Inorganica Chimica Acta, *129* (1987) 31–33

Voltammetry of Zinc Tetraphenylporphyrin in Solution and in Polymer Films: The Effect of Axial Ligands

LALCHAN PERSAUD, ANDREW CROUCH and COOPER H. LANGFORD*

Department of Chemistry, Concordia University, 1455 deMaisonneuve W., Montreal, Que., H3G 1M8, Canada

(Received September 22, 1986)

Abstract

Cyclic voltammetry at Pt electrodes is presented for the title compound in solution with added pyridine or polyvinylpyridine and $(C_6H_5)_3P$ and $(C_6H_5)_3As$ as well, and in films formed on the electrode from polyvinylpyridine with the porphyrin incorporated by axial ligation. The axial ligands have only a small effect on the one electron reversible oxidation of the porphyrin but after the second oxidation step, a slow reaction leads to a peripheral nucleophilic substitution which is reversed only at much more cathodic voltages (−0.1 V). The substituted form also displays a quasi-reversible reaction at a quite anodic potential (1.0 V) which is rendered unobservable by excess pyridine ligand.

Introduction

Recently, we have been interested in the behaviour of photocatalysts formed by depositing films of polyvinylpyridine on oxide supports and adding porphyrins such as zinc tetraphenylporphyrin (ZnTPP) to the films via axial ligation of the pendant pyridine to the porphyrin [1]. We have also studied photoelectrodes with this type of film on SnO_2 transparent electrodes [2]. In the course of this work, we have obtained spectroscopic evidence for the participation of oxidized forms of the porphyrins in the reaction cycles. It is also known that the dication of the porphyrin is susceptible to peripheral nucleophilic attack [3, 4]. The present report explores the cyclic voltammetry of the porphyrin in CH_3CN solution in the presence of added pyridine or polyvinylpyridine (and several other ligands as well) and in films of polyvinylpyridine which contain the porphyrin.

Experimental

Materials

Zinc tetraphenylporphyrin (ZnTPP) from Strem Chemical Co. was purified by chromatography on neutral alumina and elution with CH_2Cl_2. Triphenylphosphine, triphenylarsine (Eastman), poly(4-vinylpyridine) (PVP) (Eastman) and pyridine (Aldrich) were used as received. Other solvents were spectrograde and used without further purification. The supporting electrolyte $NaClO_4$ (Aldrich) was recrystallised from hot distilled water and dried prior to use.

Instrumentation

All potentials were measured using a Ag/Ag^+ reference electrode, a 1 cm^2 Pt working electrode and a Pt wire counter electrode. Potentials were applied with a Metrohm 506 Polaricord and varied with a Metrohm 616 V/A Scanner. Voltammograms were recorded with an *x–y* recorder (Hitachi). All voltammetric experiments were performed in a conventional Metrohm cell. Optical spectra were recorded on a Perkin-Elmer 552 UV–Vis spectrophotometer. Proton NMR spectra were recorded on a Bruker WP-80 SY spectrometer. For the voltammetry on modified electrodes, the working electrode was modified by dipping it into a CH_2Cl_2 solution of ZnTPP and poly vinylpyridine (93.5 mg ZnTPP and 101.1 mg PVP in 10 ml CH_2Cl_2), and then allowing the electrode to dry in a vacuum oven at 60 °C. In this way a thin film of polyvinylpyridine containing ZnTPP is formed on the surface of the Pt. The amount of ZnTPP in the polymer film on the electrode was subsequently determined by redissolving the film in CH_2Cl_2 and then measuring its optical absorbance.

Voltammetric titrations were performed by spiking the working solution of ZnTPP in CH_3CN (0.1 M $NaClO_4$ as background electrolyte) with 10 μl portions of a 10% titrant (pyridine, triphenylarsine, triphenylphosphine or PVP).

---

*Author to whom correspondence should be addressed.

