

## Heterogeneous Electron Transfer Rate Constants of Substituted Tetraphenylporphinosilver(II) Complexes

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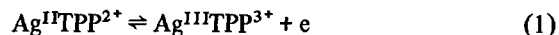
Received August 14, 1980

*Cyclic voltammetry experiments have been performed on a series of p- or m-substituted tetraphenylporphyrin complexes of silver(II) in dichloromethane. Potential separation differences were used to calculate heterogeneous electron-transfer rate constants at a platinum electrode for the  $Ag^{II}P \rightleftharpoons Ag^{III}P + e$  reaction. The  $k_s$  values obtained range from  $9.06 \times 10^{-3}$  cm/sec for  $Ag^{II}$ -p-OCH<sub>3</sub>TPP to  $1.00 \times 10^{-3}$  cm/sec for  $Ag^{II}$ TPP complex.*

### Introduction

In recent years a number of papers have reported the heterogeneous electron-transfer rate constants for the redox reactions of several metalloporphyrins [1–5]. The metalloporphyrins most extensively investigated are the iron, cobalt, and manganese complexes. From these metalloporphyrins studied it has been shown that the electron-transfer reactivities are dependent on a number of physical and chemical properties: the basicity of the porphyrin ring, the solvent and electrolyte composition, metal spin state, and the degree of axial ligation.

In the course of investigating the effect of substituents on the redox potentials of substituted *meso*-tetraphenylporphinosilver(II) complexes [6] we have also analyzed the heterogeneous electron-transfer rate constants of these complexes in dichloromethane. Silver(II) provides an ideal system for the study of electron transfer rates to an electrode surface. It being a  $d^9$  metal center with an electron in the antibonding  $d_{x^2-y^2}$  orbital of the silver(II) porphyrin [7]. The spin state for silver changes from spin of 1/2 to zero spin state and easily adapts itself to study by ESR, low energy charge transfer measurements in the UV-visible spectroscopy, emission spectra, redox potentials, and near infrared absorption. Since silver(II) porphyrin does not form axial ligation, it also provides an excellent opportunity to study the porphyrin ring basicity without inductive interferences by axial ligands. Non-coordinating solvent, dichloromethane, has been used in this study. The reaction of interest to us is the electron-transfer rate constant,  $k_s$ , of the metal center, eqn. (1)



In the present paper, electron transfer rate constants of several substituted *meso*-tetraphenylporphinosilver(II) complexes have been determined by the cyclic voltammetry method and reported herein.

### Experimental

The following synthetic porphyrins: *p*-OCH<sub>3</sub>TPP, *p*-CH<sub>3</sub>TPP, *m*-CH<sub>3</sub>TPP, H<sub>2</sub>TPP, *p*-FTPP, *p*-BrTPP, *p*-ClTPP, and 4-pyridylporphyrin were obtained from Man-Win Chemical Company. The purification, synthesis and characterization of the silver(II)-porphyrin complexes have been described in an earlier work [6]. Eastman Kodak Co., tetrabutylammonium perchlorate (TBAP) was recrystallized from an ethanol-water solution and stored in the dark under vacuum at 60 °C. The solvent dichloromethane was treated with concentrated sulfuric acid, then aqueous potassium carbonate and water, and dried over calcium chloride. It was distilled over P<sub>2</sub>O<sub>5</sub> before usage.

Cyclic voltammetry measurements were done using the three-electrode potentiostatic circuit and a MPI Model MP-1042 voltammetry Controller in conjunction with a PAR Houston Model 2000 X-Y recorder. The working electrode was a platinum bead electrode while the counter-electrode was either a platinum gauze electrode or a platinum wire. A Beckman saturated calomel electrode was used as the reference electrode. Solutions were purged with pre-purified and solvent saturated nitrogen gas for 15 minutes. The solutions were kept under the nitrogen atmosphere after purging for quiescent voltammetry scans. Careful avoidance of both water and oxygen is essential in these studies to provide clean electron transfer to the electrode without subsequent chemical reaction. All the cyclic voltammetry measurements were done at ambient room temperature at  $24 \pm 1.5$  °C.

The supporting electrolyte was 0.10 or 0.50 *M* TBAP and the silver(II)-porphyrin concentration was kept at 1 *mM* and in two cases at 0.5 *mM*. All the potentials were converted to values versus SCE.

