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ELECTROCHEMICAL INVESTIGATION OF β-ALKYLOXY SUBSTITUTED meso-TETRAPHENYLPORPHYRINS

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Abstract: The voltammetric behaviour of several β -alkyloxy substituted *meso*tetraphenylporphyrins has been investigated. The first oxidation potential of all compounds depends strongly upon the substituent constant σ^+ . In contrast to this the second oxidation potential is insensitive to this constant. Furthermore, rate constants for the first anodic electron transfer process were determined. The estimated data confirm, that the distortion of the porphyrin chromophore induced by the substituents did not affect the electrochemical rate constant significantely.

Introduction:

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Charge separation in photosynthetic organisms occurs in a chlorophyllquinone-protein complex known as the photochemical reaction center. The stucture of the photochemical reaction center of *Rhodopseudomonas viridis* was determined in 1984 by X-ray diffraction analysis.¹⁾ This investigation stimulated the synthesis of artificial model systems for photochemical reaction centers in the last years. Especially porphyrinic systems were synthesized for these investigations.²⁾ For the design and synthesis of new arificial model systems it is necessary to investigate the effect of different substituents on the chromophore properties. Especially it is necessary to get more information about the influence of substituent parameters on oxidation and reduction potentials and on spectroscopic properties.

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We recently synthesized a number of different β -alkyloxy substituted porphyrins and investigated some of their electrochemical properties.^{3,4)} In these systems (figure 1) the electronic and steric properties of the substituents were changed. Increased bulkyness of the β -substituents leads to an increased interaction with the *meso*-phenyl groups and forces the porphyrin chromophore out of plane. As a result, the porphyrinic system is now non-planar. We now report here new electrochemical investigations of the already published β alkyloxy porphyrins and of some new compounds.



Figure 1: Synthesized β -alkyloxy substituted porphyrins 1a-j.

Experimental:

All electrochemical experiments were carried out in dry CH_2Cl_2 under N_2 atmosphere. Tetrabutyl ammonium tetrafluoroborate (0.1 M) was used as supporting electrolyte. A Tacussel PJT 24 Potentiostat connected to a Tacussel IMT 1 interface and an IBM-AT computer was used for all measurements. Ohmic drop compensation was carried out electronically by the positive feed back method. A conventional three electrode cell was used. A Ag/AgCl electrode was used as reference, a Pt-electrode as counter and a Pt-mini or a Pt-micro (d = 10^{-5} m) electrode was used as working electrode. Kinetic studies were always carried out at the micro-electrode. All potentials were given with respect to the ferrocen/ferrocenium system. Electrode areas were determined by pulse voltammetry using a 10^{-3} M ferrocene/CH₂Cl₂ solution (D = 1.7×10^{-5} cm²s⁻¹). Diffusion coefficients of the investigated compounds were determined by pulse voltammetry.

Results and Discussion:

Two peaks can be clearly seen in the cyclo voltammogram of all investigated β -alkyloxy porphyrins (Figure 2).



Figure 2: Cyclo voltammogram of 1b in CH₂Cl₂/TBATFB at different scan rates. Measured against Ag/AgCl (550 mV vs. ferrocene).

Increase of the substituent constant σ^+ leads to an increase of the first oxidation potential (Table 1). From the slope of the Hammett plot we calculated an electrochemical reaction constant of 0.29 Volt for the first oxidation potential. This value indicates that the first oxidation potential strongly depends upon the electronic properties of the β -substituent. Furthermore, a decrease of the electron donating power of the substituent (examples 1h-j) leads, as expected, to an increase of the first oxidation potential. In contrast to these findings, there is no

linear correlation between the second oxidation potential and σ^+ . The potential remains constant varying σ^+ from -0.78 to -0.83. On the other hand, changing of the bulkyness of the β -substituent leads to variations in the second oxidation potential. Thus bulky substituents like i-propyloxy and neo-pentyloxy lead to a decrease of the second oxidation potential. Taking into consideration an interaction between *meso-* and β -substituents we can state that the distortion of the chromophore effects the second oxidation potential. Variations of the electronic nature of the substituent are more important for the first oxidation potential than for the second oxidation potential. In contrast to the observed dependency of the oxidation potentials from the substituent, the reduction potentials remain constant. This finding is in accordance with theoretical calculations that confirm, that only the HOMO energy is influenced by chromophore distortion and that the LUMO energy is not effected.⁵)

| | E ^{1/2} _{ox1} /V | E ^{1/2} _{ox2} /V | ΔE_{ox} /V | ${\rm E}^{1/2}_{\rm red1}$ /V | E ^{1/2} _{red2} /V |
|-----------|------------------------------------|------------------------------------|--------------------|-------------------------------|-------------------------------------|
| 1a | 0.440 | 0.630 | 0.190 | -1.765 | -2.070 |
| 1b | 0.430 | 0.630 | 0.200 | -1.770 | -2.080 |
| 1c | 0.425 | 0.630 | 0.205 | -1.765 | -2.070 |
| 1d | 0.420 | 0.620 | 0.200 | -1.770 | -2.070 |
| 1e | 0.415 | 0.610 | 0.195 | -1.770 | -2.070 |
| 1f | 0.425 | 0.610 | 0.185 | -1.765 | -2.080 |
| 1g | 0.380 | - | - | - | - |
| 1h | 0.470 | 0.660 | 0.190 | - | - |
| 1i | 0.455 | 0.630 | 0.170 | - | - |
| 1j | 0.425 | 0.635 | 0.210 | - | - |

