Theoretical Investigation of N (2D) + HOX (Cl, Br) Reaction

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Supporting Information:

Table S1. The optimized geometrical parameters of the stationary points at UCCSD(T)/aug-cc-pVTZ, UMP2/cc-pVTZ, UM06-2X/cc-pVTZ and available experimental results. Bond lengths are in angstrom (Å), and angles are in degrees.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Species | Parameters | CCSD(T) | MP2 | M06-2X | Experimental | Species | Parameters | CCSD(T) | MP2 | M06-2X | Experimental |
| HOCl | r(O-Cl) | 1.709 | 1.697 | 1.680 | 1.691a | HOBr | r(O-Br) | 1.839 | 1.825 | 1.815 | 1.834b |
| r(O-H) | 0.967 | 0.967 | 0.964 | 0.964a | r(O-H) | 0.967 | 0.967 | 0.964 | 0.961b |
| θ(H-O-Cl) | 102.52 | 101.83 | 103.84 | 102.45a | θ(H-O-Br) | 103.10 | 101.96 | 104.12 | 102.3b |
| HCl | r(H-Cl) | 1.279 | 1.273 | 1.279 | 1.275c | HBr | r(H-Br) | 1.421 | 1.407 | 1.421 | 1.414c |
| HNO | r(O-N) | 1.215 | 1.221 | 1.190 | 1.209d | NO | r(O-N) | 1.157 | 1.137 | 1.137 | 1.154c |
| r(N-H) | 1.055 | 1.050 | 1.057 | 1.090d |
| θ(H-N-O) | 107.99 | 107.51 | 108.39 | 108.05d |
| NH | r(N-H) | 1.039 | 1.031 | 1.036 | 1.036e | OH | r(O-H) | 0.973 | 0.968 | 0.971 | 0.970e |
| NCl | r(N-Cl) | 1.636 | 1.622 | 1.626 | 1.611c | NBr | r(N-Br) | 1.793 | 1.769 | 1.786 | 1.789f |
| ClO | r(O-Cl) | 1.594 | 1.571 | 1.571 | 1.596c | BrO | r(O-Br) | 1.730 | 1.708 | 1.714 | 1.718g |

aExperimental data are taken from ref.[34] bExperimental data are taken from ref.[35] cExperimental data are taken from ref.[36] dExperimental data are taken from ref.[37] eExperimental data are taken from ref.[38] fExperimental data are taken from ref.[39] gExperimental data are taken from ref.[40]

Table S2. Relative Energies (in kcal/mol) at different levels of theory for the different species involved in the reaction of N (2D) with HOCl.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **System** | **MP2/CBS a** | **M06-2X/CBS b** | **CCSD(T)c** | **CCSD(T)/CBSd** |
| HOCl+N(2D) | 0 | 0 | 0 | 0 |
| HNO+Cl | -110.94 | -103.52 | -101.30 | -100.14 |
| NO+HCl | -168.11 | -158.70 | -154.02 | -153.93 |
| NH+OCl | -45.34 | -50.14 | -41.83 | -42.21 |
| OH+NCl | -71.40 | -74.57 | -66.46 | -66.43 |
| I1a | -108.16 | -105.07 | -96.24 | -98.57 |
| I2a | -108.35 | -105.01 | -95.76 | -98.29 |
| I3a | -136.72 | -132.70 | -123.08 | -125.70 |
| I4a | -137.72 | -133.59 | -123.89 | -126.79 |
| TS1a | -95.00 | -92.14 | -82.24 | -84.56 |
| TS2a | -130.16 | -126.69 | -117.05 | -119.55 |
| TS3a | -85.00 | -97.56 | -90.76 | -93.03 |
| TS4a | -100.50 | -98.82 | -90.00 | -92.11 |

aIncluding the zero-point energy (ZPE) correction as estimated at the UMP2/cc-pVTZ level.

bIncluding the ZPE correction as estimated at the UM062X/cc-pVTZ level.

 cCalculations UCCSD(T)/cc-pVTZ//UM062X/cc-pVTZ.

dCalculations UCCSD(T)/CBS without ZPE.

Table S3. Relative Energies (in kcal/mol) at different levels of theory for the different species involved in the reaction of N (2D) with HOBr.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **System** | **MP2/CBSa** | **M06-2X/CBS b** | **CCSD(T)c** | **CCSD(T)/CBSd** |
| HOBr+N(2D) | 0 | 0 | 0 | 0 |
| HNO+Br | -112.63 | -107.96 | -102.87 | -102.86 |
| NO+HBr | -157.36 | -146.76 | -144.12 | -142.95 |
| NH+OBr | -41.03 | -46.99 | -39.87 | -39.74 |
| OH+NBr | -62.23 | -67.01 | -59.33 | -58.28 |
| I1b | -107.10 | -102.05 | -95.37 | -97.80 |
| I2b | -107.81 | -101.92 | -95.26 | -97.69 |
| I3b | -129.50 | -124.23 | -117.05 | -118.96 |
| I4b | -130.64 | -125.11 | -118.00 | -120.05 |
| TS1b | -95.80 | -90.95 | -83.19 | -85.54 |
| TS2b | -122.72 | -118.42 | -111.21 | -113.01 |
| TS3b | -85.37 | -96.98 | -90.90 | -93.37 |
| TS4b | -91.05 | -92.63 | -85.49 | -85.37 |

aIncluding the zero-point energy (ZPE) correction as estimated at the UMP2/cc-pVTZ level.

bIncluding the ZPE correction as estimated at the UM062X/cc-pVTZ level.

cCalculations UCCSD(T)/cc-pVTZ//UM062X/cc-pVTZ.

dCalculations UCCSD(T)/CBS without ZPE.

