Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

Expanding the applicability of electrostatic potentials to the realm of transition states

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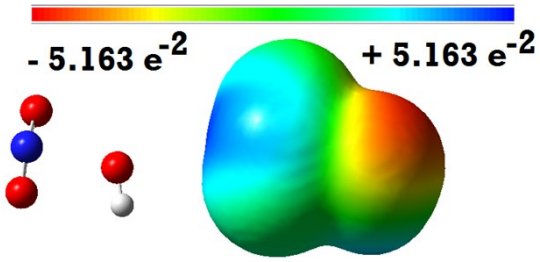
Table S1: Results for the effect of various basis sets on B3LYP method for the OH + NO_2 → HNO3 reaction potential energy surface. Where $\Delta E_1 = E_{TS} - E_{Reactants}$, $\Delta E_2 = E_{TS} - E_{Product}$ and $\Delta E_3 = E_{Reactants} - E_{Product}$. All the energies are in kcal/mol and are ZPE corrected.

Basic sets	ΔE_1	ΔE_2	ΔE_3
6-31G	32.1	69.5	37.4
6-31G(d)	31.6	77.8	46.2
6-31+G(d)	29.2	72.4	43.2
6-31++G(d)	29.2	72.5	43.3
6-31++G(d,p)	29.1	72.2	43.1
6-31++G(2df,2p)	28.3	72.4	44.1
6-31++G(2df,2pd)	28.3	72.4	44.1
6-31++G(3df,2pd)	28.4	72.5	44.1
6-31++G(3df,3pd)	28.3	72.4	44.1
Aug-CC-pVDZ	28.5	72.1	43.6
Aug-CC-PVTZ	28.2	71.5	43.3
Aug-CC-PVQZ	28.2	71.8	43.6

Table S2: Results for the effect of various methods using 6-31++G(3df,2pd) basis set for the OH + NO_2 → HNO3 reaction potential energy surface. Where $\Delta E_1 = E_{TS} - E_{Reactants}$, $\Delta E_2 = E_{TS} - E_{Product}$ and $\Delta E_3 = E_{Reactants} - E_{Product}$. All the energies are in kcal/mol and are ZPE corrected.

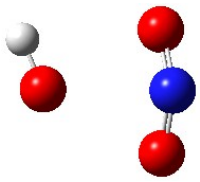
Methods	ΔE_1	ΔE_2	ΔE_3
HF	96.8	109.7	12.9
B3LYP	28.4	72.5	44.1
X3LYP	29.3	73.9	44.6
O3LYP	23.7	69.1	45.4
B3PW91	29.8	76.5	46.7
M06	26.0	76.8	50.8

Figure S1: Computed ESP map of transition state calculated from the B3LYP/6-31++G (3df,3pd) method at 0.001 au electron density surfaces. Quantitative values of electrostatic potentials are also in au.



Cartesian Coordinates of stationary points

Transition State



Transition State: X3LYP/6-31++G(3df,2pd)

Imaginary frequency 707.7086i

N	0.72070000	0.05269700	0.24207200
O	0.75354400	-1.04822500	-0.12091600
O	0.49315600	1.14152500	-0.10286900
O	-1.62302500	-0.21859000	0.03293900
H	-2.03429400	0.63343600	-0.16773700

Transition State: O3LYP/6-31++G(3df,2pd)

Imaginary frequency 631.6697i

N	0.74156300	0.03855300	0.24301900
O	0.74734100	-1.06498500	-0.12122300
O	0.55175000	1.13608700	-0.10264500
O	-1.68788400	-0.18860100	0.03284800
H	-2.08059900	0.67012100	-0.17297500

Transition State: M06/6-31++G(3df,2pd)

Imaginary frequency 730.6674i

N	0.71873700	0.05711200	0.22917000
O	0.75592600	-1.04244100	-0.11497500
O	0.47875000	1.14070600	-0.09749500
O	-1.60962600	-0.22557800	0.03255500
H	-2.03155600	0.61871200	-0.16486200

