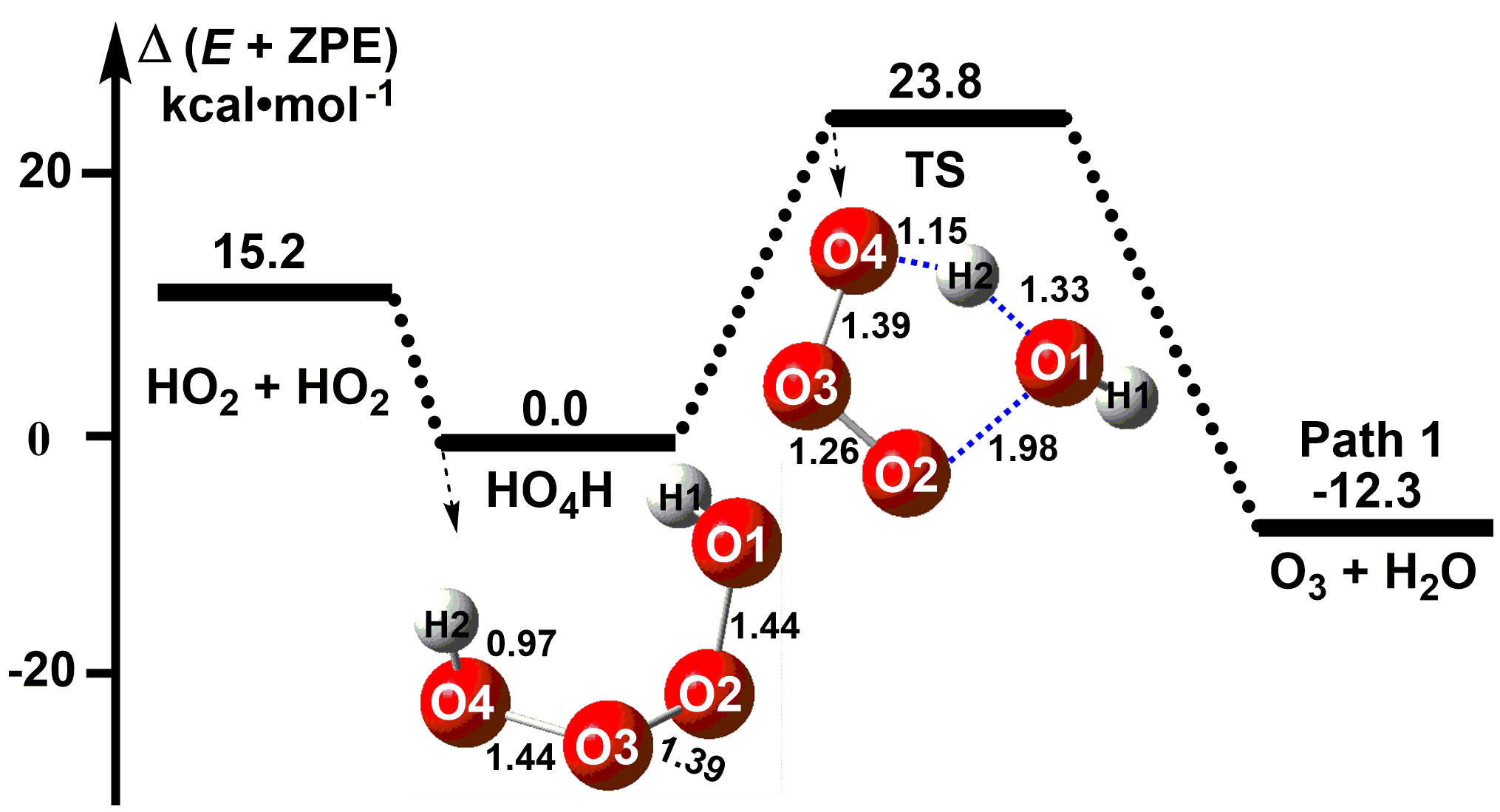
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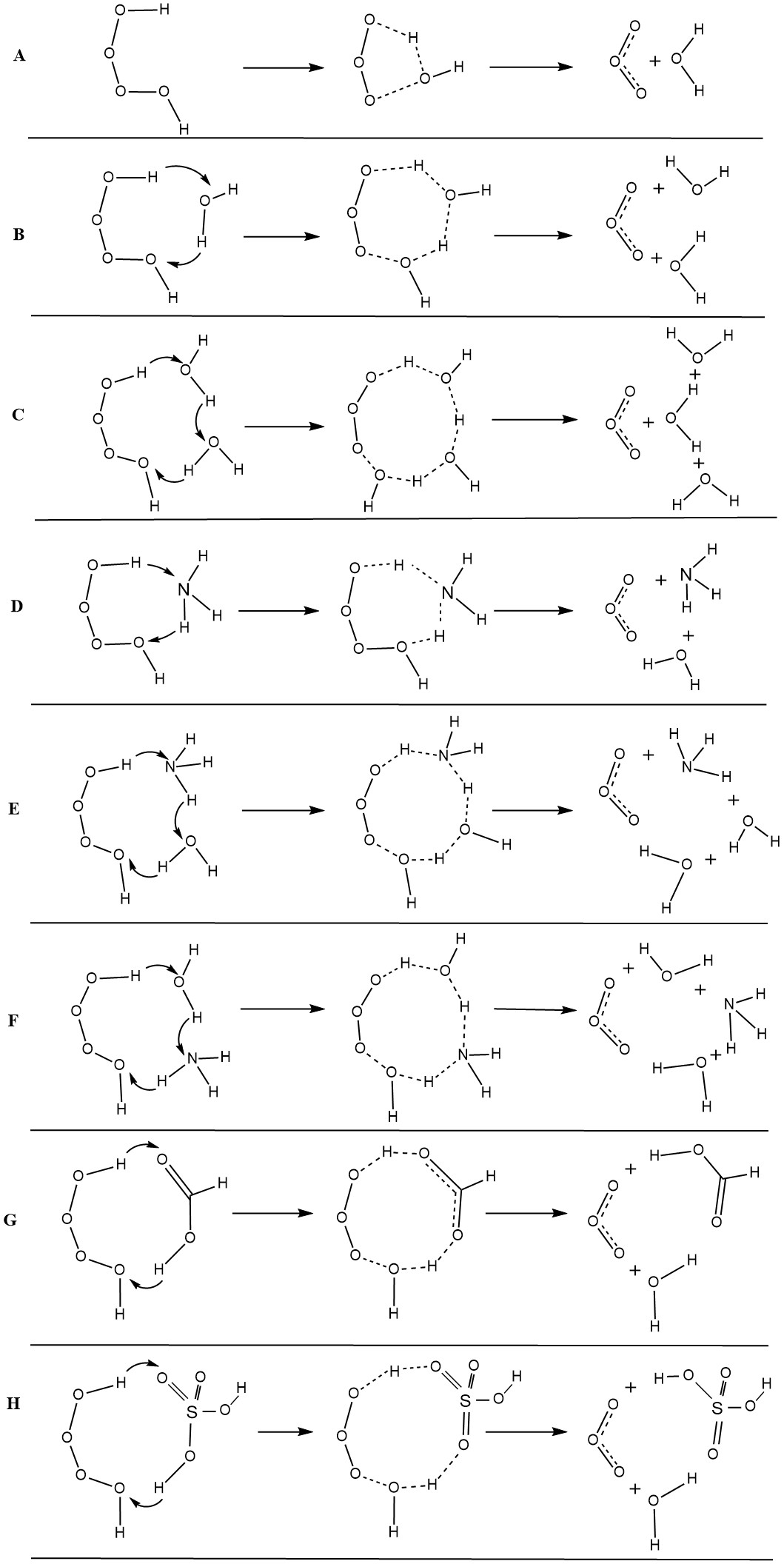
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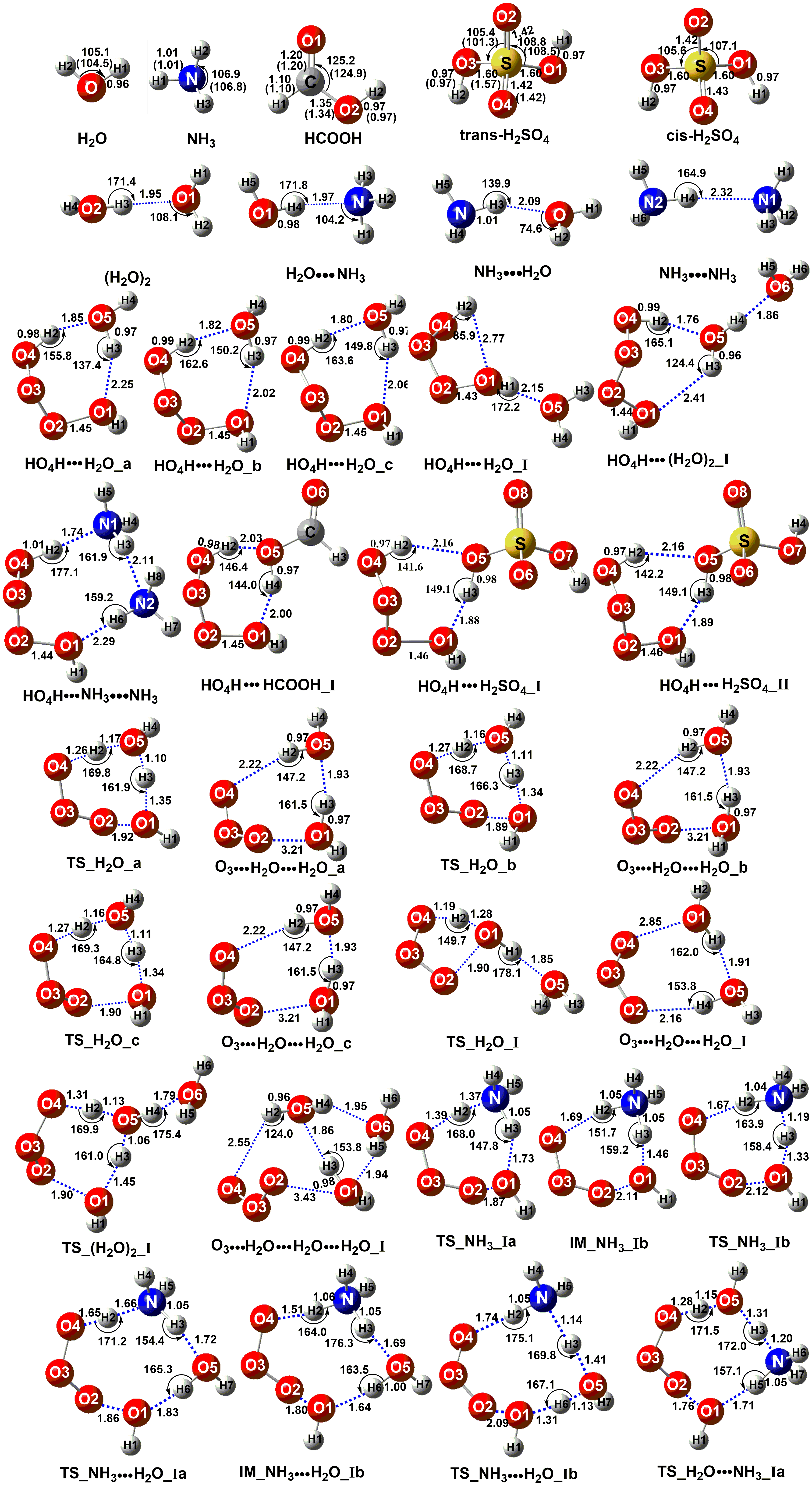
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| --- | --- |
| S. NO | Caption |
| 1 | **Figure S1** Schematic energy diagrams of the HO4H → H2O + O3 reaction without catalysts at the CCSD(T)-F12a/cc-pVDZ-F12//M06-2X/6-311+G(3*d*,2*p*) level, including the zero-point energy correction (kcal∙mol-1) |
| 2 | **Figure S2** Schematic representation of hydrogen abstraction of HO4H → O3 + H2O (A) under isolated conditions and (B–H) assisted by various catalysts (B: H2O, C: (H2O)2, D: NH3, E: NH3∙∙∙H2O, F: H2O∙∙∙NH3, G: HCOOH and H: H2SO4) |
| 3 | **Figure S3** The geometrical structures of the optimized the reactants, intermediates, transition states and products for the *X* (*X* = H2O, (H2O)2, NH3, NH3∙∙∙H2O, H2O∙∙∙NH3,HCOOH and H2SO4) catalyzed HO4H → H2O + O3 reaction at the M06-2X/6-311+G(3*d*,2*p*) level of theory |
| 4 | **Table S1** Zero point energy (ZPE/(kcal⋅mol-1)), relative energies (Δ*E* and Δ(*E +* ZPE)/(kcal⋅mol-1)), enthalpies (Δ*H*(298)/(kcal⋅mol-1)), entropy (S(298)/(cal⋅mol-1⋅K-1)), free energies (Δ*G*(298)/(kcal⋅mol-1)) , *<S2>* and *T1* of all species for the HO4H + *X* reactionat the CCSD(T)-F12a/cc-pVDZ-F12//M06-2X/ 6-311+G(3*d*,2*p*) level of theory (*X* = H2O, (H2O)2, NH3, NH3∙∙∙H2O, H2O∙∙∙NH3, HCOOH and H2SO4) |
| 5 | **Table S2** The binding energies (∆Ea, 0 K), energy barriers (∆Eb, 0 K), and reaction energies (∆Ec,0 K) of the HO4H → H2O + O3 reaction at different theoretical methods with zero-point correction involved and mean unsigned error (MUEd) (in kcal mol-1) |
| 6 | **Table** **S3** Concentrations of all the catalysts (in molecule⋅cm-3) within temperature range of 280 K – 320 K at 0 km altitude |
| 7 | **Table S4** Calculated rate constants (molecule-1⋅cm3⋅s-1) in presence of catalyst *X* (*X* = H2O, (H2O)2, NH3, NH3∙∙∙H2O, H2O∙∙∙NH3,HCOOH and H2SO4) using the results obtained from CCSD(T)-F12a/ cc-pVDZ-F12//M06-2X/6-311+G(3*d*,2*p*) level of theory |
| 8 | **Table S5** Effective rate constants (s-1) for all the catalysts within temperature range of 280 K – 320 K at 0 km altitude using catalyst *X* (*X* = H2O, (H2O)2, NH3, NH3∙∙∙H2O, H2O∙∙∙NH3,HCOOH and H2SO4) concentrations given in Table S3 |
| 9 | **Figure S4** The results of IRC calculations of all transition state for HO4H → O3 + H2O reaction with catalyst *X* (*X* = H2O, (H2O)2, NH3, NH3∙∙∙H2O, H2O∙∙∙NH3, HCOOH and H2SO4) |