Table S4. Harmonic Vibrational Frequencies and Rotational constants calculated at the UMP2/cc-pVTZ Level of Theory.

|  |  |  |
| --- | --- | --- |
| Species | Frequencies(cm-1) | Rotational Constants(GHz) |
| A | B | C |
|  |  |  |  |  |
| HOCl | 769, 1278, 3802 | 605.41 | 15.10 | 14.73 |
| HOBr | 662, 1208, 3798 | 604.58 | 10.68 | 10.50 |
| HNO | 1485,1585,3028 | 562.57 | 41.69 | 38.81 |
| NO | 3340 |  | 52.35 |  |
| HCl | 3054 |  | 318.17 |  |
| HBr | 2763 |  | 256.72 |  |
| NH | 3391 |  | 505.26 |  |
| OH | 3818 |  | 569.35 |  |
| OCl | 847 |  | 18.65 |  |
| OBr | 741 |  | 13.03 |  |
| NCl | 848 |  | 19.22 |  |
| NBr | 845 |  | 14.51 |  |
|  |  |  |  |  |
| I1a  | 308, 444, 934, 1182, 1455, 3428 | 59.49 | 6.56 | 5.91 |
| I2a | 435, 514, 750, 1086, 1459, 3423 | 61.99 | 6.62 | 5.98 |
| I3a | 339, 460, 751, 1114, 1385, 3700 | 55.62 | 6.61 | 5.91 |
| I4a | 446, 454, 770, 1093, 1391, 3773 | 60.06 | 6.60 | 5.95 |
|  |  |  |  |  |
| I1b | 244, 393, 905, 1322, 1459, 3412 | 57.88 | 4.45 | 4.14 |
| I2b | 376, 481, 734, 1101, 1463, 3415 | 59.03 | 4.49 | 4.18 |
| I3b | 332, 400, 786, 1116, 1381, 3692 | 53.58 | 4.44 | 4.10 |
| I4b | 387, 446, 744, 1091, 1388, 3763 | 56.91 | 4.44 | 4.12 |
|  |  |  |  |  |
|  |  |  |  |  |
| TS1a | 640i, 352, 875, 1039, 1429, 3366 | 48.01 | 6.96 | 6.21 |
| TS2a | 531i, 442, 760, 998, 1258, 3744 | 55.91 | 6.38 | 5.83 |
| TS3a | 703i, 330, 381, 856, 1404, 3370 | 69.96 | 5.33 | 4.95 |
| TS4a | 1970i, 507, 630, 1139, 1494, 1688 | 49.18 | 6.85 | 6.00 |
|  |  |  |  |  |
| TS1b | 581i, 302, 820, 1035, 1431, 3359 | 45.76 | 4.75 | 4.37 |
| TS2b | 552i, 391, 823, 984, 1253, 3739 | 53.28 | 4.32 | 4.05 |
| TS3b | 1241i, 403, 716, 917, 1483, 3299 | 73.51 | 3.92 | 3.74 |
| TS4b | 2541i, 312, 439, 679, 1446, 1580 | 47.91 | 4.66 | 4.25 |

Table S5. Total Energy and Zero-point Vibrational Energy for the MP2/cc-pVTZ Geometries (in hartree).

|  |  |  |
| --- | --- | --- |
| Species | MP2 | ZPE |
| N(2D) | -54.374916 | 0 |
| N(4S) | -54.496617  | 0 |
| HOCl | -535.357605 | 0.013325 |
| HOBr | -2648.351042 | 0.012912 |
| HNO | -130.273015 | 0.013893 |
| NO | -129.693582 | 0.007609 |
| HCl | -460.30945 | 0.006959 |
| HBr | -2573.286061 | 0.006294 |
| NH | -55.117975 | 0.007725 |
| OH | -75.618907 | 0.008698 |
| OCl | -534.685185 | 0.001931 |
| OBr | -2647.674804 | 0.001688 |
| NCl | -514.228827 | 0.001931 |
| NBr | -2627.208623 | 0.001705 |
| Cl | -459.643362 | 0 |
| Br | -2572.6394525  | 0 |
| I1a | -589.9044 | 0.01766 |
| I2a | -589.904619 | 0.017465 |
| I3a | -589.949671 | 0.017653 |
| I4a | -589.933102 | 0.018059  |
| I1b | -2702.896018 | 0.017622 |
| I2b | -2702.931764 | 0.017558 |
| I3b | -2702.897244 | 0.017246 |
| I4b | -2702.933689 | 0.017812 |
| TS1a | -589.882686 | 0.016087 |
| TS2a | -589.939044 | 0.016405 |
| TS3a | -589.862458 | 0.014447 |
| TS4a | -589.891888 | 0.012438 |
| TS1b | -2702.877423 | 0.015827 |
| TS2b | -2702.920883 | 0.016379 |
| TS3b | -2702.862585 | 0.015533 |
| TS4b | -2702.864669 | 0.010152 |