0020-1693/87/$3.50

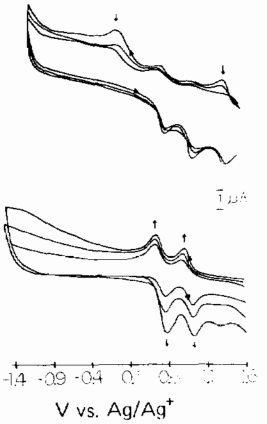

Fig. 1. (a) Cyclic voltammograms for ZnTPP in CH_2Cl_2 titrated with pyridine in increments of 0, 10, 30, and 50 μl of 10% pyridine, 50 μl corresponds to a slight excess of pyridine. As pyridine is added, the two intermediate reversible peaks decline, the extreme anodic peak grows, and the large reduction wave grows. In excess pyridine, the 'reversible' wave at the anodic extreme declines again. (b) Similar titration with a solution of polyvinylpyridine from 0 to 50 μl of titrant. Note that the major reduction wave is poorly resolved and the extreme anodic wave is missing. Scan rates 30 mV/s.

Results

Figure 1(a) shows results of the 'titration' of 5.8×10^{-2} mM ZnTPP with 10% (v/v) pyridine in CH_3CN solution. In the absence of pyridine, the cyclic voltammogram (CV) shows two quasi-reversible peaks near +0.35 and +0.65 V. These correspond to the oxidation of ZnTPP to a monocation radical and a dication as previously reported [3]. In agreement with observations reported by Dolphin *et al.* [5], as pyridine is added, the two anodic peaks remain observable, but the corresponding reduction peaks at +0.61 and +0.31 V progressively disappear. The oxidation becomes irreversible. We find rendering of the oxidations irreversible is accompanied by two new features. A new quasi-reversible pair of peaks emerges near +0.99 V and a reduction feature develops at −0.08 V. Integration of the new reduction feature at −0.08 V indicates that the coulombs passed equals the sum of the charge for the two oxidations within 6.9%. It is noteworthy that the reduction at −0.08 V completes a cycle. The voltammogram may be repeated without change on successive runs.

The remaining feature of the titration with pyridine emerges as the pyridine concentration just exceeds the concentration of porphyrin. As the pyridine concentration increases above the concentration of ZnTPP, the new quasi-reversible peak near 0.99 V declines again. Figures 2(a) and (b) show similar 'titrations' of ZnTPP with triphenylphosphine and triphenylarsine. The qualitative features are similar but the 'new' features with increasing ligand concentration are not as well defined. Titration of ZnTPP with polyvinylpyridine is shown in Fig. 1(b). This titration can be considered to resemble that with pyridine if one recognizes that all points are collected in circumstances where there is an excess of pyridine at each ZnTPP molecule affected. That is, as a ZnTPP reacts with one pyridine, it becomes associated with a polymer molecule with a large number of additional pyridine pendant groups. Figure 3 shows the cyclic voltammogram of a film of PVP containing ZnTPP. This could be consistent with the solution cyclic voltammogram with extensive broadening of peaks corresponding to considerable reduction of rates due to much reduced mobility. Unfortunately, no identifiable peaks remain.

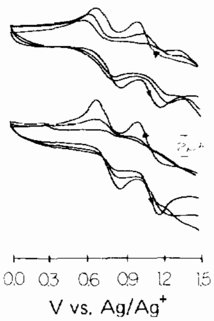

Fig. 2. (a) Titration with triphenylphosphine. (b) Titration with triphenylarsine. Conditions similar to those in Fig. 1.

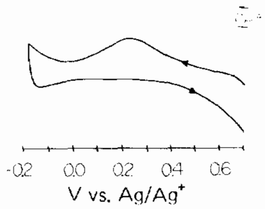

Fig. 3. Cyclic voltammogram of a film of ZnTPP/PVP on a 1 cm^2 Pt electrode. The ratio of ZnTPP to pyridine groups of PVP is 1:8.