**Figure S1** Schematic energy diagrams of the HO4H → H2O + O3 reaction without catalysts at the CCSD(T)-F12a/cc-pVDZ-F12//M06-2X/6-311+G(3*d*,2*p*) level, including the zero-point energy correction (kcal∙mol-1)



**Figure S2** Schematic representation of hydrogen abstraction of HO4H → O3 + H2O (A) under isolated conditions and (B–H) assisted by various catalysts (B: H2O, C: (H2O)2, D: NH3, E: NH3∙∙∙H2O, F: H2O∙∙∙NH3, G: HCOOH and H: H2SO4)



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**Figure S3** The geometrical structures of the optimized the reactants, intermediates, transition states and products for the *X* (*X* = H2O, (H2O)2, NH3, NH3∙∙∙H2O, H2O∙∙∙NH3,HCOOH and H2SO4) catalyzed HO4H → H2O + O3 reaction at the M06-2X/6-311+G(3*d*,2*p*) level of theory**Table S1** Zero point energy (ZPE/(kcal⋅mol-1)), relative energies (Δ*E* and Δ(*E +* ZPE)/(kcal⋅mol-1)), enthalpies (Δ*H*(298)/(kcal⋅mol-1)), entropy (S(298)/(cal⋅mol-1⋅K-1)), free energies (Δ*G*(298)/(kcal⋅mol-1)) , *<S2>* and *T1* of all species for the HO4H + *X* reactionat the CCSD(T)-F12a/cc-pVDZ-F12//M06-2X/ 6-311+G(3*d*,2*p*) level of theory (*X* = H2O, (H2O)2, NH3, NH3∙∙∙H2O, H2O∙∙∙NH3, HCOOH and H2SO4)

