Supplemental Information

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | ∆H (kcal/mol) |  |  |  |
| **E1** | **B1-A** | **C1-B1** | **D1-C1** | **overall** |
| UUU | -32.70 | -2.41 | 38.17 | 3.06 |
| UUD | -27.15 | -6.36 | 39.38 | 5.87 |
| UDU | -28.19 | -3.62 | 36.61 | 4.81 |
| UDD | -32.14 | 9.75 | 19.46 | -2.92 |
| DUU | -26.85 | -7.50 | 38.17 | 3.82 |
| DUD | -29.07 | -6.42 | 39.38 | 3.89 |
| DDU | -26.94 | -3.16 | 36.61 | 6.52 |
| DDD | -26.14 | 4.08 | 19.46 | -2.59 |
| **E2** | **B2-A** | **D2-B2** |  | **overall** |
| UUU | -32.70 | 35.76 |  | 3.06 |
| UUD | -27.15 | 33.02 |  | 5.87 |
| UDU | -28.19 | 32.99 |  | 4.81 |
| UDD | -32.14 | 29.21 |  | -2.92 |
| DUU | -26.85 | 30.67 |  | 3.82 |
| DUD | -29.07 | 32.96 |  | 3.89 |
| DDU | -26.94 | 33.45 |  | 6.52 |
| DDD | -26.14 | 23.55 |  | -2.59 |

**Table S1.** The change in enthalpy for each step of the reaction through the E1 and E2 mechanisms. The three letter combinations refer to the orientations of the hydroxide and two methyl substituents, respectively.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | ∆S(kcal/mol\*K) |  |  |  |
| **E1** | **B1-A** | **C1-B1** | **D1-C1** | **overall** |
| UUU | -0.0043 | 0.0481 | -0.0057 | 0.0382 |
| UUD | 0.0036 | 0.0396 | -0.0050 | 0.0381 |
| UDU | -0.0002 | 0.0444 | -0.0058 | 0.0383 |
| UDD | -0.0044 | 0.0459 | -0.0036 | 0.0379 |
| DUU | 0.0026 | 0.0407 | -0.0057 | 0.0376 |
| DUD | -0.0035 | 0.0466 | -0.0050 | 0.0381 |
| DDU | 0.0032 | 0.0406 | -0.0058 | 0.0379 |
| DDD | 0.0025 | 0.0392 | -0.0036 | 0.0381 |
| **E2** | **B2-A** | **D2-B2** |  | **overall** |
| UUU | -0.0043 | 0.0425 |  | 0.0382 |
| UUD | 0.0036 | 0.0346 |  | 0.0381 |
| UDU | -0.0002 | 0.0385 |  | 0.0383 |
| UDD | -0.0044 | 0.0423 |  | 0.0379 |
| DUU | 0.0026 | 0.0350 |  | 0.0376 |
| DUD | -0.0035 | 0.0416 |  | 0.0381 |
| DDU | 0.0032 | 0.0347 |  | 0.0379 |
| DDD | 0.0025 | 0.0355 |  | 0.0381 |

**Table S2.** The change in entropy for each step of the reaction through the E1 and E2 mechanisms. The three letter combinations refer to the orientations of the hydroxide and two methyl substituents, respectively.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | ∆G (kcal/mol) |  |  |  |
| **E1** | **B1-A** | **C1-B1** | **D1-C1** | **overall** |
| UUU | -31.40 | -16.77 | 39.87 | -8.30 |
| UUD | -28.22 | -18.17 | 40.88 | -5.50 |
| UDU | -28.13 | -16.84 | 38.35 | -6.61 |
| UDD | -30.84 | -3.94 | 20.55 | -14.23 |
| DUU | -27.62 | -19.65 | 39.87 | -7.39 |
| DUD | -28.03 | -20.31 | 40.88 | -7.45 |
| DDU | -27.89 | -15.25 | 38.35 | -4.78 |
| DDD | -26.89 | -7.60 | 20.55 | -13.94 |
| **E2** | **B2-A** | **D2-B2** |  | **overall** |
| UUU | -31.40 | 23.10 |  | -8.30 |
| UUD | -28.22 | 22.72 |  | -5.50 |
| UDU | -28.13 | 21.51 |  | -6.61 |
| UDD | -30.84 | 16.61 |  | -14.23 |
| DUU | -27.62 | 20.23 |  | -7.39 |
| DUD | -28.03 | 20.57 |  | -7.45 |
| DDU | -27.89 | 23.10 |  | -4.78 |
| DDD | -26.89 | 12.95 |  | -13.94 |