Transition State: HF/6-31++G(3df,2pd)

Imaginary frequency 750.1492i

N	0.73097400	0.26118900	0.00000700
O	1.29515100	-0.69703600	0.00003400
O	-0.07981200	0.98012200	-0.00001800
O	-1.54990100	-0.48808300	-0.00012000
H	-2.44031100	-0.18835100	0.00077400

Transition State: B3PW91/6-31++G(3df,2pd)

Imaginary frequency 713.0316i

N	0.72126100	0.05389900	0.23798600
O	0.75270400	-1.04619100	-0.11865900
O	0.48913900	1.13998100	-0.10153000
O	-1.61939500	-0.22018500	0.03184500
H	-2.02841600	0.63387100	-0.15915000

Transition State: B3LYP/6-31G

Imaginary frequency 720.1156i

N	0.67910900	0.15153000	-0.29653200
O	0.22163200	1.18799700	0.13952300
O	0.98354800	-0.93482400	0.12787000
O	-1.53605400	-0.43209900	0.00493400
H	-2.10676900	0.37070600	-0.10288900

Transition State: B3LYP/6-31G(d)

Imaginary frequency 722.0501i

N	0.69783600	0.11158500	-0.28101700
O	0.33262500	1.16121600	0.12921700
O	0.88677800	-0.97819600	0.12638700
O	-1.57648500	-0.34572200	-0.00701400
H	-2.02819500	0.52052500	-0.02159700

Transition State: B3LYP/6-31+G(d)

Imaginary frequency 681.5423i

N	0.72077400	0.06169100	-0.25803400
O	0.47347800	1.15190900	0.11111400
O	0.78152900	-1.04313700	0.12637700
O	-1.62723000	-0.23972900	-0.02919400

H	-2.06764100	0.61582600	0.13985600

Transition State: B3LYP/6-31+G(d,p)

N	0.721195	0.060981	0.257547
O	0.781181	-1.043807	-0.126867
O	0.475400	1.151744	-0.110343
O	-1.629356	-0.237823	0.030985
H	-2.066162	0.612216	-0.153032

Transition State: B3LYP/6-31++G(d)

Imaginary frequency 681.1372i

N	0.72097200	0.06182700	-0.25797100
O	0.47319300	1.15196900	0.11106000
O	0.78198800	-1.04301700	0.12638500
O	-1.62761500	-0.24006100	-0.02927100
H	-2.06733700	0.61609100	0.14041300

Transition State: B3LYP/6-31++G(d,p)

Imaginary frequency 680.0879i

N	0.72127600	0.06063400	-0.25751800
O	0.47636000	1.15163700	0.11028900
O	0.78050400	-1.04418700	0.12690000
O	-1.62971900	-0.23715000	-0.03108200
H	-2.06609200	0.61316000	0.15377300

Transition State: B3LYP/6-31++G(2df,2p)

Imaginary frequency 698.0726i

N	0.72191600	0.05197600	-0.24318400
O	0.49675300	1.14246100	0.10330300
O	0.75466500	-1.04979600	0.12141500
O	-1.62764500	-0.21737900	-0.03296700
H	-2.04359300	0.63388200	0.16828800

Transition State: B3LYP/6-31++G(2df,2pd)

Imaginary frequency 698.2202i

N	0.72195200	0.05165000	-0.24312200
O	0.49759900	1.14234200	0.10328200
O	0.75390300	-1.05014400	0.12139500
O	-1.62767800	-0.21655100	-0.03300900
H	-2.04425800	0.63327900	0.16850700

Transition State: B3LYP/6-31++G(3df,2pd)

Imaginary frequency 695.3579i

N	0.72279500	0.05174500	-0.24443800
O	0.49818000	1.14226100	0.10392100
O	0.75511800	-1.05028700	0.12180000
O	-1.63088900	-0.21698300	-0.03256500
H	-2.03883400	0.63785600	0.16581900

Transition State: B3LYP/6-31++G(3df,3pd)