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Catalyst | System | ZPE | S | △*E* | △(*E* + ZPE) | △*H* | △*G* | <S2> | *T1* |
| Nake  Reaction | HO2 + HO2 | 18.5 | 109.2 | 18.6 | 15.2 | 16.5 | 4.2 | 0.750, 0.750 | 0.029, 0.029 |
| HO4H | 21.9 | 67.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000 | 0.020 |
| TS | 18.5 | 65.6 | 27.2 | 23.8 | 23.6 | 24.2 | 0.000 | 0.020 |
| O3 + H2O | 18.1 | 101.9 | -8.5 | -12.3 | -10.7 | -21.0 | 0.000, 0.000 | 0.020, 0.011 |
| Nake Reaction\_I | HO2 + HO2 | 18.5 | 109.2 | 18.0 | 14.2 | 14.2 | 3.1 | 0.750, 0.750 | 0.029, 0.029 |
| HO4H\_I | 22.3 | 67.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000 | 0.020 |
| TS\_I | 19.2 | 65.1 | 30.4 | 27.3 | 26.9 | 27.6 | 0.000 | 0.020 |
| O3 + H2O | 18.7 | 101.7 | -7.1 | -10.7 | -9.3 | -19.5 | 0.000, 0.000 | 0.020, 0.011 |
| H2O | HO2 + HO2 + H2O | 32.0 | 154.2 | 17.3 | 13.3 | 14.7 | 2.3 | 0.750, 0.750, 0.000 | 0.029, 0.029, 0.011 |
| HO4H + H2O | 36.0 | 112.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020, 0.011 |
| HO4H∙∙∙H2O | 38.1 | 80.3 | -11.6 | -9.5 | -10.3 | -0.7 | 0.000 | 0.018 |
| TS\_H2O | 34.0 | 74.7 | 15.0 | 12.9 | 11.4 | 22.6 | 0.000 | 0.016 |
| O3∙∙∙H2O∙∙∙H2O | 36.0 | 93.5 | -19.9 | -19.9 | -19.4 | -13.7 | 0.000 | 0.020 |
| O3 + (H2O)2 | 34.3 | 125.5 | -14.9 | -16.7 | -15.8 | -19.7 | 0.000, 0.000 | 0.020, 0.011 |
| H2O\_a | HO2 + HO2 + H2O | 31.3 | 154.2 | 17.3 | 13.3 | 14.7 | 2.3 | 0.750, 0.750, 0.000 | 0.029, 0.029, 0.011 |
| HO4H + H2O | 35.6 | 112.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020, 0.011 |
| HO4H∙∙∙H2O\_a | 36.8 | 81.0 | -9.7 | -7.1 | -7.8 | 1.6 | 0.000 | 0.018 |
| TS\_H2O\_a | 33.4 | 75.1 | 17.6 | 14.1 | 14.3 | 23.4 | 0.000 | 0.019 |
| O3∙∙∙H2O∙∙∙H2O\_a | 34.9 | 94.2 | -19.2 | -19.2 | -19.3 | -14.9 | 0.000 | 0.020 |
| O3 + (H2O)2 | 33.7 | 126.7 | -14.3 | -17.6 | -16.6 | -20.3 | 0.000, 0.000 | 0.020, 0.011 |
| H2O\_b | HO2 + HO2 + H2O | 31.3 | 154.2 | 17.3 | 13.3 | 14.7 | 2.3 | 0.750, 0.750, 0.000 | 0.029, 0.029, 0.011 |
| HO4H + H2O | 35.6 | 112.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020, 0.011 |
| HO4H∙∙∙H2O\_b | 37.1 | 82.4 | -9.4 | -6.9 | -7.6 | 1.8 | 0.000 | 0.018 |
| TS\_H2O\_b | 33.3 | 76.0 | 17.6 | 13.5 | 14.7 | 25.9 | 0.000 | 0.020 |
| O3∙∙∙H2O∙∙∙H2O\_b | 34.9 | 98.4 | -20.2 | -19.9 | -19.0 | -14.5 | 0.000 | 0.020 |
| O3 + (H2O)2 | 34.3 | 125.5 | -14.9 | -16.7 | -15.8 | -19.7 | 0.000, 0.000 | 0.020, 0.011 |
| H2O\_c | HO2 + HO2 + H2O | 31.3 | 154.2 | 17.3 | 13.3 | 14.7 | 2.3 | 0.750, 0.750, 0.000 | 0.029, 0.029, 0.011 |
| HO4H + H2O | 34.6 | 112.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020, 0.011 |
| HO4H∙∙∙H2O\_c | 37.0 | 82.7 | -9.0 | -6.5 | -7.2 | 2.1 | 0.000 | 0.018 |
| TS\_H2O\_c | 33.3 | 76.0 | 18.2 | 14.1 | 15.3 | 26.5 | 0.000 | 0.020 |
| O3∙∙∙H2O∙∙∙H2O\_c | 34.9 | 98.4 | -20.3 | -19.9 | -19.0 | -14.5 | 0.000 | 0.020 |
| O3 + (H2O)2 | 34.3 | 125.5 | -14.9 | -16.7 | -15.8 | -19.7 | 0.000, 0.000 | 0.020, 0.011 |
| H2O\_I | HO2 + HO2 + H2O | 31.3 | 154.2 | 17.3 | 13.3 | 14.7 | 2.3 | 0.750, 0.750, 0.000 | 0.029, 0.029, 0.011 |
| HO4H + H2O | 34.6 | 112.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020, 0.011 |
| HO4H∙∙∙H2O\_I | 36.4 | 88.5 | -5.2 | -3.4 | -3.79 | 3.8 | 0.000 | 0.018 |
| TS\_H2O\_I | 33.4 | 87.5 | 20.3 | 16.2 | 18.6 | 26.4 | 0.000 | 0.020 |
| O3∙∙∙H2O∙∙∙H2O\_I | 34.9 | 98.8 | -19.9 | -19.6 | -18.7 | -14.3 | 0.000 | 0.020 |
| O3 + (H2O)2 | 34.3 | 125.5 | -14.9 | -16.7 | -15.8 | -19.7 | 0.000, 0.000 | 0.020, 0.011 |
| (H2O)2 | HO2 + HO2 + H2O + H2O | 45.6 | 199.3 | 22.5 | 16.0 | 18.0 | -0.9 | 0.750, 0.750, 0.000, 0.000 | 0.029, 0.029, 0.011, 0.011 |
| HO4H + (H2O)2 | 52.1 | 136.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020, 0.011 |
| HO4H∙∙∙(H2O)2 | 52.8 | 97.3 | -16.4 | -15.6 | -16.2 | -4.6 | 0.000 | 0.017 |
| TS\_(H2O)2 | 48.6 | 87.4 | 11.7 | 8.3 | 6.4 | 20.9 | 0.000 | 0.020 |
| O3∙∙∙H2O∙∙∙H2O∙∙∙H2O | 50.9 | 112.6 | -23.7 | -24.8 | -24.0 | -17.0 | 0.000 | 0.020 |
| O3 + (H2O)3 | 51.4 | 135.1 | -20.8 | -21.4 | -21.4 | -21.1 | 0.000, 0.000 | 0.020, 0.011 |
| (H2O)2\_I | HO2 + HO2 + H2O + H2O | 44.7 | 199.5 | 20.3 | 14.7 | 16.5 | -1.9 | 0.750, 0.750, 0.000, 0.000 | 0.029, 0.029, 0.011, 0.011 |
| HO4H + (H2O)2 | 52.1 | 136.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020, 0.011 |
| HO4H∙∙∙(H2O)2\_I | 52.2 | 106.3 | -11.3 | -9.3 | -9.5 | -0.1 | 0.000 | 0.017 |
| TS\_(H2O)2\_I | 49.1 | 98.3 | 12.4 | 8.6 | 7.2 | 21.9 | 0.000 | 0.020 |
| O3∙∙∙H2O∙∙∙H2O∙∙∙H2O\_I | 51.1 | 113.2 | -24.6 | -21.7 | -22.2 | -15.1 | 0.000 | 0.020 |
| O3 + (H2O)3 | 51.4 | 135.1 | -20.8 | -21.4 | -21.4 | -21.1 | 0.000, 0.000 | 0.020, 0.011 |
| NH3 | HO2 + HO2 + NH3 | 40.2 | 155.1 | 17.3 | 13.3 | 14.7 | 2.3 | 0.750, 0.750, 0.000 | 0.029, 0.029, 0.009 |
| HO4H + NH3 | 44.2 | 113.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020, 0.009 |
| HO4H∙∙∙NH3 | 45.5 | 85.6 | -12.9 | -11.6 | -11.9 | -3.6 | 0.000 | 0.018 |
| TS\_NH3 | 43.2 | 77.6 | 11.9 | 10.9 | 9.7 | 20.4 | 0.000 | 0.019 |
| O3∙∙∙NH3∙∙∙H2O | 43.6 | 96.8 | -20.5 | -21.1 | -20.2 | -15.3 | 0.000 | 0.020 |
| O3 + H2O∙∙∙NH3 | 42.6 | 125.0 | -16.3 | -18.0 | -17.3 | -20.7 | 0.000, 0.000 | 0.020, 0.010 |
| NH3\_I | HO2 + HO2 + NH3 | 40.2 | 155.1 | 17.3 | 13.3 | 14.7 | 2.3 | 0.750, 0.750, 0.000 | 0.029, 0.029, 0.009 |
| HO4H + NH3 | 44.2 | 113.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020, 0.009 |
| HO4H∙∙∙NH3 | 45.5 | 85.6 | -12.9 | -11.6 | -11.9 | -3.6 | 0.000 | 0.018 |
| TS\_NH3\_Ia | 41.7 | 77.2 | 18.6 | 15.1 | 16.2 | 27.3 | 0.000 | 0.019 |
| IM\_NH3\_Ib | 44.1 | 78.7 | 12.0 | 10.9 | 10.1 | 20.8 | 0.000 | 0.019 |
| TS\_NH3\_Ib | 42.2 | 79.8 | 6.9 | 5.5 | 6.3 | 16.8 | 0.000 | 0.018 |
| O3∙∙∙NH3∙∙∙H2O | 43.6 | 96.8 | -20.5 | -21.1 | -20.2 | -15.3 | 0.000 | 0.020 |
| O3 + NH3∙∙∙H2O | 42.6 | 125.0 | -16.3 | -18.0 | -17.3 | -20.7 | 0.000, 0.000 | 0.020, 0.010 |
| NH3∙∙∙H2O | HO2 + HO2 + NH3 + H2O | 53.8 | 200.3 | 16.1 | 10.9 | 13.1 | -6.0 | 0.750, 0.750, 0.000, 0.000 | 0.029 , 0.029 , 0.009 , 0.011 |