## Results and Discussion

The redox behavior of several metal centers located with porphyrin rings has been studied for quite some time. An excellent summary was done by Fuhrhop, Kadish, and Davis [8]. Silver(II) porphyrin have several oxidations and reductions. Some redox couples which are very reversible belong to oxidation-reduction reactions associated with the porphyrin rings and only one redox couple is associated with the metal center. It is fortunate that the porphyrin oxidations occur above +1.00 V vs SCE and the porphyrin reductions occur below -1.00 V vs SCE. The oxidation of Ag(II) with the most electron-withdrawing substituents attached to the phenyl rings occurred at +0.60 V vs SCE and with the most electron-donating group at +0.46 V vs SCE [6]. This permits the use of the cyclic voltammetry technique to study the rates of electron transfer.

In cyclic voltammetry, a triangular wave potential is applied as a function of time such that the oxidized species produced at the electrode surface during the forward sweep is reduced to give the cathodic peak in the return sweep. Furthermore, when the potential scan rate is increased, the cathodic and the anodic peaks will be shifted along the potential axis. Such shifts with potential scan rates are an indication of quasi-reversible electron transfers and the electron-transfer rate constants,  $k_s$ , can be calculated by using the equation developed by Nicholson [9].

$$\psi = k_s \left[ \frac{D_0}{D_R} \right]^{\alpha/2} \left[ \frac{\pi n F \nu D_0}{RT} \right]^{-1/2}$$

Where  $D_0$  and  $D_R$  are the diffusion coefficients of the oxidized and reduced forms;  $n$ , the number of electrons transferred;  $\nu$ , the scan rate;  $\alpha$ , the transfer coefficient;  $k_s$ , the heterogeneous rate constant in cm per sec., and  $\pi$ ,  $F$ , and  $RT$  have their usual significance. The  $\psi$  is calculated by Nicholson as a function of peak separation,  $\Delta E_p$ , at  $\alpha = 0.5$ .

The charge transfer coefficient,  $\alpha$ , has been assumed to be 0.5 for all cases of the silver(II)-porphyrin because of their close similarity in structures and charges. Values for  $\alpha$  can be estimated from the shift of the cathodic peak with scan rate and have been found to range from 0.44 to 0.65 with a mean value of 0.53. It is because of the relatively insensitivity of  $k_s$  to the value of  $\alpha$  that 0.5 is used in all the calculations.

Table I lists the heterogeneous rate constants,  $k_s$ , at various scan rates for the reaction (1) in dichloromethane. The good agreement of the  $k_s$  values calculated shows that the electron transfer is kinetically controlled. Table II lists all the heterogeneous rate constants for all the silver(II)-porphyrins studied at scan rate of 100 mv per sec., except for the 4-pyridylporphyrinat silver(II) which was studied at 1 V per

TABLE I. Calculation of  $k_s$  for the Electrode Reaction  $\text{Ag}^{\text{II}}-p\text{-CH}_3\text{TPP} \rightleftharpoons \text{Ag}^{\text{III}}-p\text{-CH}_3\text{TPP} + e$ .<sup>a</sup>

| scan rate, mv/sec | $10^3 k_s$ , cm/sec     |
|-------------------|-------------------------|
| 100               | 1.66                    |
| 200               | 1.90                    |
| 500               | 2.66                    |
|                   | average $2.07 \pm 0.39$ |

<sup>a</sup> 1 mM complex in 0.1 M TBAP and  $\text{CH}_2\text{Cl}_2$  at 24 °C.

TABLE II. Diffusion Coefficients and Heterogeneous Rate Constants of Silver(II)(*p*- or *m*-X)TPP in  $\text{CH}_2\text{Cl}_2$ .<sup>a</sup>

|  | $10^6 D_0$ , $\text{cm}^2/\text{sec}$ | $10^3 k_s$ , cm/sec |
|--|---------------------------------------|---------------------|
| $\text{Ag}^{\text{II}}-p\text{-OCH}_3\text{TPP}$ | 9.06                                  | 9.01                |
| $\text{Ag}^{\text{II}}-p\text{-CH}_3\text{TPP}$  | 17.4                                  | 1.66                |
| $\text{Ag}^{\text{II}}-m\text{-CH}_3\text{TPP}$  | 2.78                                  | 1.45                |
| $\text{Ag}^{\text{II}}\text{-TPP}$               | 0.55                                  | 1.00                |
| $\text{Ag}^{\text{II}}-p\text{-FTPP}$            | 3.43                                  | 2.03                |
| $\text{Ag}^{\text{II}}-p\text{-ClTPP}$           | 0.86                                  | 2.27                |
| $\text{Ag}^{\text{II}}-p\text{-BrTPP}$           | 8.58                                  | 1.11                |
| $\text{Ag}^{\text{II}}-4\text{-pyP}$             | 2.36                                  | (1.85 at 1 v/sec)   |

