Disproportionation of iron(III) porphyrin π-cation radicals in the presence of sterically hindered pyridines. Spectroscopic detection of asymmetric highly oxidized intermediates.

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Streszczenie

The reactivity of iron(III) tetraphenylporphyrin π-cation radical $(TPP^{\bullet})Fe^{III}(ClO_4)_2$, (**1**-1) iron(III) tetra-*p*-tolylporphyrin π-cation radical $(TTP^{\bullet})Fe^{III}(ClO_4)_2$ (**1**-2) and iron(III) tetramesitylporphyrin π-cation radical $(TMP^{\bullet})Fe^{III}(ClO_4)_2$ (**1**-3) complexes with 2,4,6-collidine, 2,3,6-collidine, 2-picoline, 2,6-di-*tert*-butylpyridine, and 2,6-dibromopyridine has been examined by ^1H NMR spectroscopy in dichloromethane-d_2 solution at low temperatures. These complexes undergo hydration processes which are essential in the generation of highly oxidized species via acid base/equilibria of coordinated water followed by disproportionation pathway, giving as sole stable products $[(TPP^{\bullet})Fe^{III}OFe^{III}(TPP)]^+$ (**4**-1), $[(TTP^{\bullet})Fe^{III}OFe^{III}(TTP)]^+$ (**4**-2), and $(TMP)Fe^{III}(OH)$ (**6**) respectively. The sterically hindered pyridines act as efficient proton scavengers. Two novel highly oxidized iron complexes have been detected by ^1H NMR spectroscopy after addition of 2,4,6-collidine to $(TTP^{\bullet})Fe^{III}(ClO_4)_2$ or $(TPP^{\bullet})Fe^{III}(ClO_4)_2$ in dichloromethane-d_2 solution at 202 K. New intermediates have been identified as iron porphyrin *N*-oxide complexes, i.e., iron(III) porphyrin *N*-oxide cation radical (**2**-*n*) and iron(IV) porphyrin *N*-oxide radical (**3**-*n*). The ^1H NMR results indicate that the D_{4h} symmetry of the parent iron(III) π-cation radical is drastically reduced upon disproportionation in the presence of proton scavengers. Both species are very unstable and were observed from 176 to 232 K. The intermediate **2**-2 has a ^1H NMR spectrum which demonstrates large hyperfine shifts (ppm) for the meso *p*-tolyl substituents (ortho 98.0, 94.8, 92.9, 91.7; meta −34.8, −38.7, −41.5, −42.3; *p*-CH_3 −86.3, −88.0) which are consistent with presence of an N-substituted iron porphyrin radical in the product mixture. The characteristic ^1H NMR spectrum of **2**-2 includes six pyrrole resonances at 149.6, 118.2, 115.4, 88.3, 64.6, and 55.7 ppm at 202 K, i.e., in the positions corresponding to iron(III) high-spin porphyrins. On warming to 222 K, the pyrrole resonances broaden and then coalesce pairwaise. Such dynamic behavior is accounted for by a rearrangement mechanism which involves an inversion of the porphyrin puckering. The pattern of *p*-tolyl resonances revealed the cation radical electronic structure of **3**-2. The *p*-tolyl resonances are divided in two distinct sets showing opposite direction of the isotropic shift for the same ring positions. The pyrrole resonances of **3**-2 also demonstrated downfield and upfield shifts. A disproportionation mechanism of the hydrated iron porphyrin cation radicals to generate **2** and **3** has been proposed. Both intermediates react with triphenylphosphine to produce triphenylphosphine oxide and high-spin iron porphyrins. Addition of 2,4,6-collidine to $(TMP^{\bullet})Fe^{III}(ClO_4)_2$ does not produce analogs of **2** and **3** found for sterically unprotected porphyrins. It results instead in the formation of a variety of $X(TMP^{\bullet})Fe^{IV}O$ (**5**) complexes also accounted for by the disproportionation process.

Słowa kluczowe

Cations, Iron, Phenyls, Pyrroles, Quantum mechanics

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