| HO4H + NH3∙∙∙H2O | 58.9 | 133.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020 , 0.010 |
| HO4H∙∙∙NH3∙∙∙H2O | 61.3 | 98.9 | -19.2 | -19.1 | -17.8 | -10.1 | 0.000 | 0.020 |
| TS\_NH3∙∙∙H2O | 54.7 | 96.7 | 19.4 | 15.5 | 16.6 | 28.4 | 0.000 | 0.015 |
| O3∙∙∙NH3∙∙∙H2O∙∙∙H2O | 59.6 | 115.3 | -30.3 | -29.9 | -28.4 | -23.5 | 0.000 | 0.020 |
| O3 + NH3∙∙∙H2O∙∙∙H2O | 58.9 | 136.8 | -21.3 | -25.4 | -21.7 | -26.2 | 0.000, 0.000 | 0.020 , 0.011 |
| NH3∙∙∙H2O\_I | HO2 + HO2 + NH3 + H2O | 53.8 | 200.3 | 16.1 | 10.9 | 13.1 | -6.0 | 0.750, 0.750, 0.000, 0.000 | 0.029, 0.029, 0.009, 0.011 |
| HO4H + NH3∙∙∙H2O | 58.9 | 133.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020, 0.010 |
| HO4H∙∙∙NH3∙∙∙H2O | 61.3 | 98.9 | -19.2 | -19.1 | -17.8 | -10.1 | 0.000 | 0.020 |
| TS\_NH3∙∙∙H2O\_Ia | 55.6 | 96.3 | 45.7 | 43.1 | 42.6 | 53.3 | 0.000 | 0.019 |
| IM\_NH3∙∙∙H2O\_Ib | 59.9 | 95.3 | 4.3 | 3.3 | 5.2 | 16.1 | 0.000 | 0.020 |
| TS\_NH3∙∙∙H2O\_Ib | 57.4 | 92.9 | 1.2 | 0.5 | 0.6 | 10.8 | 0.000 | 0.020 |
| O3∙∙∙NH3∙∙∙H2O∙∙∙H2O | 59.6 | 115.3 | -30.3 | -29.9 | -28.4 | -23.5 | 0.000 | 0.020 |
| O3 + NH3∙∙∙H2O∙∙∙H2O | 58.9 | 136.8 | -21.3 | -25.4 | -21.7 | -26.2 | 0.000, 0.000 | 0.020, 0.011 |
| H2O∙∙∙NH3 | HO2 + HO2 + H2O + NH3 | 53.8 | 200.3 | 20.7 | 15.2 | 16.6 | -0.6 | 0.750, 0.750, 0.000, 0.000 | 0.029, 0.029, 0.009， 0.011 |
| HO4H + H2O∙∙∙NH3 | 57.4 | 134.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020 , 0.010 |
| HO4H∙∙∙H2O∙∙∙NH3 | 61.7 | 99.2 | -12.1 | -8.8 | -8.4 | -0.1 | 0.000 | 0.017 |
| TS\_H2O∙∙∙NH3 | 52.5 | 85.5 | 9.6 | 8.9 | 7.9 | 21.0 | 0.000 | 0.020 |
| O3∙∙∙H2O∙∙∙NH3∙∙∙H2O | 59.5 | 117.5 | -25.1 | -24.0 | -21.1 | -15.8 | 0.000 | 0.020 |
| O3 + H2O∙∙∙NH3∙∙∙H2O | 51.6 | 191.0 | -3.8 | -7.3 | -6.3 | -21.0 | 0.000, 0.000 | 0.020, 0.011 |
| H2O∙∙∙NH3\_I | HO2 + HO2 + H2O +NH3 | 53.8 | 200.3 | 20.7 | 15.2 | 16.6 | -0.6 | 0.750, 0.750, 0.000, 0.000 | 0.029, 0.029, 0.009, 0.011 |
| HO4H + H2O∙∙∙NH3 | 57.4 | 134.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020, 0.010 |
| HO4H∙∙∙ H2O∙∙∙NH3 | 61.7 | 99.2 | -12.1 | -8.8 | -8.4 | -0.1 | 0.000 | 0.017 |
| TS\_H2O∙∙∙NH3\_Ia | 53.5 | 92.1 | 33.8 | 28.9 | 31.1 | 40.6 | 0.000 | 0.016 |
| IM\_H2O∙∙∙NH3\_Ib | 58.4 | 90.0 | 13.3 | 14.8 | 14.8 | 28.8 | 0.000 | 0.020 |
| TS\_H2O∙∙∙NH3\_Ib | 56.3 | 95.3 | 3.3 | 3.2 | 2.9 | 15.1 | 0.000 | 0.019 |
| O3∙∙∙H2O∙∙∙NH3∙∙∙H2O\_I | 58.5 | 117.5 | -25.1 | -24.0 | -21.1 | -15.8 | 0.000 | 0.017 |
| O3 + H2O∙∙∙NH3∙∙∙H2O | 51.6 | 191.0 | -3.8 | -7.3 | -6.3 | -21.0 | 0.000 | 0.020, 0.011 |
| NH3∙∙∙NH3 | HO2 + HO2 + NH3 + NH3 | 58.4 | 199.3 | 16.4 | 11.7 | 12.6 | -1.9 | 0.750, 0.750, 0.000, 0.000 | 0.029, 0.029,0.011, 0.011 |
| HO4H + NH3∙∙∙NH3 | 63.2 | 140.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020, 0.009 |
| HO4H∙∙∙NH3∙∙∙NH3 | 65.1 | 101.4 | -15.4 | -16.9 | -15.6 | -2.4 | 0.000 | 0.017 |
| TS\_NH3∙∙∙NH3 | 62.4 | 85.8 | 42.0 | 35.7 | 33.3 | 51.6 | 0.000 | 0.020 |
| O3∙∙∙NH3∙∙∙NH3∙∙∙H2O | 64.7 | 122.5 | -21.3 | -20.0 | -19.3 | -16.1 | 0.000 | 0.019 |
| O3 + NH3∙∙∙NH3∙∙∙H2O | 63.5 | 140.6 | -20.8 | -21.4 | -21.3 | -20.8 | 0.000, 0.000 | 0.020, 0.010 |
| HCOOH | HO2 + HO2 + HCOOH | 40.1 | 168.4 | 17.3 | 13.3 | 14.7 | 2.3 | 0.750, 0.750, 0.000 | 0.029, 0.029, 0.017 |
| HO4H + HCOOH | 44.1 | 126.7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020, 0.017 |
| HO4H∙∙∙HCOOH | 45.2 | 88.4 | -15.3 | -14.1 | -14.4 | -3.0 | 0.000 | 0.019 |
| TS\_HCOOH | 40.3 | 84.0 | 9.3 | 5.5 | 4.7 | 17.4 | 0.000 | 0.020 |
| O3∙∙∙H2O∙∙∙HCOOH | 43.4 | 99.2 | -21.6 | -22.3 | -21.4 | -13.2 | 0.000 | 0.020 |
| O3 + H2O∙∙∙HCOOH | 42.6 | 129.8 | -20.3 | -21.9 | -21.3 | -22.2 | 0.000, 0.000 | 0.020, 0.016 |
| HCOOH\_I | HO2 + HO2 + HCOOH | 40.1 | 168.4 | 17.3 | 13.3 | 14.7 | 2.3 | 0.750, 0.750, 0.000 | 0.029, 0.029, 0.017 |
| HO4H + HCOOH | 44.1 | 126.7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020, 0.017 |
| HO4H∙∙∙HCOOH\_I | 45.5 | 94.3 | -2.2 | -5.3 | -5.7 | 1.5 | 0.000 | 0.019 |
| TS\_HCOOH\_I | 39.9 | 87.2 | 20.3 | 16.1 | 16.5 | 27.1 | 0.000 | 0.020 |
| O3∙∙∙H2O∙∙∙HCOOH\_I | 41.5 | 112.7 | -21.6 | -23.4 | -20.8 | -16.2 | 0.000 | 0.020 |
| O3 + H2O∙∙∙HCOOH\_I | 43.9 | 108.6 | -18.9 | -19.7 | -18.9 | -20.6 | 0.000, 0.000 | 0.020, 0.016 |
| H2SO4 | HO2 + HO2 + H2SO4 | 39.2 | 181.6 | 12.3 | 10.0 | 11.2 | 0.3 | 0.750, 0.750, 0.000 | 0.029, 0.029, 0.016 |
| HO4H + H2SO4 | 41.1 | 140.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020, 0.016 |
| HO4H∙∙∙H2SO4 | 43.2 | 100.6 | -12.1 | -10.3 | -10.6 | 1.2 | 0.000 | 0.018 |
| TS\_H2SO4 | 38.1 | 95.9 | 2.6 | 2.1 | 1.7 | 13.3 | 0.000 | 0.017 |
| O3∙∙∙H2O∙∙∙H2SO4 | 39.9 | 115.1 | -31.5 | -27.7 | -27.6 | -26.0 | 0.000 | 0.020 |
| O3 + H2O∙∙∙H2SO4 | 39.2 | 174.2 | -26.3 | -26.4 | -25.1 | -25.1 | 0.000, 0.000 | 0.020, 0.015 |
| H2SO4\_I | HO2 + HO2 + H2SO4 | 39.2 | 181.6 | 12.3 | 10.0 | 11.2 | 0.3 | 0.750, 0.750, 0.000 | 0.029, 0.029, 0.016 |
| HO4H + H2SO4 | 41.1 | 140.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020, 0.016 |
| HO4H∙∙∙H2SO4\_I | 41.3 | 110.1 | -5.9 | -4.7 | -4.6 | 2.5 | 0.000 | 0.018 |
| TS\_H2SO4\_I | 39.5 | 102.8 | 7.3 | 5.6 | 5.9 | 16.3 | 0.000 | 0.020 |
| O3 ∙∙∙H2O∙∙∙H2SO4\_I | 40.1 | 123.6 | -27.4 | -27.0 | -26.5 | -14.5 | 0.000 | 0.020 |
| O3 + H2O∙∙∙H2SO4\_I | 39.2 | 174.2 | -26.3 | -26.4 | -25.1 | -25.1 | 0.000, 0.000 | 0.020, 0.015 |
| H2SO4\_II | HO2 + HO2 + H2SO4 | 42.3 | 181.8 | 15.3 | 11.9 | 13.2 | 1.0 | 0.750, 0.750, 0.000 | 0.029, 0.029, 0.016 |
| HO4H + H2SO4 | 45.7 | 139.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.000, 0.000 | 0.020, 0.016 |
| HO4H∙∙∙H2SO4\_II | 46.7 | 105.6 | -5.4 | -5.9 | -4.3 | 3.6 | 0.000 | 0.018 |
| TS\_H2SO4\_II | 43.8 | 100.7 | 7.6 | 5.8 | 6.4 | 16.8 | 0.000 | 0.020 |
| O3 ∙∙∙H2O∙∙∙H2SO4\_II | 40.6 | 120.3 | -29.1 | -28.2 | -18.4 | -13.7 | 0.000 | 0.020 |
| O3 + H2O∙∙∙H2SO4\_II | 39.2 | 171.2 | -26.3 | -26.4 | -25.1 | -25.1 | 0.000, 0.000 | 0.020, 0.015 |

