Electronic Supplementary Information

Unveiling the Electrophilic Aromatic Substitution Reactions of Pyridine Derivatives with Nitronium Ion through Molecular Electron Density Theory

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Table S1. *ω*B97X-D/6-311G(d,p) enthalpies, H in a.u., entropies, S in kcal·mol^{-1}K^{-1}, and Gibbs free energies, G in a.u., computed in water at r.t., of the stationary points involved in in the EAS nitration reaction of pyridine **3** with nitronium NO_2^+ ion **13**.

	H	S	G
Py **3**	-248.163114	68.5	-248.195676
NO_2^+ **13**	-204.804600	51.0	-204.828826
HSO_4^-	-699.763184	69.0	-699.795952
H_2SO_4	-700.184899	72.1	-700.219138
CM-I-m	-452.968308	95.2	-453.013563
TS-I-o	-452.960214	84.2	-453.000227
TS-I-m	-452.964222	85.1	-453.004647
TS-I-p	-452.943732	85.2	-452.984198
IN-I-o	-452.968236	85.3	-453.008752
IN-I-m	-452.977331	85.9	-453.018127
IN-I-p	-452.956511	85.3	-452.997018
P-I-o	-452.650537	84.2	-452.690535
P-I-m	-452.647477	83.6	-452.687210
P-I-p	-452.646227	83.8	-452.686061

Table S2. *ω*B97X-D/6-311G(d,p) enthalpies, H in a.u., entropies, S in kcal·mol^{-1}K^{-1}, and Gibbs free energies, G in a.u., computed in water at r.t., of the stationary points involved in in the EAS nitration reaction of protonated pyridine **4** with nitronium NO_2^+ ion **13**.

	H	S	G
PyO^+ **4**	-248.601074	68.9	-248.633805
CM-II-m	-453.406106	89.4	-453.448570
TS-II-o	-453.346596	83.9	-453.386465
TS-II-m	-453.354062	85.2	-453.394539
TS-II-p	-453.333847	83.8	-453.373674
IN-II-o	-453.345816	85.2	-453.386309
IN-II-m	-453.356982	84.3	-453.397045
IN-II-p	-453.335019	85.6	-453.375669
P-II-o	-453.065618	83.4	-453.105253
P-II-m	-453.040738	77.1	-453.077362
P-II-p	-453.335019	85.6	-453.375669

Table S3. *ω*B97X-D/6-311G(d,p) enthalpies, H in a.u., entropies, S in kcal·mol^{-1}K^{-1}, and Gibbs free energies, G in a.u., computed in water at r.t., of the stationary points involved in in the EAS nitration reaction of protonate pyridine-N-oxide **14** with nitronium NO_2^+ ion **13**.

	H	S	G
PyOH **14**	-323.751703	75.0	-323.787361
CM-III-m	-528.555211	103.3	-528.604270
TS-III-o	-528.495853	89.9	-528.538574
TS-III-m	-528.500631	90.5	-528.543624
TS-III-p	-528.491427	90.4	-528.534375
IN-III-o	-528.496479	90.4	-528.539422
IN-III-m	-528.502604	89.9	-528.545325
IN-III-p	-528.492919	89.3	-528.535348
P-III-o	-528.208575	88.0	-528.250376
P-III-m	-528.219941	91.2	-528.263259
P-III-p	-528.220534	90.3	-528.263428

Table S4. *ω*B97X-D/6-311G(d,p) enthalpies, H in a.u., entropies, S in kcal·mol^{-1}K^{-1}, and Gibbs free energies, G in a.u., computed in water at r.t., of the stationary points involved in in the EAS nitration reaction of pyridine-N-oxide **7** with nitronium NO_2^+ ion **13**.

	H	S	G
PyO **7**	-323.322211	72.8	-323.356814
CM-IV-p	-528.126762	101.2	-528.174835
TS-IV-o	-528.128902	92.9	-528.173041
TS-IV-m	-528.111122	88.7	-528.153433
TS-IV-p	-528.125674	93.3	-528.169991
TS-IV-ipso	-528.130458	92.4	-528.174337
IN-IV-o	-528.142192	85.7	-528.182906
IN-IV-m	-528.116892	89.6	-528.159476
IN-IV-p	-528.150949	86.0	-528.191831
P-IV-ipso	-528.130280	93.0	-528.174470
P-IV-o	-527.790390	87.9	-527.832150
P-IV-m	-527.801309	87.9	-527.843080
P-IV-p	-527.805821	87.1	-527.847227

Table S5. *ω*B97X-D/6-311G(d,p) electronic energies, E in a.u., enthalpies, H in a.u., entropies, S in kcal·mol^{-1}K^{-1}, and Gibbs free energies, G in a.u., computed in water at r.t., of **TS-IV-o-solv** and **TS-IV-p-solv**.

	E	H	S	G
TS-IV-o-solv	-2627.681916	-2627.464078	176.7	-2627.548011
TS-IV-p-solv	-2627.681704	-2627.461859	188.6	-2627.551480

Table S6. Populations, in average number of electrons e, of the more relevant ELF valence basin of **TS-I-m** and **TS-IV-o**.

TS-I-m		**TS-IV-o**	
V(N1)	2.72	V(N1,C2)	2.73
V(N1,C2)	2.30	V(C2,C3)	2.97
V(C2,C3)	2.58	V(C3,C4)	2.79
V(C3,C4)	2.47	V(C4,C5)	2.61
V(C4,C5)	2.55	V(C5,C6)	3.06
18 V(C5,C6)	2.47	V(N1,6)	2.75
V(N1,C6)	2.86	V(N1,O7)	1.45
		V(O7)	2.95
		V(O7)	2.92
V(N7)	1.77	V(N8)	1.14
V(N7,O9)	2.00	V(N8,O9)	2.39
V(N7,O8)	2.01	V(N8,O10)	2.33
V(O8)	2.87	V(O9)	3.62
V’(O8)	2.42	V’(O9)	1.36
V(O9)	2.88	V(O10)	2.13
V’(O9)	2.39	V’(O10)	2.95