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Effect of Porphyrin Ring Distortion on Redox Potentials of β-Brominated-Pyrrole Iron(III) Tetraphenylporphyrins

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A variety of metallotetraphenylporphyrins having halogen substituents on the pyrrole β positions of the macrocycle have been shown to be good catalysts in oxygen atom transfer reactions.[1] These electron-withdrawing groups will lower the energy of the highest occupied molecular level (HOMO) and raise that of the lowest unoccupied molecular level (LUMO) with respect to those of the unsubstituted derivatives. This effect should, in principle, be additive such that $E_{1/2}$ for oxidation or reduction of the porphyrin should change in a linear fashion with the number of electron-withdrawing substituents on the macrocycle.[2] This is the case for oxidation or reduction of tetraphenylporphyrins having substituents located on the para or meta positions of the four phenyl rings[2] as well as for reduction of Cu(II),[3] Co(II),[4] and free-base[3] β-substituted-pyrrole tetraphenylporphyrins. It is not the case for oxidation of the same β-substituted-pyrrole compounds despite the fact that an increase in the number of electron-withdrawing halogen substituents from 0 to 8 should make the porphyrin ring more electron deficient and hence should lead to a more difficult oxidation. However, one must also consider the steric constraints caused by addition of up to eight bulky groups on the periphery of the macrocycle which can also alter the redox potentials because of ring deformation.

X-ray structural data for tetra- and octabrominated porphyrins reveal that the degree of porphyrin ring distortion is maximum for the octabrominated porphyrin as compared to either the tetrabrominated or unsubstituted free-base derivatives.[5,6] Weiss, Fajer, and coworkers[6] evaluated these structural data and, after comparison with the redox potentials for the same series of compounds, suggested that the oxidation potentials were governed not only by inductive effects of the halogens but also by saddle deformations of the porphyrin ring. A similar conclusion was reached by an electrochemical investigation of three different brominated short basket handle porphyrins where the data are interpreted in terms of ring distortion.[7] However, in this system, the macrocycle was already distorted prior to bromination as a result of the short chain connecting the opposite phenyl rings of the tetraphenylporphyrin entity.

Theoretical calculations indicate that conformational variations will shift both the HOMO and LUMO molecular orbitals of the porphyrin ring while the magnitude of the shift in the HOMO level will be higher than that of the LUMO.[8] This has been experimentally demonstrated for the case of octaalkyl- and octaaryl-substituted tetraphenylporphyrins,[9] but a quantitative measure of how the distortion of the porphyrin ring will affect the redox potentials of β-substituted-pyrrole metalloporphyrins has never been systematically demonstrated as a function of substituents upon going from zero to eight halogen groups.

We now report the results of electrochemical investigations on β-substituted-pyrrole tetraphenylporphyrins where the number of Br groups on the porphyrin ring has been systematically varied between 0 and 8. The investigated compounds are represented as (Br$_x$TPP)FeCl where Br$_x$TPP is the dianion of *meso*-tetraphenylporphyrin and x indicates the number of Br groups on the pyrrole β positions of the macrocycle.[10]

Each (Br$_x$TPP)FeCl derivative undergoes two reversible one-electron oxidations and three one-electron reductions in PhCN containing 0.1 M TBAP.[12] The first oxidation results in formation of a porphyrin π cation radical, while the first reduction involves formation of an iron(II) species[12] similar to what has been reported for (TPP)FeCl under similar experimental conditions.[2,13] Both electrode reactions are reversible for all investigated compounds, and an evaluation of their $E_{1/2}$ values thus provides an excellent measure of how both the oxidation and reduction potentials change as a function of systematically increasing the number of Br groups from 0 to 8 on (Br$_x$TPP)FeCl.[14]

A representative cyclic voltammogram illustrating the first oxidation and first reduction of (Br$_7$TPP)FeCl is shown in Figure

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(1) (a) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411. (b) Bruice, T. C. In *Mechanistic Principles of Enzyme Activity*; Liberman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1988; Chapter 8. (c) Traylor, T. G.; Byun, Y. S.; Traylor, P. S.; Battioni, P.; Mansuy, D. *J. Am. Chem. Soc.* **1991**, *113*, 7821. (d) Ostovic, D.; Bruice, T. C. *Acc. Chem. Res.* **1992**, *25*, 314. (e) Grinstaff, M. W.; Hill, M. G.; Labinger, J. A.; Gray, H. B. *Science* **1994**, *264*, 1311.