**Table S2** The binding energies (∆Ea, 0 K), energy barriers (∆Eb, 0 K), and reaction energies (∆Ec,0 K) of the HO4H → H2O + O3 reaction at different theoretical methods with zero-point correction involved and mean unsigned error (MUEd) (in kcal mol-1)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Methods | *∆E*a | ∆*E*b | ∆*E*c | MUEd |
| W3X-l//M06-2X/aug-cc-pVTZ | -14.5 | 7.7 | -28.8 | 0.00 |
| W2X//M06-2X/aug-cc-pVTZ | -14.8 | 9.5 | -27.7 | 1.06 |
| CCSD(T)-F12a/cc-pVDZ-F12//M06-2X/aug-cc-pVTZ | -15.2 | 8.6 | -27.5 | 0.96 |

a The binding energies with respect to HO4H. b The energy barriers with respect to HO4H → H2O + O3 reaction. c The reaction barriers with respect to HO4H → H2O + O3 reaction. d Mean unsigned error averaged over the three previous columns

**Table** **S3** Concentrations of *X* (*X =* H2O, (H2O)2, NH3, NH3∙∙∙H2O, H2O∙∙∙NH3, HCOOH and H2SO4) (in molecule⋅cm-3) within temperature range of 280 K – 320 K at 0 km altitude

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| catalyst |  | | 280 K | 290 K | 298 K | 300 K | 310 K | 320 K |
| NH3 | 0.1 ppbv | | 2.6×109 | 2.5×109 | 2.5×109 | 2.4×109 | 2.4×109 | 2.3×109 |
| 10 ppbv | | 2.6×1011 | 2.5×1011 | 2.5×1011 | 2.4×1011 | 2.4×1011 | 2.3×1011 |
| 2900 ppbv | | 7.6×1013 | 7.3×1013 | 7.1×1013 | 7.1×1013 | 6.9×1013 | 6.7×1013 |
| NH3∙∙∙NH3 | 0.1 ppbv | | 3.9×10-4 | 3.4×10-4 | 3.0×10-4 | 2.9×10-4 | 2.6×10-4 | 2.3×10-4 |
| 10 ppbv | | 3.93 | 3.38 | 3.02 | 2.93 | 2.57 | 2.28 |
| 2900 ppbv | | 3.3×105 | 2.8×105 | 2.5×105 | 2.5×105 | 2.2×105 | 1.9×105 |
| NH3∙∙∙H2O | 20%RH | 0.1 ppbv | 2.4×106 | 3.3×106 | 4.2×106 | 4.4×106 | 5.8×106 | 7.3×106 |
| 10 ppbv | 2.4×108 | 3.3×1008 | 4.2×108 | 4.4×108 | 5.8×108 | 7.3×108 |
| 2900 ppbv | 6.9×1010 | 9.5×1010 | 1.2×1011 | 1.3×1011 | 1.7×1011 | 2.1×1011 |
| 100%RH | 0.1 ppbv | 1.2×107 | 1.6×107 | 2.1×107 | 2.2×107 | 2.9×107 | 3.6×107 |
| 10 ppbv | 1.2×109 | 1.6×109 | 2.1×109 | 2.2×109 | 2.9×109 | 3.6×109 |
| 2900 ppbv | 3.5×1011 | 4.8×1011 | 6.1×1011 | 6.4×1011 | 8.4×1011 | 1.1×1012 |
| H2O∙∙∙NH3 | 20%RH | 0.1 ppbv | 1.8×105 | 2.5×105 | 3.3×105 | 3.4×105 | 4.7×105 | 5.1×105 |
| 10 ppbv | 1.8×107 | 2.5×107 | 3.3×107 | 3.4×107 | 4.6×107 | 5.1×107 |
| 2900 ppbv | 5.4×109 | 7.4×109 | 9.3×109 | 1.0×1010 | 1.3×1010 | 1.5×1010 |
| 100%RH | 0.1 ppbv | 9.2×105 | 1.3×106 | 1.7×106 | 1.7×106 | 2.4×106 | 2.9×106 |
| 10 ppbv | 9.2×107 | 1.3×108 | 1.7×108 | 1.7×108 | 2.4×108 | 2.9×108 |
| 2900 ppbv | 2.7×1010 | 3.7×1010 | 4.8×1010 | 5.1×1010 | 6.9×1010 | 8.4×1010 |
| H2O | 20% RH | | 5.2×1016 | 9.6×1016 | 1.5×1017 | 1.7×1017 | 2.9×1017 | 4.1×1017 |
| 40% RH | | 1.0×1017 | 1.9×1017 | 3.1×1017 | 3.4×1017 | 5.8×1017 | 9.4×1017 |
| 60% RH | | 1.5×1017 | 2.9×1017 | 4.5×1017 | 5.1×1017 | 8.8×1017 | 1.4×1017 |
| 80% RH | | 2.1×1017 | 2.9×1017 | 6.2×1017 | 6.9×1017 | 1.2×1017 | 1.9×1017 |
| 100% RH | | 2.6×1017 | 4.8×1017 | 7.7×1017 | 8.6×1017 | 1.5×1018 | 2.3×1018 |
| (H2O)2 | 20% RH | | 8.2×1012 | 2.4×1013 | 5.4×1013 | 6.5×1013 | 1.6×1014 | 3.7×1014 |
| 40% RH | | 3.3×1013 | 5.0×1013 | 2.2×1014 | 2.6×1014 | 6.5×1014 | 1.5×1015 |
| 60% RH | | 7.4×1013 | 2.1×1014 | 4.9×1014 | 5.8×1014 | 1.5×1015 | 3.3×1015 |
| 80% RH | | 1.1×1014 | 3.8×1014 | 8.7×1014 | 1.0×1015 | 2.6×1015 | 5.9×1015 |
| 100% RH | | 2.0×1014 | 5.9×1014 | 1.4×1015 | 1.6×1015 | 4.0×1015 | 9.2×1015 |
| HCOOH | 10 ppbv | | 2.6×1011 | 2.5×1011 | 2.4×1011 | 2.4×1011 | 2.4×1011 | 2.3×1011 |
| 0.01 ppbv | | 2.6×108 | 2.5×108 | 2.4×108 | 2.4×108 | 2.4×108 | 2.3×108 |
| 2 ppbv | | 2.0×1010 | 1.9×1010 | 1.9×1010 | 1.9×1010 | 1.8×1010 | 1.8×1010 |
| H2SO4 | | | 3.9×108 | 3.8×108 | 3.7×108 | 3.7×108 | 3.6×108 | 3.4×108 |

