3720 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3720—3723 (1973) [Vol. 46, No. 12

Determination of Electrochemical Kinetic Parameters of Porphyrins and Metalloporphyrins in *N,N'*-Dimethylformamide by Radio Frequency Polarographic Method

Tadaaki KAKUTANI and Mitsugi SENDA

Department of Agricultural Chemistry, Faculty of Agriculture, Kyoto University, Kyoto 606

(Received June 22, 1973)

Electrochemical kinetic parameters were determined for the first two reduction steps of some porphyrins and divalent metalloporphyrins in DMF containing 0.5 M TEAP at 25 °C by use of radio frequency polarographic method. The results were discussed in view of their molecular structures and the diffuse double layer effect on the kinetic parameters.

It has been found [1–4] that in aprotic solvent such as dimethylformamide(DMF) porphyrins and their divalent metal complexes give three or four well-defined reduction waves, of which the first two are in general reversible one-electron reduction steps with negligible complications by specific adsorption. The products produced at the first two steps have been found to be reasonably stable. These findings have made it possible to study the electrode kinetics of these compounds in quantitative way.

In this study the kinetic parameters for the first two reduction steps of some porphyrins and divalent metal complexes in DMF were determined by use of the radio frequency polarographic method.[5–8] The results were discussed in view of their molecular structures and the diffuse double layer effect on the kinetic parameters.

Experimental

Materials: Protoporphyrin IX dimethylester (PPDM), mesoporphyrin IX dimethylester(MPDM), Cu(II)-PPDM, Ni(II)-PPDM, Co(II)-PPDM, Zn(II)-PPDM and Mn(III)-Cl·H_2O-PPDM were prepared and purified by previously described methods.[4] The supporting electrolyte, tetraethylammonium perchlorate(TEAP), was prepared and purified as described elsewhere.[9] The solvent, DMF, was purified as described previously.[4]

Electrochemical Measurements. Conventional DC polarograms and square wave polarograms were measured with a Yanagimoto polarograph PF-500 and auxiliary potentiometer. The Faradaic rectification current at the DME or the radio frequency polarographic current was measured also with a Yanagimoto polarograph PF-500 equipped with a laboratory-made RF (0.05 to 2 MHz) generator and appropriate low-pass filter circuits, using the square wave amplitude modulation technique developed by Barker.[5] Differential capacity was measured with a Grahame's AC bridge at 1 kHz.[10]

The polarographic cell was described elsewhere.[4] All potential measurements were made with respect to an aqueous saturated calomel electrode (SCE). The capillary characteristics were $m=1.07_8$ mg/s and $t=5.8$ s at $h=70$ cmHg in DMF containing 0.1 M TEAP at -0.5 v *vs.* SCE.

When the RF and SW polarographic currents were measured, the drop time was controlled by an electro-mechanical synchronizer and the RF current pulse or SW voltage pulse was applied to the DME at the last stage of a drop life, usually from $t=2.0$ to 3.0 s. Measurements were carried out, under dried nitrogen atmosphere, usually with nearly saturated solution(approx. 4×10^{-4} M, but for Cu(II)-complex approx. 2×10^{-4} M) of porphyrins or metalloporphyrins in DMF containing 0.5 M TEAP at 25 ± 0.1 °C. Under the conditions total cell resistance varied from 200 to 300Ω depending on drop area.

Results

As described in the previous work,[4] the first two reduction steps of PPDM, MPDM, Cu(II)-PPDM, Ni(II)-PPDM, and Zn(II)-PPDM and the second reduction step of Co(II)-PPDM and Mn(III)Cl-H_2O-PPDM are characterized by simple one-electron transfer reaction. Furthermore, for these steps the specific adsorption seems to have no or little effect on the electrode processes. Accordingly we applied the Faradaic rectification method to determine the kinetic parameters of the electrode charge transfer reactions of these reduction steps.

Determination of Kinetic Parameters. Computation of the kinetic parameters, *i.e.*, the (measured) rate constant of charge transfer at the standard redox potential, k_{sm}, and the (measured) transfer coefficient, α_{m}, was based on analysis of the rectification voltage, $\Delta\bar{E}_\infty$, or $\phi(=4RT\Delta\bar{E}_\infty/nFV_{\mathrm{A}}^2)$ against applied DC potential, E_{DC}, curves,[7,8] where n is the number of electrons involved per reacting molecule or ion, F the Faraday, R the gas constant and T the absolute temperature. The rectification voltage was evaluated by the comparison method, *i.e.*, by comparison of RF

---

[1] C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, Inc., New York (1970).