Imaginary frequency 695.9760i

N	0.72258100	0.05302100	-0.24437500
O	0.49492600	1.14283400	0.10409700
O	0.75788600	-1.04904800	0.12149300
O	-1.63006300	-0.21965600	-0.03191400
H	-2.04005600	0.63580800	0.16122000

Transition State: B3LYP/Aug-CC-pVDZ

Imaginary frequency 691.4846i

N	0.72156500	0.05904300	-0.24965700
O	0.47927700	1.14791000	0.10705300
O	0.77168400	-1.04488900	0.12312100
O	-1.62667700	-0.23291200	-0.03027200
H	-2.04522700	0.62582200	0.14838700

Transition State: B3LYP/Aug-CC-pVTZ

Imaginary frequency 699.2081i

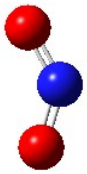
N	0.72413900	0.04965600	-0.23941000
O	0.50393900	1.13788100	0.10116300
O	0.75071900	-1.04929900	0.12030000
O	-1.63289000	-0.21186200	-0.03429900
H	-2.04311300	0.63864900	0.17856100

Transition State: B3LYP/Aug-CC-pVQZ

Imaginary frequency 700.4789i

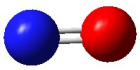
N	-0.72363800	0.04987400	0.23899900
O	-0.50304700	1.13718300	-0.10115900
O	-0.75102800	-1.04823600	-0.11983800
O	1.63191600	-0.21231000	0.03362500
H	2.04274700	0.63778100	-0.17401300

Geometry of NO_2:B3LYP/6-31+G(d,p)



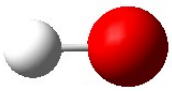
N	0.000000	0.000000	0.326575
O	0.000000	1.106215	-0.142877
O	0.000000	-1.106215	-0.142877

Geometry of NO:B3LYP/6-31+G(d,p)



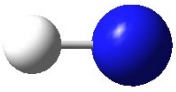
O	0.000000	0.000000	0.540241
N	0.000000	0.000000	-0.617418

Geometry of OH:B3LYP/6-31+G(d,p)



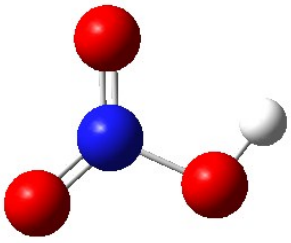
O	0.000000	0.000000	0.108890
H	0.000000	0.000000	-0.871121

Geometry of NH:B3LYP/6-31+G(d,p)



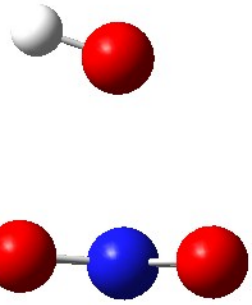
N	0.000000	0.000000	0.130641
H	0.000000	0.000000	-0.914485

Geometry of the product HNO_3:B3LYP/6-31+G(d,p)



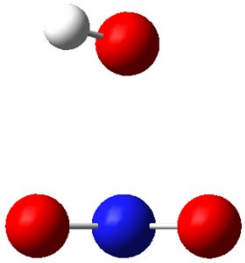
N	-0.148211	0.034479	-0.000119
O	-1.044289	-0.767762	0.000105
O	-0.182339	1.252003	0.000036
O	1.139414	-0.543149	-0.000040
H	1.735192	0.229907	0.000031

Geometry of the OH + NO_2 transition state:B3LYP/6-31+G(d,p)



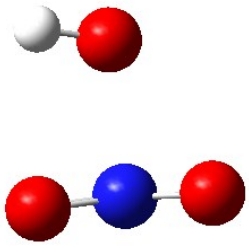
N	0.721195	0.060981	0.257547
O	0.781181	-1.043807	-0.126867
O	0.475400	1.151744	-0.110343
O	-1.629356	-0.237823	0.030985
H	-2.066162	0.612216	-0.153032

