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# Hidden Complexities in the Reaction of $H_2O_2$ and HNO Revealed by Ab Initio Quantum Chemical Investigations

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## Supporting Information

Table S1: Post-Hartree-Fock activation energies at the aug-cc-pVDZ basis used in the NEVPT2 extrapolation described in the Methods section of the main text, CCSD(T) and BD(T) calculations performed with an RHF reference wavefunction. Results at the aug-cc-pVTZ basis for CCSD(T) and BD(T) and the extrapolated aug-cc-pVTZ basis for NEVPT2 and CASSCF can be seen in the main text in Table 7. Columns 3 and 5 report the difference between the aug-cc-pVTZ and aug-cc-pVDZ energies, as described in Equation 1, for CCSD(T) and BD(T). The deltas obtained for CCSD(T) and BD(T) are nearly identical. Energies in kcal/mol relative to associated complexes as illustrated in Figure 1 of the main text. Geometries optimized at the UB3LYP/aug-cc-pVTZ level of theory.

| | CCSD(T)/augdz | ΔCCSD(T) | BD(T)/augdz | ΔBD(T) | NEVPT2/augdz |
|---|---|---|---|---|---|
| TS1 | 28.9 | 2.3 | 28.8 | 2.4 | 27.0 |
| TS2-grott | 24.5 | −0.7 | 24.4 | −0.7 | 24.0 |
| TS2-inter | 40.6 | −0.7 | 40.6 | −0.7 | 40.4 |
| TS2-intra | 55.8 | −0.2 | 55.8 | −0.2 | 54.8 |
| TS3 | 11.9 | −0.0 | 11.9 | −0.0 | 10.7 |

Table S2: Post-Hartree-Fock activation energies at the cc-pVDZ basis used in the CASSCF extrapolation described in the Methods section of the main text, CCSD(T) and BD(T) calculations performed with an RHF reference wavefunction. Results at the aug-cc-pVTZ basis for CCSD(T) and BD(T) and the extrapolated aug-cc-pVTZ basis for CASSCF and NEVPT2 can be seen in the main text in Table 7. Columns 3 and 5 report the difference between the aug-cc-pVTZ and cc-pVDZ energies, as described in Equation 1, for CCSD(T) and BD(T). The deltas obtained for CCSD(T) and BD(T) are nearly identical. Energies in kcal/mol relative to associated complexes as illustrated in Figure 1 of the main text. Geometries optimized at the B3LYP/aug-cc-pVTZ level of theory. NEVPT2/cc-pVDZ barriers included as comparison.

| | CCSD(T)/dz | ΔCCSD(T) | BD(T)/dz | ΔBD(T) | CASSCF/dz | NEVPT2/dz |
|---|---|---|---|---|---|---|
| TS1 | 33.6 | –2.4 | 33.6 | –2.5 | 36.6 | 33.1 |
| TS2-grott | 21.7 | 2.1 | 21.6 | 2.1 | 24.9 | 22.7 |
| TS2-inter | 43.3 | –3.4 | 43.3 | –3.4 | 42.5 | 42.2 |
| TS2-intra | 57.4 | –1.7 | 57.4 | –1.7 | 60.8 | 55.7 |
| TS3 | 12.4 | –0.6 | 12.5 | –0.6 | 13.0 | 11.6 |

Table S3: UB3LYP/aug-cc-pVTZ optimized structures and zero-point corrected energy, in Hartree, of each transition state and intermediate as shown in Figures 1, 3, and 5 of the main text.

| Reactant Complex | E= −282.130540 | | |
|---|---|---|---|
| N | −1.101187 | −0.377701 | 1.596220 |
| H | −0.741944 | −1.009137 | 0.835503 |
| O | −1.791462 | 0.473294 | 1.095767 |
| O | −1.613456 | 0.048846 | −1.785738 |
| O | −1.144750 | −1.258108 | −1.367333 |
| H | −1.797486 | −1.832460 | −1.786502 |
| H | −1.870708 | 0.420159 | −0.924967 |

| Reactant to Int1 TS | E= −282.127181 | | |
|---|---|---|---|
| N | −0.978180 | 0.513310 | 0.733004 |
| H | −1.406552 | −0.199716 | 1.381890 |
| O | 0.199219 | 0.303269 | 0.628607 |
| O | −2.300001 | −1.324177 | −1.007621 |
| O | −1.433136 | −1.058758 | −2.133182 |
| H | −0.911579 | −0.314863 | −1.801049 |
| H | −3.142528 | −0.987272 | −1.338271 |

| Int1 | E= −282.130304 | | |
|---|---|---|---|
| N | −0.797887 | 0.056252 | 0.861600 |
| H | −0.393113 | −0.904302 | 1.020778 |
| O | −1.937511 | 0.092537 | 1.221896 |
| O | 1.485964 | 1.157508 | −0.583893 |
| O | 1.501689 | −0.218890 | −1.038290 |
| H | 1.399102 | −0.099032 | −1.990226 |
| H | 0.647392 | 1.158931 | −0.088974 |

| TS1 | E= −282.094397 | | |
|---|---|---|---|
| N | −0.416688 | 1.811231 | 0.373860 |
| H | 0.289802 | 1.784190 | 1.139107 |
| O | −1.199153 | 0.902817 | 0.374830 |
| O | 0.717922 | 2.036769 | −0.986609 |
| O | 2.035557 | 1.519156 | −2.071022 |
| H | 2.667330 | 2.155058 | −1.709937 |
| H | 0.085207 | 1.985614 | −1.715245 |