**Table S4** Calculated rate constants (molecule-1⋅cm3⋅s-1) in presence of catalyst *X* (*X* = H2O, (H2O)2, NH3, NH3∙∙∙H2O, H2O∙∙∙NH3,HCOOH and H2SO4) using the results obtained from CCSD(T)-F12a/ cc-pVDZ-F12//M06-2X/6-311+G(3*d*,2*p*) level of theory

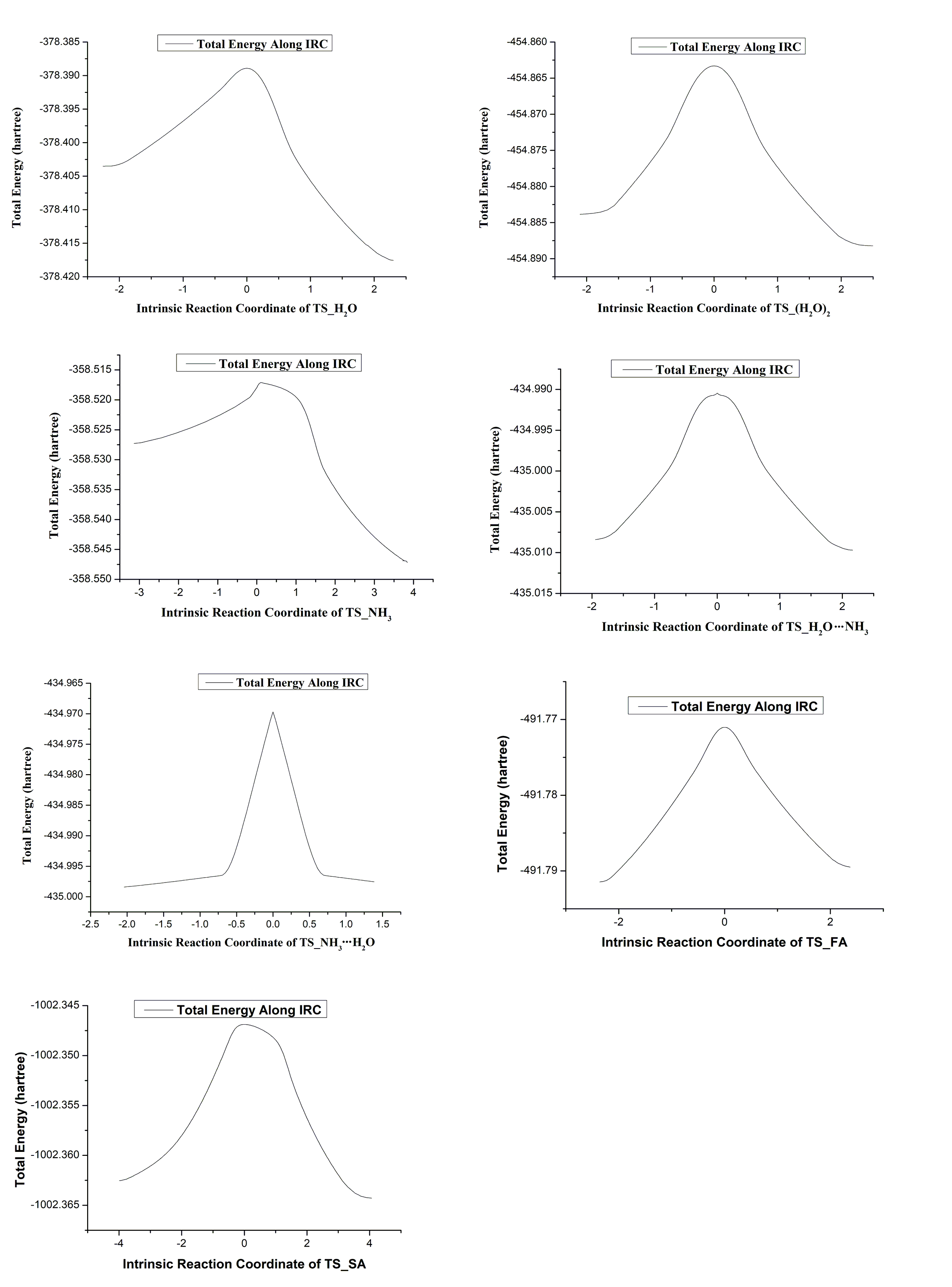
|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Catalyst | Rate Constant | Temperature(K) | | | | | | | | |
| 213 K | 230 K | 259 K | 280 K | 290 K | 298 K | 300 K | 310 K | 320 K |
| Nake | *kb* | 1.21×10-7 | 3.27×10-7 | 8.95×10-6 | 3.07×10-5 | 7.19×10-5 | 9.19×10-5 | 2.47×10-4 | 3.06×10-4 | 1.47×10-3 |
| H2O | Keq | 5.06×10-17 | 8.94×10-18 | 7.96×10-19 | 1.91×10-19 | 1.04×10-19 | 6.63×10-20 | 5.95×10-20 | 3.51×10-21 | 9.52×10-21 |
| *k*uni | 4.42×10-9 | 3.79×10-8 | 1.47×10-6 | 1.81×10-5 | 5.59×10-5 | 1.33×10-4 | 1.65×10-4 | 4.61×10-4 | 2.79×10-3 |
| *kb* | 2.23×10-25 | 3.39×10-25 | 1.17×10-24 | 3.46×10-24 | 5.83×10-24 | 8.83×10-24 | 9.79×10-24 | 1.62×10-23 | 2.66×10-23 |
| H2O\_a | Keq | 1.66×10-17 | 3.32×10-18 | 3.55×10-19 | 9.50×10-20 | 5.44×10-20 | 3.59×10-20 | 3.25×10-20 | 2.00×10-20 | 1.28×10-20 |
| *k*uni | 2.00×10-9 | 1.75×10-8 | 7.12×10-7 | 8.97×10-6 | 2.79×10-5 | 6.67×10-5 | 8.26×10-5 | 2.32×10-4 | 6.22×10-4 |
| *kb* | 3.31×10-26 | 5.82×10-26 | 2.53×10-25 | 8.52×10-25 | 1.52×10-24 | 2.39×10-24 | 2.68×10-24 | 4.66×10-24 | 7.96×10-24 |
| H2O\_b | Keq | 2.06×10-17 | 3.83×10-18 | 3.67×10-19 | 9.22×10-20 | 5.12×10-20 | 3.30×10-20 | 2.97×10-20 | 1.79×10-20 | 1.11×10-20 |
| *k*uni | 2.05×10-9 | 2.00×10-8 | 9.39×10-7 | 1.27×10-5 | 4.09×10-5 | 1.00×10-4 | 1.25×10-4 | 3.60×10-4 | 9.89×10-4 |
| *kb* | 4.22×10-26 | 7.65×10-26 | 3.44×10-25 | 1.17×10-24 | 2.09×10-24 | 3.31×10-24 | 3.70×10-24 | 6.45×10-24 | 1.10×10-23 |
| H2O\_c | Keq | 9.86×10-18 | 1.96×10-18 | 2.05×10-19 | 5.45×10-20 | 3.10×10-20 | 2.03×10-20 | 1.84×10-20 | 1.13×10-20 | 7.16×10-21 |
| *k*uni | 1.43×10-9 | 1.31×10-8 | 5.85×10-7 | 7.80×10-6 | 2.51×10-5 | 6.15×10-5 | 7.64×10-5 | 2.21×10-4 | 6.10×10-4 |
| *kb* | 1.41×10-26 | 2.57×10-26 | 1.20×10-25 | 4.25×10-25 | 7.76×10-25 | 1.25×10-24 | 1.40×10-24 | 2.50×10-24 | 4.37×10-24 |
| H2O\_I | Keq | 5.05×10-20 | 1.82×10-20 | 4.42×10-21 | 1.94×10-21 | 1.37×10-21 | 1.05×10-21 | 9.90×10-22 | 7.36×10-22 | 5.57×10-22 |
| *k*uni | 1.19×10-6 | 3.87×10-6 | 3.88×10-5 | 2.27×10-4 | 5.33×10-4 | 1.05×10-3 | 1.24×10-3 | 2.85×10-3 | 6.45×10-3 |
| *kb* | 6.00×10-26 | 7.05×10-26 | 1.71×10-25 | 4.41×10-25 | 7.29×10-25 | 1.11×10-24 | 1.23×10-24 | 2.10×10-24 | 3.59×10-24 |
| (H2O)2 | Keq | 1.03×10-13 | 7.56×10-15 | 1.95×10-16 | 2.22×10-17 | 8.86×10-18 | 4.44×10-18 | 3.76×10-18 | 1.69×10-18 | 7.98×10-19 |
| *k*uni | 5.59×10-11 | 7.72×10-10 | 5.44×10-8 | 8.97×10-7 | 3.09×10-6 | 7.91×10-6 | 9.95×10-6 | 3.01×10-5 | 8.60×10-5 |
| *kb* | 5.77×10-24 | 5.84×10-24 | 1.06×10-23 | 2.00×10-23 | 2.73×10-23 | 3.51×10-23 | 3.74×10-23 | 5.09×10-23 | 6.86×10-23 |
| (H2O)2\_I | Keq | 1.50×10-16 | 2.39×10-17 | 1.85×10-18 | 4.07×10-19 | 2.15×10-19 | 1.33×10-19 | 1.18×10-19 | 6.80×10-20 | 4.06×10-20 |
| *k*uni | 9.57×10-9 | 2.17×10-7 | 1.51×10-5 | 5.29×10-5 | 1.23×10-4 | 1.31×10-4 | 1.63×10-4 | 3.87×10-4 | 8.36×10-4 |
| *kb* | 1.43×10-24 | 5.17×10-24 | 2.79×10-23 | 2.15×10-23 | 2.65×10-23 | 1.75×10-23 | 1.93×10-23 | 2.63×10-23 | 3.39×10-23 |
| NH3 | Keq | 1.51×10-14 | 1.98×10-15 | 1.17×10-16 | 2.21×10-17 | 1.09×10-17 | 6.43×10-18 | 5.66×10-18 | 3.07×10-18 | 1.74×10-18 |
| *k*uni | 3.43×10-13 | 1.73×10-11 | 4.20×10-9 | 1.10×10-7 | 4.40×10-7 | 1.25×10-6 | 1.61×10-6 | 4.40×10-6 | 1.38×10-5 |
| *kb* | 5.18×10-27 | 3.42×10-26 | 4.92×10-25 | 2.43×10-24 | 4.80×10-24 | 8.04×10-24 | 9.10×10-24 | 1.35×10-23 | 2.40×10-23 |
| NH3\_I | Keq | 1.51×10-14 | 1.98×10-15 | 1.17×10-16 | 2.21×10-17 | 1.09×10-17 | 6.43×10-18 | 5.65×10-18 | 3.07×10-18 | 1.74×10-18 |
| *k*uni | 3.62×10-12 | 2.55×10-10 | 2.14×10-9 | 5.66×10-8 | 2.57×10-7 | 4.26×10-7 | 5.42×10-7 | 8.04×10-7 | 2.27×10-6 |
| *kb* | 5.47×10-26 | 5.04×10-25 | 2.51×10-25 | 1.25×10-24 | 2.81×10-24 | 2.74×10-24 | 3.07×10-24 | 2.47×10-24 | 3.93×10-24 |
| NH3∙∙∙H2O | Keq | 1.82×10-25 | 2.49×10-25 | 5.39×10-25 | 1.08×10-24 | 1.56×10-24 | 2.11×10-24 | 2.28×10-24 | 3.37×10-24 | 5.02×10-24 |
| *k*uni | 2.44×10-16 | 1.34×10-15 | 2.40×10-14 | 6.12×10-14 | 1.42×10-13 | 1.62×10-13 | 2.07×10-13 | 5.75×10-13 | 1.55×10-12 |
| *kb* | 4.45×10-41 | 3.34×10-40 | 1.30×10-38 | 6.62×10-38 | 2.23×10-37 | 3.43×10-37 | 4.71×10-37 | 1.94×10-36 | 7.79×10-36 |
| NH3∙∙∙H2O\_I | Keq | 9.24×10-46 | 4.08×10-45 | 7.47×10-44 | 7.76×10-43 | 2.53×10-42 | 6.65×10-42 | 8.49×10-42 | 2.95×10-41 | 1.05×10-40 |
| *k*uni | 3.55×10-37 | 8.25×10-36 | 1.78×10-33 | 2.80×10-32 | 1.56×10-31 | 3.60×10-31 | 5.47×10-31 | 3.70×10-30 | 2.44×10-29 |
| *kb* | 3.28×10-82 | 3.37×10-80 | 1.33×10-76 | 2.18×10-74 | 3.96×10-73 | 2.40×10-72 | 4.64×10-72 | 1.09×10-70 | 2.56×10-69 |