(2) Kadish, K. M. *Prog. Inorg. Chem.* **1986**, *34*, 435.

(3) (a) Giraudeau, A.; Callot, H. J.; Jordan, J.; Ezhar, I.; Gross, M. *J. Am. Chem. Soc.* **1979**, *101*, 3857. (b) Giraudeau, A.; Callot, H. J.; Gross, M. *Inorg. Chem.* **1979**, *18*, 201.

(4) D'Souza, F.; Villard, A.; Van Caemelbecke, E.; Franzen, M.; Boschi, T.; Tagliatesta, P.; Kadish, K. M. *Inorg. Chem.* **1993**, *32*, 4042.

(5) (a) Scheidt, W. R.; Lee, Y. J. *Struct. Bonding (Berlin)* **1987**, *64*, 1. (b) Mandon, D.; Oschsenbein, P.; Fischer, J.; Weiss, R.; Jayaraj, K.; Austin, R. N.; Gold, A.; White, P. S.; Brigaud, O.; Battioni, P.; Mansuy, D. *Inorg. Chem.* **1992**, *31*, 2044. (c) Bhyrappa, P.; Nethaji, M.; Krishnan, V. *Chem. Lett.* **1993**, 869.

(6) Ochsenbein, P.; Ayougou, K.; Mandon, D.; Fischer, J.; Weiss, R.; Austin, R. N.; Jayaraj, K.; Gold, A.; Terner, J.; Fajer, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 348.

(7) Reddy, D.; Ravikanth, M.; Chandrashekar, T. K. *J. Chem. Soc., Dalton Trans.* **1993**, 3575.

(8) (a) Barkigia, K. M.; Chantranupong, L.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* **1988**, *110*, 7566. (b) Barkigia, K. M.; Renner, M. W.; Furenlid, L. R.; Medforth, C. J.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* **1993**, *115*, 3627.

(9) (a) Barkigia, K. M.; Berber, M. D.; Fajer, J.; Medforth, C. J.; Renner, M.; Smith, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 8851. (b) Shelnutt, J. A.; Medforth, C. J.; Berber, M. D.; Barkigia, K. M.; Smith, K. M. *J. Am. Chem. Soc.* **1991**, *113*, 4077. (c) Sparks, L. D.; Medforth, C. J.; Park, M.-S.; Chamberlain, J. R.; Ondrias, M. R.; Senge, M. O.; Smith, K. M.; Shelnutt, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 581.

(10) The (Br$_x$TPP)H$_2$ derivatives were synthesized by literature methods.[3,4] Iron was inserted using the ferrous sulfate hydrate method[11a] and/or the iron carbonyl method.[11b] All synthesized derivatives gave satisfactory elemental analysis and mass spectral results.

(11) (a) *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Chapter 19. Elsevier: New York, 1975; (b) Groves, J. T.; Myers, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 5741.

(12) A complete spectroscopic study of the products formed in the various redox reactions will be published elsewhere.

(13) Phillippi, M. A.; Goff, H. M. *J. Am. Chem. Soc.* **1979**, *101*, 7641. (b) Phillippi, M. A.; Goff, H. M. *J. Am. Chem. Soc.* **1982**, *104*, 6026.