Geometry of the OH + NO_2 transition state: uB3LYP/6-31+G(d,p) with guess=mix



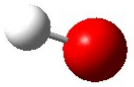
N	0.026846	0.031320	0.016208
O	0.029476	-0.014828	1.193878
O	0.798024	0.095352	-0.880378
O	0.732522	-2.304861	0.199943
H	1.513231	-2.472610	-0.359690

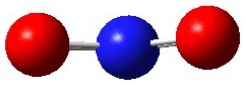
Geometry of the OH + NO_2 transition state:wB97xD/6-31+G(d,p)



N	0.710657	0.069396	0.245468
O	0.769624	-1.030361	-0.121801
O	0.437889	1.147944	-0.106215
O	-1.574609	-0.250826	0.031471
H	-2.037826	0.580169	-0.145911

Geometry of the OH + NO_2 transition state:uwB97xD/6-31+G(d,p) – Broken Symmetry – Guess=mix option.





N	0.755779	0.066229	0.267471
O	0.779497	-1.020784	-0.187332
O	0.535036	1.177732	-0.076763
O	-1.669993	-0.239678	0.158270
H	-2.094584	0.532824	-0.258634

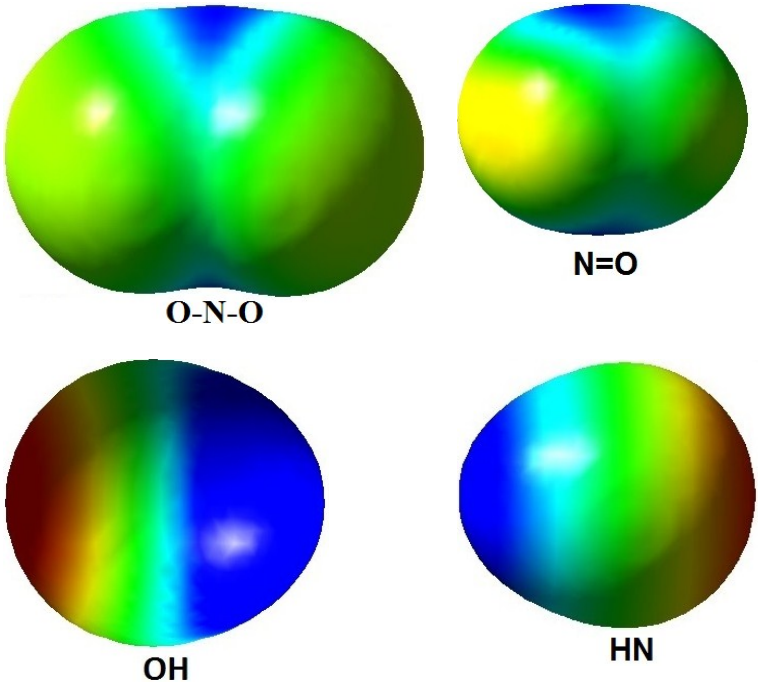


Figure S2: Computed ESP maps of OH, NH, NO, and NO_2, using B3LYP/6-31+G (d,p) method at 0.001 au electron density surfaces. ESP colour scheme: Red represents regions of negative and blue represents regions of positive electrostatic potentials.

Analysis of the ESP maps for the reactants HN and OH are quite similar. In both the cases there are positive electrostatic potentials around the H-atoms and negative electrostatic potentials around the N-atom and O-atom. Analysis of the ESP of the NO_2 shows that the regions of the positive electrostatic potential are above and below the central N-atom (above and below the plane of NO_2). These positive regions are usually referred as π-holes. In NO_2, accumulation of the π-holes above and below the N-atom can be explained as, "because of the more electronegative O-atoms, π-bonding electrons are drawn sufficiently towards the O-atoms, so that the associated rearrangement of the electronic density leaves a region of positive potentials above and below the N-atom". Analysis of the ESP map of NO shows that, there is a positive π-hole region above and below the N=O π-bond. The π-hole region is almost on the central region of the NO molecule with a partial shifted in densities towards N-atom of the NO.