| Int2 | E= −282.228122 | | |
|---|---|---|---|
| N | −0.306951 | −0.458446 | 0.006176 |
| H | −0.075892 | −0.806839 | −0.946180 |
| O | 0.292415 | −0.969808 | 0.924897 |
| O | −1.150150 | 0.416334 | 0.055864 |
| O | −2.002752 | 1.613551 | 2.799557 |
| H | −1.488657 | 1.160810 | 3.472160 |
| H | −1.718225 | 1.223388 | 1.965408 |

| Int2 to Int3 TS | E= −282.227909 | | |
|---|---|---|---|
| N | −0.108837 | −0.575257 | −0.328587 |
| H | −0.542264 | −0.237920 | −1.211703 |
| O | −0.368568 | −1.711485 | −0.005040 |
| O | 0.596455 | 0.226757 | 0.253284 |
| O | −1.346089 | 0.906121 | 2.475862 |
| H | −1.438048 | 0.312554 | 3.225110 |
| H | −0.453155 | 0.760018 | 2.146815 |

| Int3 | E= −282.235447 | | |
|---|---|---|---|
| N | −0.622402 | −0.189438 | 0.493184 |
| H | 0.224531 | 0.031717 | −0.080133 |
| O | −0.442649 | −0.867611 | 1.488175 |
| O | −1.681749 | 0.255889 | 0.091051 |
| O | 1.721469 | 0.420752 | −1.095680 |
| H | 2.550038 | −0.059829 | −1.017082 |
| H | 1.674611 | 0.732894 | −2.003445 |

| TS2-grott | E= −282.202061 | | |
|---|---|---|---|
| N | −0.579491 | 0.058739 | 0.320863 |
| H | 0.777168 | 0.247420 | −0.032770 |
| O | −1.285975 | −0.387969 | 1.177547 |
| O | −1.073415 | 0.607382 | −0.731514 |
| O | 1.284454 | 0.782813 | −0.929470 |
| H | 1.742998 | 0.157871 | −1.502043 |
| H | 0.233406 | 0.884708 | −1.231384 |

| TS2-inter | E= −282.174427 | | |
|---|---|---|---|
| N | −0.971375 | 0.255613 | 0.266265 |
| H | 0.531063 | 0.303873 | 0.039013 |
| O | −0.393958 | −0.811745 | 0.698627 |
| O | −2.162868 | 0.388303 | 0.406627 |
| O | 1.562606 | 0.506801 | −0.322546 |
| H | 1.990833 | −0.363320 | −0.351099 |
| H | 1.519959 | 0.876794 | −1.216552 |

| TS2-intra | E= −282.152018 | | |
|---|---|---|---|
| N | −0.705670 | −0.115780 | 0.637042 |
| H | −0.480127 | −0.510882 | 1.737187 |
| O | −1.725669 | −0.418414 | 1.396792 |
| O | −0.822805 | 0.286517 | −0.475303 |
| O | 2.171346 | 0.537653 | −0.955735 |
| H | 2.591140 | 0.842243 | −1.763502 |
| H | 1.224031 | 0.575832 | −1.126801 |

| Int4 | E= −282.245762 | | |
|---|---|---|---|
| N | −0.987070 | −0.075843 | −0.020953 |
| H | 0.874714 | 0.143608 | 0.112274 |
| O | −1.936268 | −0.377041 | 0.598799 |
| O | 0.175226 | −0.129123 | 0.745261 |
| O | 2.085449 | 0.661882 | −1.136715 |
| H | 1.708014 | 0.738388 | −2.017957 |
| H | 2.592993 | 1.465938 | −0.995431 |

| TS3 | E= −282.227641 | | |
|---|---|---|---|
| N | −1.391236 | −0.320468 | 0.290114 |
| H | 0.305835 | 0.624492 | −0.043869 |
| O | −1.155635 | −1.298985 | 0.869882 |
| O | −0.435414 | 0.741138 | 0.591944 |
| O | 1.714819 | 0.463196 | −1.174654 |
| H | 1.880032 | 1.217769 | −1.747034 |
| H | 2.555280 | 0.259856 | −0.754376 |

| Product Complex | E= −282.244238 | | |
|---|---|---|---|
| N | −0.840434 | −0.350440 | 0.747287 |
| H | 0.152308 | 0.835004 | −0.394769 |
| O | 0.065991 | −1.101133 | 0.588003 |
| O | −0.712054 | 0.840047 | 0.095832 |
| O | 1.728712 | 0.643280 | −1.237804 |
| H | 2.489513 | 1.226513 | −1.167438 |
| H | 1.996389 | −0.202511 | −0.862061 |

| TS2-grott2x | E= −358.679594 | | |
|---|---|---|---|
| N | −0.495867 | 0.027860 | 0.335072 |
| H | 0.946205 | −0.057800 | 0.039514 |
| O | −1.049404 | −0.039810 | 1.403862 |
| O | −1.199185 | 0.180574 | −0.723071 |
| O | 1.885881 | −0.053791 | −0.531011 |
| H | 2.390513 | −0.855800 | −0.363912 |
| H | 1.402392 | 0.000525 | −1.600849 |
| O | 0.546072 | 0.214355 | −2.491443 |
| H | 0.447821 | −0.476997 | −3.151805 |
| H | −0.305064 | 0.211249 | −1.839430 |