0020-1669/94/1333-5169$04.50/0

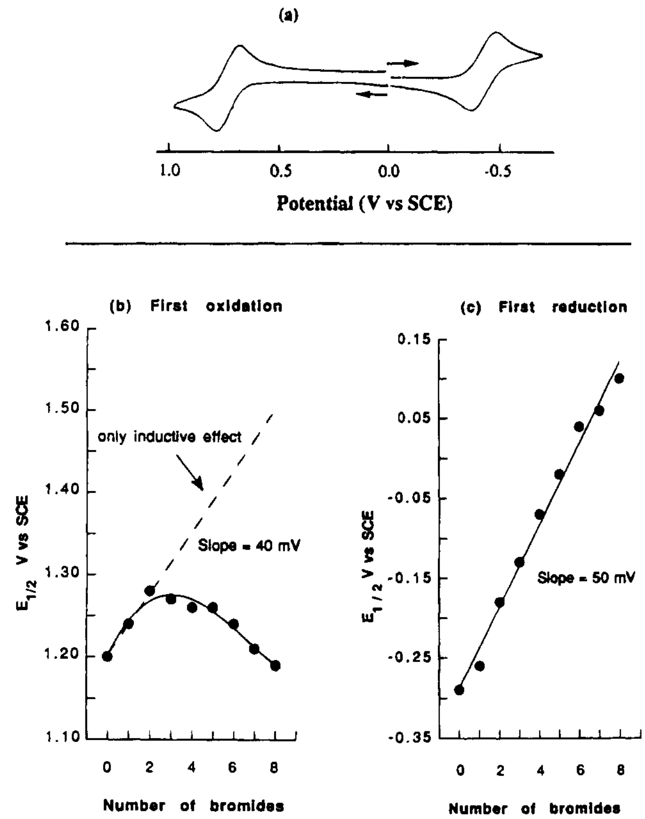

Figure 1. (a) Cyclic voltammogram of $(Br_7TPP)FeCl$ in PhCN containing 0.1 M TBAP and dependence of $E_{1/2}$ on the number of Br groups of $(Br_xTPP)FeCl$ for (b) the first oxidation and (c) the first reduction in PhCN containing 0.1 M TBAP.

Table 1. Half-Wave Potentials (V vs SCE)[a] and Positions of the Soret Bands[b] for the Investigated Iron(III) Porphyrins

compound	1st oxidn	1st redn	λ_{max}, nm[c]	ΔE_{ox},[d] mV
(TPP)FeCl	1.20	−0.29	417	0
$(Br_1TPP)FeCl$	1.24	−0.26	418	0
$(Br_2TPP)FeCl$	1.28	−0.18	424	0
$(Br_3TPP)FeCl$	1.27	−0.13	427	50
$(Br_4TPP)FeCl$	1.26	−0.07	432	93
$(Br_5TPP)FeCl$	1.26	−0.02	436	118
$(Br_6TPP)FeCl$	1.24	0.04	446	186
$(Br_7TPP)FeCl$	1.21	0.06	451	256
$(Br_8TPP)FeCl$	1.19	0.10	461	309

[a] Measured in PhCN containing 0.1 M TBAP. [b] In $CHCl_3$. [c] Additional bands in the visible region are also observed.[12] [d] Potential difference between the experimental $E_{1/2}$ values for oxidation of each $(Br_xTPP)FeCl$ complex and the extrapolated linear Hammet plot for the first three derivatives in Figure 1b.