**Table S3.** The change in free energy for each step of the reaction through the E1 and E2 mechanisms. The three letter combinations refer to the orientations of the hydroxide and two methyl substituents, respectively.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | ∆U(kcal/mol) |  |  |  |
| **E1** | **B1-A** | **C1-B1** | **D1-C1** | **overall** |
| UUU | -32.44 | -15.86 | 37.91 | -10.38 |
| UUD | -26.89 | -19.80 | 39.12 | -7.57 |
| UDU | -27.93 | -17.06 | 36.35 | -8.63 |
| UDD | -30.84 | -3.94 | 20.55 | -14.23 |
| DUU | -26.59 | -20.95 | 37.91 | -9.62 |
| DUD | -28.81 | -19.86 | 39.12 | -9.55 |
| DDU | -26.68 | -16.60 | 36.35 | -6.93 |
| DDD | -25.88 | -41.04 | 20.55 | -46.37 |
| **E2** | **B2-A** | **D2-B2** |  | **overall** |
| UUU | -31.40 | 23.10 |  | -8.30 |
| UUD | -28.22 | 22.72 |  | -5.50 |
| UDU | -28.13 | 21.51 |  | -6.61 |
| UDD | -30.84 | 16.61 |  | -14.23 |
| DUU | -27.62 | 20.23 |  | -7.39 |
| DUD | -28.03 | 20.57 |  | -7.45 |
| DDU | -27.89 | 23.10 |  | -4.78 |
| DDD | -26.89 | 12.95 |  | -13.94 |

**Table S4.** The change in free energy for each step of the reaction through the E1 and E2 mechanisms. The three letter combinations refer to the orientations of the hydroxide and two methyl substituents, respectively.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | T∆S (kcal/mol) |  |  |  |
| **E1** | **B1-A** | **C1-B1** | **D1-C1** | **overall** |
| UUU | -1.27 | 14.36 | -1.70 | 11.39 |
| UUD | 1.07 | 11.81 | -1.50 | 11.37 |
| UDU | -0.06 | 13.22 | -1.74 | 11.42 |
| UDD | -1.30 | 13.69 | -1.09 | 11.31 |
| DUU | 0.77 | 12.14 | -1.70 | 11.22 |
| DUD | -1.04 | 13.90 | -1.50 | 11.35 |
| DDU | 0.95 | 12.10 | -1.74 | 11.30 |
| DDD | 0.75 | 11.68 | -1.09 | 11.35 |
| **E2** | **B2-A** | **D2-B2** |  | **overall** |
| UUU | -1.27 | 12.66 |  | 11.39 |
| UUD | 1.07 | 10.30 |  | 11.37 |
| UDU | -0.06 | 11.48 |  | 11.42 |
| UDD | -1.30 | 12.61 |  | 11.31 |
| DUU | 0.77 | 10.44 |  | 11.22 |
| DUD | -1.04 | 12.39 |  | 11.35 |
| DDU | 0.95 | 10.35 |  | 11.30 |
| DDD | 0.75 | 10.59 |  | 11.35 |

**Table S5.** The temperature times the change in entropy for each step of the reaction through the E1 and E2 mechanisms. The three letter combinations refer to the orientations of the hydroxide and two methyl substituents, respectively.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | H-L Gap | (hartree) |  |  |
| **E1** | **starting** | **int 1** | **int 2** | **product** |
| UUU | 0.22127 | 0.21698 | 0.09395 | 0.18748 |
| UUD | 0.22357 | 0.18534 | 0.10306 | 0.18535 |
| UDU | 0.22219 | 0.20997 | 0.09889 | 0.18450 |
| UDD | 0.22360 | 0.21993 | 0.12892 | 0.18708 |
| DUU | 0.22477 | 0.18944 | 0.09395 | 0.18748 |
| DUD | 0.22127 | 0.21494 | 0.10306 | 0.18535 |
| DDU | 0.22589 | 0.19123 | 0.09889 | 0.18450 |
| DDD | 0.22357 | 0.19456 | 0.12892 | 0.18708 |

**Table S6.** The HOMO-LUMO Gap for each step of the reaction through the E1 mechanism. The three letter combinations refer to the orientations of the hydroxide and two methyl substituents, respectively.