<sup>a</sup> Except for the TPP and *p*-ClTPP complexes, the concentration of the complexes is 1 mM. The exceptions were at 5 and 0.5 mM, respectively. The electrolyte is 0.1 M–0.5 M TBAP and at 24 °C.

sec. The diffusion coefficients of the oxidized and reduced forms were calculated using the Randles [10] and Sevcik [11] equation which relates the peak current to the other experimental parameters of the stationary-electrode in polarography. The  $D_0$  values varied from 0.5 to  $17 \times 10^{-6} \text{ cm}^2/\text{sec}$ ., and are also listed in Table II.

Only the 4-pyridylporphyrinat silver(II) has an electron transfer rate constant so slow at 100 mv/sec scan rate that it was considered irreversible. However, when the scan rate was increased to 1 v/sec, a  $k_s$  value of  $1.85 \times 10^{-3} \text{ cm/sec}$ . was obtained. From Table II, it is evidenced that the rate of electron transfer of the silver(II) is slightly influenced by the electronic effect of the substituents on the phenyl groups of the porphyrin ring. This is in agreement with the general trend observed by Kadish *et al.* [5], for the Fe(*p*-X)-TPP series. The small variation in  $k_s$  is expected since the electron donating and the electron withdrawing substituents are located at least six atoms distance for the *m*-substituents and seven atoms distance for the *p*-substituents on an aromatic ring which is not coplanar with the porphyrin ring.

The metal redox rate constants for porphyrin complexes of Co, Fe, and Mn are listed in Table III for comparison with Ag(II). It is apparent that the

TABLE III. Metal Electron Transfer Rate Constants.

| Complex  | $10^3 k_s$ , cm/sec                            | Ref.      |
|--|--|-----------|
| CoTPP  | 3.3 (in CH <sub>2</sub> Cl <sub>2</sub> )      | 2         |
| ClMn( <i>p</i> -ClTPP)                           | 1 (in DMSO)                                    | 4         |
| Fe( <i>p</i> -XTPP)                              | 0.79–9.12 (in BN)                              | 5         |
| Ag <sup>II</sup> ( <i>p</i> - or <i>m</i> -XTPP) | 1.0–9.01 (in CH <sub>2</sub> Cl <sub>2</sub> ) | This work |

metal electron transfer rate constants for those that have no axial ligation (Co, Fe, Ag) are very close and in the order of  $10^{-3}$  to  $10^{-2}$  cm/sec. Comparison between the 3d and 4d transition metals electron transfer rate constants is not plausible at this stage, since data have been obtained under different conditions. However, one thing is certain; that is, axial ligation as in Mn reduces the  $k_s$  values.

Attempts were made to correlate  $k_s$  of the Ag<sup>II</sup>TPP and the FeTPP series with Hammett  $\sigma$  values. Only the general trend reported earlier is observed except for the *p*-OCH<sub>3</sub>TPP complexes. Within the experimental errors, the rate of electron transfer of the metal center can be observed to be, in general, not influenced by the substituent's electronic contribution from the distant phenyl ring, although the redox potentials have been altered somewhat by the substituents. Perhaps, because the metal center such as Ag(II) is at such a distance that the  $k_s$  can be due entirely to the rate of removal of the metal d electron and only when an electron donating group as good as *p*-OCH<sub>3</sub> is used that a significant enhancement is observed. A factor of four to nine in rate enhancement is observed when Ag<sup>II</sup>-*p*-OCH<sub>3</sub>TPP is compared

with the other *p*- or *m*-substituted Ag<sup>II</sup>-TPP. It is unknown at this time why in particular *p*-OCH<sub>3</sub>TPP complexes enhanced the metal electron transfer rates.

### Acknowledgment

We would like to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We would also like to thank Dr. K. D. Legg of Instrumental Lab. for his many helpful suggestions.

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