1a,[15] and the relevant half-wave potentials in PhCN are summarized in Table 1. The relationship between $E_{1/2}$ for the first oxidation and the number of Br groups on $(Br_xTPP)FeCl$ is shown in Figure 1b, while that between $E_{1/2}$ for the first reduction and the number of Br groups is shown in Figure 1c. The positive shift in $E_{1/2}$ with increase in the number of Br groups is additive for the metal-centered (Fe^{III}/Fe^{II}) electroreduction (Figure 1c), and this is similar to what has been reported for ring- and/or metal-centered electroreductions of $(Br_xTPP)Co$ ($x = 0, 6, 7, 8$),[4] $(Br_xTPP)Cu$ ($x = 0-4$),[3] and $(Br_xTPP)H_2$ ($x = 0-4$)[3] under similar experimental conditions. The slope of the straight-line plot in Figure 1c is 51 mV/Br group, and this compares to a slope of 63 mV/Br for the metal-centered Co^{II}/Co^{I} reaction of $(Br_xTPP)Co^{II}$.[4]

In contrast, a nonlinear relationship is observed between $E_{1/2}$ for the first oxidation of $(Br_xTPP)FeCl$ and the number of Br groups on the compound (Figure 1b). The oxidation potential initially shifts in the expected positive direction (by 40 mV/Br group) and reaches a maximum at $(Br_2TPP)FeCl$, after which it changes direction and then shifts negatively upon going from $x = 3$ to $x = 8$. This results in an inverted parabolic behavior such that the first one-electron oxidation of $(Br_8TPP)FeCl$ occurs at a more negative half-wave potential than that for the same electrode reaction of (TPP)FeCl, even though the former compound has eight Br groups attached directly to the porphyrin macrocycle. Thus, the difference between $E_{1/2}$ for reduction of the unbrominated and octabrominated compounds is 390 mV, while that between oxidation of the same two compounds is virtually zero (see Table 1).

The Soret band positions of the neutral Fe(III) complexes are listed in Table 1 and are red-shifted with each stepwise increase in the number of Br groups on $(Br_xTPP)FeCl$. It has earlier been shown that the red shift is due to both the effect of ring substitution and the increasingly distorted conformation of the porphyrin macrocycle in solution.[6,8,9] The correlation in Figure 1b illustrates that only inductive effects are operative for the first three macrocycles while, for the other compounds, the distortion of the macrocycle caused by the presence of additional bulky substituents will dominate the inductive effects of the halogens in determining the half-wave potentials.

The degree of ring distortion increases with each stepwise increase in the number of Br groups beyond $(Br_2TPP)FeCl$, and this results in a decreased stability of the HOMO level, thus making the oxidation easier upon going from $(Br_3TPP)FeCl$ to $(Br_8TPP)FeCl$. A quantitative measure of how the degree of ring distortion relates to the redox potentials can best be illustrated by examining the potential difference between the experimental $E_{1/2}$ values and the extrapolated straight line originated from the first three $E_{1/2}$ values in Figure 1b for the planar macrocycles. This difference in potential, ΔE_{ox}, increases with increasing number of Br groups above 2 and ranges from 50 mV for $(Br_3TPP)FeCl$ to 309 mV for $(Br_8TPP)FeCl$ (see Table 1). It is also important to note that a deviation in the plot of the experimental data occurs after addition of only three bromides to $(Br_xTPP)FeCl$, and this contrasts with the earlier suggested deviation after addition of four bromides to a similar free-base porphyrin.[6]

As expected, the first reduction of the investigated compounds is linearly related to the number of Br groups and becomes easier with increase in the number of Br groups. Theory[8] predicts that the ring deformation should have a minimum effect on the reduction potentials, and hence the observed linear trend in Figure 1c can be simply explained by inductive effects of the electron-withdrawing halogen substituents. On the other hand, the site of electron transfer, which in this case is the metal center, may also account in part for the difference in behavior between the oxidation and reduction. It is expected that the metal-centered reactions may not fully experience the effect of porphyrin ring distortion as in oxidation, since the bulky substituents are in direct conjugation with the macrocycle.

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(14) The $E_{1/2}$ values for oxidation and reduction are expected not to vary appreciably for the different geometric isomers of $(Br_2TPP)FeCl$ and $(Br_6TPP)FeCl$ as has been reported for free-base and Cu(II) derivatives of dibrominated porphyrins (see ref 3).

(15) The instrumentation employed in this study has been described in an earlier publication.[4]