Table 1. Electrochemical data of the 2-alkyloxy-5,10,15,20tetraphenylporphyrins **1a-1h.** T = 296 K, c = 10^{-3} M, scan-rate 100 mV/s. Pt-elektrode. All potentials measured against Ag/AgCl and referenced against ferrocene/ferrocenium. Furthermore we investigated the effect of the different substituents on the electrochemical rate constant k_s . This rate constant was calculated from the current function Ψ , which is given by equation (1):

(1)
$$\Psi = \gamma^{\alpha} k_{s} (\pi n F \upsilon D_{o} / R T)^{1/2}$$

 Ψ was obtained from a working curve using Nicholson and Shain's⁶ tables. The transfer coefficient α was calculated from equation (2):

(2)
$$\alpha = (1.857 \text{ R T} / \text{n F})(E_p - E_{p/2})^{-1}$$

The obtained values for k_s and D are summarized in table 2. From these data it is obvious, that the conformational changes induced by steric interaction between *meso-* and β -substituents leads only to small changes in the electrode kinetics.

| the second s | | | | | |
|--|---------|--------|--------------|-------|-----------------------|
| | υ / V/s | ΔΕ / V | $D / cm^2/s$ | Х | k _s / cm/s |
| 1a | 0.1 | 0.107 | 4.60 | 0.475 | 0.0036 |
| 1b | 0.1 | 0.105 | 5.13 | 0.445 | 0.0035 |
| 1c | 0.1 | 0.066 | 3.55 | 0.660 | 0.0044 |
| 1d | 0.1 | 0.078 | 4.88 | 1.100 | 0.0055 |
| 1h | 0.1 | 0.086 | 7.27 | 0.925 | 0.0087 |
| 1i | 0.1 | 0.098 | 5.92 | 0.620 | 0.0053 |

Table 2. Electrokinetic data of β -alkyloxy substituted porphyrins. T = 298 K, c = 10⁻³ M. Pt-electrode.

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Calculation of k_s from working curves has some disadvantages. Especially for small values of ΔE , the error in X is significant.⁷ Therefore we used a second method for determining the k_s values. In 1981 Kochi and Klingler⁸ developed a method for determining the rate constant k_s which circumvent the above mentioned disadvantages. According to these authors k_0 is given by equation (3)

(3) $k_s = 2.18$ (D α n F υ / R T)^{1/2} exp [(- α^2 n F /R T)($E_p^{a} - E_p^{c}$)]

Using equation (3) we calculated k_s for different scan rates. The calculated data were fitted by a 2nd order polynome ($y = ax^2 + bx + c$) and the maximum value of k_s was calculated by equation (4).

(4)
$$k_s^{max} = -b^2 / 4 a + c$$

The electrochemical parameter k_s^{max} and the determined coefficients a, b and c are summarized in table 3. From the calculated data and from figure 3 and 4 it is obvious, that the distortion of the porphyrin ring system did not affect k_s^{max} significantly. It is also obvious, that introduction of a polar group into the substituent (examples 1h and 1i) leads to an increase in k_s^{max} .

| | α | a x 10 ² | b | с | k _s ^{max} / cm/s |
|----|-------|---------------------|--------|--------|--------------------------------------|
| 1a | 0.578 | -2.0042 | 1.9174 | 3.7685 | 0.049 |
| 1b | 0.597 | -1.4226 | 1.5405 | 4.7721 | 0.046 |
| 1c | 0.616 | -1.3706 | 1.5489 | 3.1070 | 0.047 |
| 1d | 0.683 | -2.1007 | 1.7139 | 3.9922 | 0.039 |
| 1h | 0.637 | -1.9207 | 2.3602 | 5.4331 | 0.078 |
| 1i | 0.684 | -2.3653 | 2.1291 | 4.2813 | 0.052 |

Table 3. Electrokinetic parameters α and k_s^{max} estimated for β -alkyloxy substituted porphyrins. The value of k_s^{max} was calculated from equation (4)



Figure 3: Plot of k_s calculated from equation (3) vs scan-rate for 1h (fit 2) and 1i (fit 1).



Figure 4: Plot of k_s calculated from equation (3) vs scan-rate for 1a-d.

As a preliminary conclusion we can say that two different factors are responsible for changes in the oxidation potential. The electronic nature of the substituents affects mainly the first oxidation potential. The second oxidation potential is much less sensitive to variation of the electronic nature of the substituent. Furthermore a steric effect is operative. The steric interaction between the *meso-* and β -substituents affects the first and the second oxidation potential significantly. The rate constant of the first electron transfer is mainly controlled by the electronic nature of the substituent and not by steric interaction between the substituents.

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Mechanism of Corrosion Inhibition of Ni and Ni-Mo-Fe Alloy

in Dilute Nitric Acid by some Azole Compounds

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Abstract

Inhibition of corrosion of nickel and nickel base (Ni-Mo-Fe) alloy in 4 percent nitric acid has been studied in the presence of some azole compounds, using electrochemical polarization technique, at various concentrations of inhibitors and at different temperatures (25, 35, 45°C). All the inhibitors investigated were able to suppress both the anodic and cathodic processes appreciably for both the systems. However, in each case the inhibition afforded by these molecules towards the corrosion of nickel in nitric acid is always greater than those for nickel base alloynitric acid system. Among these inhibitors, 2-mercaptobenzothiazole was found to be the most effective inhibitor for both the systems. These inhibitor molecules, though structurally similar do not follow the same mechanism of inhibition. Either of the two mechanisms, viz., adsorption or surface complex formation or sometimes both of these have been found valid for individual inhibitors.