BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (5), 1435—1436 (1976)

Reduction and Oxidation Potentials of Metal-free and Cobalt Tetra(*p*-substituted phenyl)porphyrins

Meguru TEZUKA, Yasukazu OHKATSU, and Tetsuo OSA*
Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received September 26, 1975)

Synopsis. Both reduction and oxidation potentials of metal-free and cobalt tetra(*p*-substituted phenyl)porphyrins were determined by means of cyclic voltammetry. They are correlated with Hammett σ values of the substituents when the electron transfer occurs at the porphin ring, but not in the electron transfer step in which the cobalt atom participates.

Great interest has been shown in the electrochemistry of porphyrins and metalloporphyrins from the standpoint that their redox properties play a significant role in biological systems.[1-4] Felton and Linschitz studied the polarographic reduction of various metallotetraphenylporphyrins (MTPP) in order to see if they were reduced step-wise through a one-electron transfer to yield the porphyrin anion radicals followed by the formation of the dianions; in the case of cobalt tetraphenylporphyrin (CoTPP), however, the central metal was reduced in the first electron transfer step.[5] On the other hand, Wolberg and Manassen investigated the oxidation of transition metal complexes of tetraphenylporphyrins and phthalocyanines and concluded that in the cases of Fe, Co, and Ni tetraphenylporphyrins, the central metal was oxidized first, whereas oxidation of the ligand was observed for Cu and Zn porphyrins, subsequent oxidation occurring at the ligand in all cases.[6] From these results, Manassen discussed the catalytic behavior of MTPP in a few pure chemical reactions, such as oxidative dehydrogenation and symmetry-forbidden rearrangement.[7]

Although a number of studies have been made on porphyrins and metalloporphyrins, little has been done to make a systematic examination of the substituent effect on their redox properties. We have determined both reduction and oxidation potentials of metal-free and cobalt (*p*-substituted phenyl)porphyrins by the cyclic voltammetric method. The effects of substituents on the redox properties and on the catalytic activity in the autoxidation of acetaldehyde are discussed.

Experimental

Materials. Metal-free tetraphenylporphyrin (H_2TPP) and its *p*-substituted derivatives, *viz.*, tetra(*p*-methylphenyl)porphyrin[$H_2(p\text{-}CH_3)TPP$], tetra(*p*-methoxyphenyl)porphyrin [$H_2(p\text{-}OCH_3)TPP$] and tetra(*p*-chlorophenyl)porphyrin[$H_2(p\text{-}Cl)TPP$] as well as the cobalt complexes of these porphyrins were synthesized and purified according to conventional methods. *N,N*-Dimethylformamide (DMF) was dried over "Drierite" for several days and distilled twice under reduced pressure of nitrogen. Tetraethylammonium perchlorate (TEAP) was synthesized and purified according to conventional methods.

Cyclic Voltammetry. Cyclic voltammograms of the saturated solutions of porphyrins in DMF were recorded with a platinum plate of 0.40 cm² at 25 °C. TEAP was used as a supporting electrolyte. The concentration of porphyrins was less than 2 mM in most cases. The potential was referred to saturated calomel electrode (SCE).

TABLE 1. CYCLIC VOLTAMMETRY OF METAL-FREE AND COBALT TETRA(*p*-SUBSTITUTED PHENYL)PORPHYRINS

Porphyrin	Peak potential (V)			
	Oxidation		Reduction	
H_2TPP		+1.13	−1.04	−1.42
$H_2(p\text{-}CH_3)TPP$		+1.08	−1.06	−1.48
$H_2(p\text{-}OCH_3)TPP$		+1.02	−1.08	−1.50
$H_2(p\text{-}Cl)TPP$		+1.18	−0.98	−1.36
CoTPP	+0.58	+1.20	−0.80	−1.90
$Co(p\text{-}CH_3)TPP$	+0.57	+1.16	−0.80	−1.88
$Co(p\text{-}OCH_3)TPP$	+0.62	+1.10	−0.80	−1.90
$Co(p\text{-}Cl)TPP$	+0.75	+1.26	−0.76	−1.79

Measurements were made on a platinum electrode in 0.1 M TEAP-DMF solution at 25 °C. The concentration of porphyrins was less than 2 mM in most cases. Potential sweep rate: 0.10 V/s. (V *vs.* SCE).

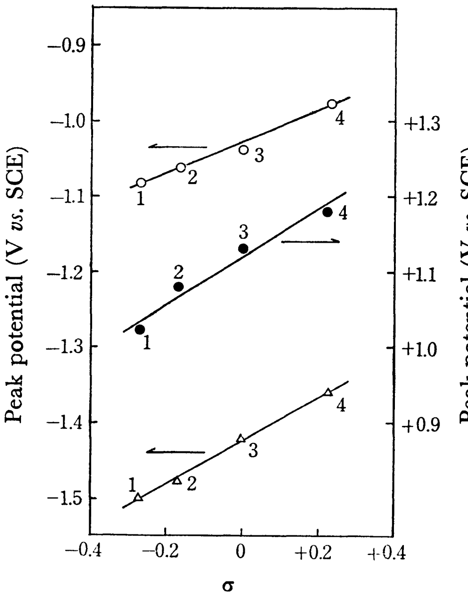

Fig. 1. Relation of peak potentials for the first (○), the second (△) reduction and oxidation (●) of metal-free tetra(p-substituted phenyl)porphyrins in DMF to Hammett substituent constants: 1, $H_2(p\text{-}OCH_3)$-TPP. 2, $H_2(p\text{-}CH_3)TPP$. 3, H_2TPP. 4, $H_2(p\text{-}Cl)$-TPP.