The dication product of the oxidation of ZnTPP could also be produced by chemical oxidation of ZnTPP using aqueous Ce(IV). The equivalence is documented by the optical spectra. Using chemical oxidation, it was possible to obtain a sample of the pyridine adduct of the ZnTPP dication. Figure 4 presents the visible spectral data available. It is clear from the visible spectra at different points in the titration of ZnTPP with pyridine that the pyridine becomes axially ligated only after its concentration exceeds that of the ZnTPP in solution. Axial ligation is recognised from the increase in intensity of the bands in the visible spectrum [6]. It is therefore reasonable to associate the adduct which

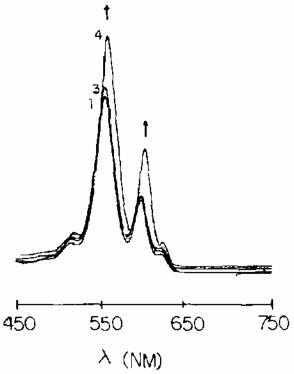

Fig. 4. Visible spectrum of ZnTPP during titration with pyridine. Curves 1–4 correspond to the concentrations in Fig. 1(a). Notice the growth of both bands when an excess of pyridine is finally achieved (curve 4).

gives the reversible voltammetric peak at +1.0 V with a ring substituted product.

Discussion

Dolphin and his collaborators have described the attack of pyridine on the dication of ZnTPP (5), suggesting substitution into the pyrrole ring to give a beta-pyridinium porphyrin cation. This has been supported by a very recent communication [4]. Nothing in the present results requires us to challenge this conclusion. Principally, the present results add to the picture.

The substitution of pyridine into the porphyrin dication creates a cationic site centred on the quaternized pyridine nitrogen and releases a proton to the solution. In effect, this 'rereduces' the porphyrin ring and accounts for the absence of reduction waves and the introduction of the new quasi-reversible wave at the anodic limit (+0.99) of the cyclic voltammogram. This new wave may be considered an analog to the one electron oxidation of the parent porphyrin which was near +0.35 V. The reduction wave found near −0.08 V is quite plausibly reduction of the quaternized pyridine which initiates the two electron reduction in an EC mechanism. It is noteworthy that one electron reduction of bipyridine centres such as methyl viologen occur at potentials near the −0.1 V region. The final feature is the loss of the anodic peak at high pyridine concentration. Either an axial pyridine reduces the rate of the electron transfer or shifts the potential to a still more anodic value outside of the range. The second explanation is not too plausible because the axial pyridines seem to shift the oxidation of the original ZnTPP very little. A change of kinetics seems more likely.

The experiments do not give us a similarly complete picture of the behaviour of the other cases. The voltammetry in the presence of triphenylarsine and triphenylphosphine hints at the features of the pyridine case and could be plausibly interpreted as displaying similar chemistry with reduced rates of electron tranfer for the new species resulting from nucleophilic attack on the porphyrin ring.

The species generated in the presence of polyvinylpyridine present special problems. It is not possible to add a nucleophile to the peripheral position without, at the same time, placing additional pyridine groups in favourable positions for axial ligation. Consequently, we see in the CVs only those features corresponding to those that appear with pyridine monomer at large excess. From this point of view the PVP results are entirely consistent with those for pyridine.

Finally, we come to the film on the electrode. Here, as we should expect, peaks become very broad because mobilities are limited. A plausible interpretation of the events is that the same chemistry takes place at considerably reduced rates but the lack of direct evidence is disappointing.

References

1 C. H. Langford, C. Saint-Joly, E. Pelletier, L. Persaud, A. Crouch and C. Arbour, in S. Kaliaguine and A. Mahay (eds.), 'Catalysis on the Energy Scene', Elsevier, Amsterdam, 1984, p. 291.
2 H. Kido and C. H. Lanford, *J. Chem. Soc., Chem. Commun.*, 350 (1983).
3 H. J. Shine, A. G. Padilla and S. M. Wu, *J. Org. Chem., 23,* 4096 (1979).
4 L. ElKahaf, M. ElMeray, M. Gross and A. Giradeau, *J. Chem. Soc., Chem. Commun.*, 621 (1986).
5 D. Dolphin, D. J. Halke, E. C. Johnson and K. Rosseau, in F. R. Longo (ed.), 'Porphyrin Chemistry Advances', Ann Arbor Science, Ann Arbor, Mich., 1979, p. 119.
6 M. Nappa and J. S. Valentine, *J. Am. Chem. Soc., 100,* 5075 (1978).