**Electronic Supplementary Information**

**Theoretical insights into the reduction mechanism of neptunyl nitrate by hydrazine derivatives**

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**Figure S1:** Optimized structures and bond distances (Å) of pathway II for reaction of [NpVIO2(H2O)2(NO3)2] with HOC2H4N2H3 in aqueous phase at the B3LYP/ECP60MWB/6-31G(d) level of theory. Values in parentheses are transition state imaginary frequencies (cm-1).



**Figure S2:** Optimized structures and bond distances (Å) of pathway II for reaction of [NpVIO2(H2O)2(NO3)2] with CHON2H3 in aqueous phase at the B3LYP/ECP60MWB/6-31G(d) level of theory. Values in parentheses are transition state imaginary frequencies (cm-1).

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**Figure S3:** Two-dimensional ELF diagrams on the Np-Oax-N plane of the structures in pathways I-II for the reaction of [NpVIO2(H2O)2(NO3)2] with HOC2H4N2H3 at the B3LYP/ECP60MWB/6-31G(d) level of theory.



**Figure S4:** Two-dimensional ELF diagrams on the Np-Oax-N plane of the structures in pathways I-II for the reaction of [NpVIO2(H2O)2(NO3)2] with CHON2H3 at the B3LYP/ECP60MWB/6-31G(d) level of theory.

Table S1. The O=Np=O bond angle (°) of in the structures for the reaction of [NpVIO2(H2O)2(NO3)2] with N2H4 at the B3LYP/ECP60MWB/6-31G(d) level of theory

|  |  |  |  |
| --- | --- | --- | --- |
| structures |  | structures |  |
| **ic1** | 179.70 | **ic3** | 179.93 |
| **ts1** | 179.21 | **ts3** | 174.94 |
| **int1** | 179.18 | **int3** | 174.92 |
| **ic2** | 179.41 | **ic4** | 179.98 |
| **ts2** | 179.40 | **ts4** | 179.75 |
| **int2** | 177.44 | **int4** | 179.72 |

Table S2. The O=Np=O bond angle (°) of in the structures of pathways I and II in the reaction of [NpVIO2(H2O)2(NO3)2] with HOC2H4N2H3 and CHON2H3 at the B3LYP/ECP60MWB/6-31G(d) level of theory

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | HOC2H4N2H3 CHON2H3 | | | |
| structures | Pathway I | Pathway II | Pathway I | Pathway II |
| **ic1** | 179.84 | 179.93 | 179.86 | 179.60 |
| **ts1** | 179.16 | 179.67 | 178.46 | 177.54 |
| **int1** | 179.11 | 179.22 | 178.43 | 177.51 |
| **ic2** | 179.77 | 179.42 | 179.31 | 179.24 |
| **ts2** | 179.15 | 179.40 | 176.95 | 177.33 |
| **int2** | 179.10 | 177.25 | 176.92 | 177.30 |

Table S3. Mayer bond order of N-H/Oax-H bonds in the structures of pathways I and II in the reaction of [NpVIO2(H2O)2(NO3)2] with HOC2H4N2H3 and CHON2H3 at the B3LYP/ECP60MWB/6-31G(d) level of theory

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | HOC2H4N2H3 CHON2H3 | | | |
| structures | Pathway I | Pathway II | Pathway I | Pathway II |
| **ic1** | 0.594/0.158 | 0.621/0.149 | 0.531/0.198 | 0.522/0.207 |
| **ts1** | 0.307/0.414 | 0.304/0.410 | 0.388/0.342 | 0.268/0.473 |
| **int1** | 0.163/0.542 | 0.182/0.530 | 0.111/0.600 | 0.104/0.615 |
| **ic2** | 0.492/0.220 | 0.483/0.228 | 0.384/0.292 | 0.713/0.057 |
| **ts2** | 0.321/0.357 | 0.322/0.354 | 0.248/0.477 | 0.245/0.482 |
| **int2** | 0.149/0.550 | 0.163/0.541 | 0.120/0.593 | 0.107/0.603 |