---

* Present address: Pharmaceutical Institute, Tohoku University, Aramaki, Sendai 980.

Results and Discussion

The cyclic voltammetric results are given in Table 1. Metal-free porphyrins were reduced step-wise through a reversible one-electron transfer step to give porphyrin anion radicals followed by the formation of the dianions.[5] The irreversible waves, ascribed to the formation of porphyrin cation radicals, were also observed in the oxidation. These peak potentials of reduction and oxidation are correlated with Hammett σ values (Fig. 1). Each correlation is expressed as follows.

First reduction:

$$E_{\mathrm{p}} = 0.205\sigma - 1.030\mathrm{V} \qquad (1)$$

Second reduction:

$$E_{\mathrm{p}} = 0.295\sigma - 1.426\mathrm{V} \qquad (2)$$

Oxidation:

$$E_{\mathrm{p}} = 0.317\sigma + 1.118\mathrm{V} \qquad (3)$$

The equations show that the electron-donating group increases the electron density on the porphin ring through the phenyl group, and consequently these peak potentials shift toward a negative direction while the reverse is seen for the electron-withdrawing group.

The reduction of cobalt porphyrins also proceeded reversibly through two one-electron steps. The first step has been accepted to be the addition of electron to cobalt, Co(II)→Co(I), and the second step also seems to involve the change in the valency of cobalt.[5,8] The oxidation consists of the two consecutive steps, the first and second steps being attributed to the oxidation of cobalt and porphin ring, respectively.[6] Contrary to the case of metal-free porphyrins, a good correlation with Hammett σ values was obtained in the second oxidation step (Fig. 2):

$$E_{\mathrm{p}} = 0.296\sigma + 1.198\mathrm{V} \qquad (4)$$

whereas no distinct correlation was found in the first oxidation and reduction steps.

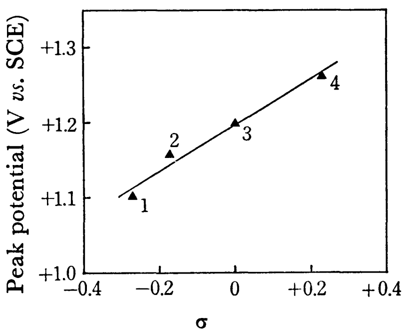

Fig. 2. Relation of peak potentials for the second oxidation of cobalt tetra(*p*-substituted phenyl)porphyrins to Hammett substituent constants: 1, Co(*p*-OCH_3)-TPP. 2, Co(*p*-CH_3)TPP. 3, CoTPP. 4, Co(*p*-Cl)-TPP.

It is thus concluded that the peak potentials are correlated well with Hammett σ values when the electron transfer occurs at the porphin ring as in the case of metal-free porphyrins or the second oxidation of cobalt porphyrins. This can be understood in terms of the resonance interaction between the substituents on phenyl groups and the porphin ring.[9] No correlation is substantially obtained when the electron transfer occurs at the cobalt atom. This indicates that the redox properties of central metal do not directly reflect those of the porphin ring.

CoTPP activates an oxygen molecule to the superoxide state through the electron donation from the central metal. The activated oxygen abstracts the hydrogen of acetaldehyde to initiate autoxidation. It was found that Co(*p*-CH_3)TPP possesses a remarkably high catalytic activity, almost ten times as much as those of the other cobalt porphyrins. The extraordinary activity of Co(*p*-CH_3)TPP cannot be explained in terms of the oxidation potentials of porphyrins. This is ascribed to the fact that the potentials indicate only the ease of the activation process of oxygen molecule. It seems that the substituent effect on the reactivity of an oxygen molecule which has been in activated condition should also be taken into account for clarifying the effect in autoxidation of acetaldehyde.

We would like to express our thanks to Prof. Taiseki Kunugi for his valuable advice and discussion.

References

1) J. H. Fuhrhop and D. Mauzerall, *J. Am. Chem. Soc.*, **91**, 4174 (1969).

D) J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *J. Am. Chem. Soc.*, **92**, 3451 (1970).

3) N. E. Tokel, V. Katonić, K. Farmery, L. B. Anderson, and B. H. Busch, *J. Am. Chem. Soc.*, **92**, 400 (1970).

4) K. M. Kadish, G. Larson, D. Lexa, and M. Momenteau, *J. Am. Chem. Soc.*, **97**, 282 (1975).

5) R. H. Felton and H. Linschitz, *J. Am. Chem. Soc.*, **88**, 1113 (1966).

6) A. Wolberg and J. Manassen, *J. Am. Chem. Soc.*, **92**, 2982 (1970).

7) J. Manassen, *Catal. Rev.*, **8**, 223 (1974).

8) L. D. Rollmann and R. T. Iwamoto, *J. Am. Chem. Soc.*, **90**, 1455 (1968).

9) P. Zuman, "Substituent Effects in Organic Polarography," Plenum Press, New York (1967).