To be Continued

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Catalyst | Rate Constant | Temperature(K) | | | | | | | | |
| 213 | 230 | 259 | 280 | 290 | 298 | 300 | 310 | 320 |
| H2O∙∙∙NH3 | Keq | 1.56×10-13 | 1.13×10-14 | 2.90×10-16 | 3.30×10-17 | 1.32×10-17 | 6.60×10-18 | 5.58×10-18 | 2.51×10-18 | 1.19×10-18 |
| *k*uni | 8.42×10-11 | 1.42×10-9 | 9.81×10-8 | 1.24×10-6 | 4.02×10-6 | 9.60×10-6 | 1.20×10-5 | 3.33×10-5 | 8.52×10-5 |
| *kb* | 1.31×10-23 | 1.60×10-23 | 2.84×10-23 | 4.10×10-23 | 5.54×10-23 | 6.34×10-23 | 6.69×10-23 | 8.35×10-23 | 1.01×10-22 |
| H2O∙∙∙NH3\_I | Keq | 1.56×10-13 | 1.13×10-14 | 2.90×10-16 | 3.30×10-17 | 1.32×10-17 | 6.60×10-18 | 5.58×10-18 | 2.51×10-18 | 1.19×10-18 |
| *k*uni | 1.16×10-26 | 2.78×10-25 | 6.19×10-23 | 9.51×10-22 | 5.04×10-21 | 1.08×10-20 | 1.59×10-20 | 9.22×10-20 | 4.88×10-19 |
| *kb* | 1.81×10-39 | 3.13×10-39 | 1.79×10-38 | 3.14×10-38 | 6.65×10-38 | 7.10×10-38 | 8.90×10-38 | 2.32×10-37 | 5.81×10-37 |
| NH3∙∙∙NH3 | Keq | 1.49×10-12 | 8.73×10-14 | 1.66×10-15 | 1.58×10-16 | 5.85×10-17 | 2.76×10-17 | 2.31×10-17 | 9.72×10-18 | 4.33×10-18 |
| *k*uni | 1.53×10-33 | 3.51×10-32 | 7.40×10-30 | 1.16×10-28 | 6.39×10-28 | 1.45×10-27 | 2.19×10-27 | 1.42×10-26 | 8.75×10-26 |
| *kb* | 2.28×10-45 | 3.06×10-48 | 1.23×10-44 | 1.83×10-44 | 3.74×10-44 | 4.01×10-44 | 5.06×10-44 | 1.38×10-43 | 3.79×10-43 |
| HCOOH | Keq | 8.08×10-14 | 6.87×10-15 | 2.21×10-16 | 2.90×10-17 | 1.23×10-17 | 6.45×10-18 | 5.52×10-18 | 2.62×10-18 | 1.31×10-18 |
| *k*uni | 1.17×10-5 | 6.79×10-5 | 1.42×10-3 | 1.16×10-2 | 3.02×10-2 | 6.30×10-2 | 7.55×10-2 | 1.82×10-1 | 4.20×10-1 |
| *kb* | 9.43×10-19 | 4.67×10-19 | 3.12×10-19 | 3.38×10-19 | 3.71×10-19 | 4.07×10-19 | 4.17×10-19 | 4.76×10-19 | 5.48×10-19 |
| HCOOH\_I | Keq | 3.63×10-21 | 1.28×10-21 | 3.02×10-22 | 1.31×10-22 | 9.21×10-23 | 7.09×10-23 | 6.66×10-23 | 4.93×10-23 | 3.73×10-23 |
| *k*uni | 1.14×10-9 | 7.99×10-9 | 3.59×10-7 | 5.79×10-6 | 2.07×10-5 | 5.58×10-5 | 7.12×10-5 | 2.33×10-4 | 7.30×10-4 |
| *kb* | 4.14×10-30 | 1.02×10-29 | 1.09×10-28 | 7.57×10-28 | 1.91×10-27 | 3.96×10-27 | 4.74×10-27 | 1.15×10-26 | 2.72×10-26 |
| H2SO4 | Keq | 1.47×10-13 | 1.27×10-14 | 4.21×10-16 | 5.63×10-17 | 2.41×10-17 | 1.27×10-17 | 1.09×10-17 | 5.22×10-18 | 2.62×10-18 |
| *k*uni | 4.91×10-4 | 7.54×10-3 | 5.00×10-1 | 5.88 | 1.46×101 | 2.97×101 | 3.55×101 | 8.43×101 | 1.95×102 |
| *kb* | 7.21×10-17 | 9.58×10-17 | 2.10×10-16 | 3.31×10-16 | 3.50×10-16 | 3.78×10-16 | 3.87×10-16 | 4.40×10-16 | 5.10×10-16 |
| H2SO4\_I | Keq | 6.68×10-18 | 1.25×10-18 | 1.23×10-19 | 3.12×10-20 | 1.75×10-20 | 1.14×10-20 | 1.03×10-20 | 6.24×10-21 | 3.92×10-21 |
| *k*uni | 8.53×10-5 | 5.53×10-4 | 1.38×10-2 | 1.30×10-1 | 3.59×10-1 | 7.87×10-1 | 9.54×10-1 | 2.44 | 5.98 |
| *kb* | 5.70×10-22 | 6.93×10-22 | 1.70×10-21 | 4.06×10-21 | 6.30×10-21 | 8.97×10-21 | 9.80×10-21 | 1.52×10-20 | 2.34×10-20 |
| H2SO4\_II | Keq | 3.81×10-18 | 7.80×10-19 | 8.64×10-20 | 2.37×10-20 | 1.38×10-20 | 9.16×10-21 | 8.30×10-21 | 5.19×10-21 | 3.35×10-21 |
| *k*uni | 1.37×10-04 | 9.59×10-4 | 2.66×10-2 | 2.65×10-1 | 7.49×10-1 | 1.67 | 2.04 | 5.31 | 1.33×101 |
| *kb* | 5.22×10-22 | 7.48×10-22 | 2.30×10-21 | 6.29×10-21 | 1.03×10-20 | 1.53×10-20 | 1.69×10-20 | 2.76×10-20 | 4.44×10-20 |

**Table S5** Effective rate constants (s-1) for all the catalysts within temperature range of 280 K – 320 K at 0 km altitude using catalyst *X* (*X* = H2O, (H2O)2, NH3, NH3∙∙∙H2O, H2O∙∙∙NH3,HCOOH and H2SO4) concentrations given in Table S3

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Catalyst | Concentrations. | | 280 K | 290 K | 298 K | 300 K | 310 K | 320 K |
| H2O | 20% RH | | 1.80×10-7 | 5.60×10-7 | 1.32×10-6 | 1.66×10-6 | 4.71×10-6 | 1.09×10-5 |
| 40% RH | | 3.46×10-7 | 1.11×10-6 | 2.74×10-6 | 3.33×10-6 | 9.42×10-6 | 2.50×10-5 |
| 60% RH | | 5.19×10-7 | 1.69×10-6 | 3.97×10-6 | 4.99×10-6 | 1.43×10-5 | 3.72×10-6 |
| 80% RH | | 7.26×10-7 | 1.69×10-6 | 5.47×10-6 | 6.75×10-6 | 1.95×10-6 | 5.05×10-6 |
| 100% RH | | 8.99×10-7 | 2.80×10-6 | 6.80×10-6 | 8.42×10-6 | 2.44×10-5 | 6.11×10-5 |
| (H2O)2 | 20% RH | | 1.64×10-10 | 6.56×10-10 | 1.90×10-9 | 2.43×10-9 | 8.14×10-9 | 2.54×10-8 |
| 40% RH | | 6.59×10-10 | 1.37×10-9 | 7.73×10-9 | 9.72×10-9 | 3.31×10-8 | 1.03×10-7 |
| 60% RH | | 1.48×10-9 | 5.74×10-9 | 1.72×10-8 | 2.17×10-8 | 7.63×10-8 | 2.27×10-7 |
| 80% RH | | 2.20×10-9 | 1.04×10-8 | 3.06×10-8 | 3.74×10-8 | 1.32×10-7 | 4.05×10-7 |
| 100% RH | | 3.99×10-9 | 1.61×10-8 | 4.92×10-8 | 5.98×10-8 | 2.03×10-7 | 6.32×10-7 |
| NH3 | 0.1 ppbv | | 6.32×10-15 | 1.20×10-14 | 2.01×10-14 | 2.18×10-14 | 3.24×10-14 | 5.52×10-14 |
| 10 ppbv | | 6.32×10-13 | 1.20×10-12 | 2.01×10-12 | 2.18×10-12 | 3.24×10-12 | 5.52×10-12 |
| 2900 ppbv | | 1.85×10-10 | 3.50×10-10 | 5.71×10-10 | 6.46×10-10 | 9.32×10-10 | 1.61×10-9 |
| NH3∙∙∙H2O | 20%RH | 0.1  ppbv | 1.59×10-31 | 7.36×10-31 | 1.44×10-30 | 2.07×10-30 | 1.12×10-29 | 5.68×10-29 |
| 10  ppbv | 1.59×10-29 | 7.36×10-29 | 1.44×10-28 | 2.07×10-28 | 1.12×10-27 | 5.68×10-27 |
| 2900  ppbv | 4.57×10-27 | 2.12×10-26 | 4.11×10-26 | 6.12×10-26 | 3.29×10-25 | 1.63×10-24 |
| 100%RH | 0.1  ppbv | 7.94×10-31 | 3.57×10-30 | 7.20×10-30 | 1.04×10-29 | 5.62×10-29 | 2.80×10-28 |
| 10  ppbv | 7.94×10-29 | 3.57×10-28 | 7.20×10-28 | 1.04×10-27 | 5.62×10-27 | 2.80×10-26 |
| 2900  ppbv | 2.32×10-26 | 1.07×10-25 | 2.09×10-25 | 3.01×10-25 | 1.63×10-24 | 8.56×10-24 |
| H2O∙∙∙NH3 | 20%RH | 0.1  ppbv | 7.51×10-18 | 1.40×10-17 | 2.07×10-17 | 2.27×10-17 | 3.88×10-17 | 5.21×10-17 |
| 10  ppbv | 7.51×10-16 | 1.40×10-15 | 2.07×10-15 | 2.27×10-15 | 3.88×10-15 | 5.21×10-15 |
| 2900  ppbv | 2.19×10-13 | 4.08×10-13 | 5.86×10-13 | 6.71×10-13 | 1.12×10-12 | 1.52×10-12 |
| 100%RH | 0.1  ppbv | 3.75×10-17 | 6.98×10-17 | 1.06×10-16 | 1.15×10-16 | 2.01×10-16 | 2.92×10-16 |
| 10  ppbv | 3.75×10-15 | 6.98×10-15 | 1.06×10-14 | 1.15×10-14 | 2.01×10-14 | 2.92×10-14 |
| 2900  ppbv | 1.10×10-12 | 2.04×10-12 | 3.01×10-12 | 3.39×10-12 | 5.77×10-12 | 8.52×10-12 |
| HCOOH | 10 ppbv | | 8.78×10-8 | 9.27×10-8 | 9.76×10-8 | 1.00×10-7 | 1.14×10-7 | 1.26×10-7 |
| 2 ppbv | | 6.75×10-9 | 7.05×10-9 | 7.73×10-9 | 7.92×10-9 | 8.56×10-9 | 9.86×10-9 |
| 0.01 ppbv | | 8.78×10-11 | 9.27×10-11 | 9.76×10-11 | 1.00×10-10 | 1.14×10-10 | 1.26×10-10 |
| H2SO4 | | | 1.29×10-7 | 1.33×10-7 | 1.40×10-7 | 1.43×10-7 | 1.58×10-7 | 1.74×10-7 |



**Figure S4** The results of IRC calculations of transition state for HO4H → O3 + H2O reactions with catalyst *X* (*X* = H2O, (H2O)2, NH3, NH3∙∙∙H2O, H2O∙∙∙NH3, HCOOH and H2SO4)

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