[2] J. Jordan, M. Gross and R. S. Marano, "Electrochemistry in Non-aqueous Solvents and its Application to Analytical Chemistry, U.S.-Japan CSS, March 1973, Tokyo," Extended Abstract, p. 75.

[3] L. G. Lanese and G. S. Wilson, *J. Electrochem. Soc.*, **119**, 1039 (1972); see also three previous papers of the same author (G.S.W.) and co-workers.

[4] T. Kakutani, S. Totsuka, and M. Senda, This Bulletin, **46**, 3652 (1973).

[5] G. C. Barker, "Transaction of the Symposium on Electrode Processes, Philadelphia, 1959," ed. by E. Yeager, John Wiley & Sons, Inc., New York, (1961), p. 325.

[6] W. A. Brocke and W. Nürnberg, *Z. Instr.*, **75**, 291, 315, 355 (1969).

[7] P. Delahay, M. Senda, and C. H. Weis, *J. Amer. Chem. Soc.*, **83**, 312 (1961).

[8] M. Senda and P. Delahay, *J. Phys. Chem.*, **65**, 1580 (1961).

[9] M. Senda, T. Ikeda, and T. Nishioka, *Nippon Kagaku Zasshi*, **91**, 957 (1970).

[10] D. C. Grahame, *J. Amer. Chem. Soc.*, **68**, 301 (1946); **71**, 2975 (1949).

polarographic current at a given E_{DC} with SW polarographic current at the same E_{DC}, with the same and one electrolysis solution. V_A is the amplitude of RF voltage applied to the electrode interface and was caluclated from the differential double layer capacity which was measured with DMF solution containing only a supporting electrolyte and the amplitude of RF current pulse applied to the electrode interface. ϕ *vs.* E_{DC} curves were obtained at several frequencies, *i.e.*, 0.05, 0.1, 0.25, 0.5 and 1.0 MHz. The diffusion coefficient of PPDM was estimated by Ilković equation to be 3.7×10^{-6} cm^2/s, and this value was employed for all porphyrin compounds studied here. It was also assumed that the neutral molecule, the monoanion radical, and the dianion possesed equal diffusion coefficient.

Figure 1 shows the first two steps of MPDM as observed by DC, SW, and RF polarography, and Figs. 2 and 3 show ϕ–E_{DC} curves of the first and second steps, respectively.

According to the theory,[7] the rectification voltage for a simple charge transfer reaction ($O + ne = R$) may be represented by

$$\phi = \frac{4RT}{nFV_A^2}\Delta\bar{E}_\infty = (2\alpha_m - 1) + \left[(1-2\alpha_m) + \frac{P-1}{P+1}\right]F(\xi) \qquad (1)$$

where

$$F(\xi) = \frac{2\xi^2+\xi}{2\xi^2+2\xi+1}, \qquad (2)$$

$$\xi = \frac{k_{sm}}{\sqrt{2\omega D}}(1+P)P^{-\alpha_m}, \qquad (3)$$

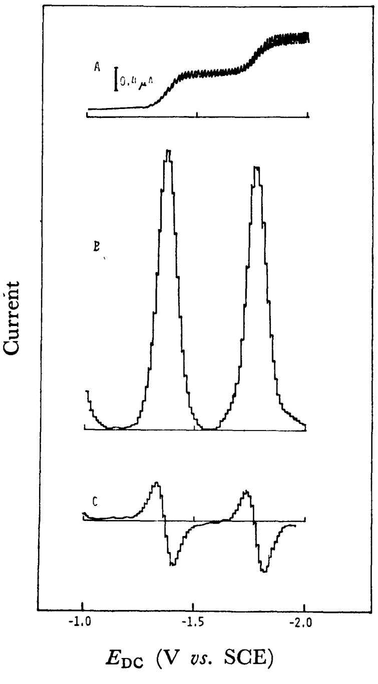

Fig. 1. Polarograms of MPDM in DMF containing 0.5 M TEAP at 25 °C.
Concentration: about 4×10^{-4} M. (A) DC, (B) SW frequency: 200 Hz; SW voltage: 5.4 mV (p-p), (C) ratio frequency: 1.0 MHz; RF voltage: $V_A = 22$ mV (p-p) at −1.4 V.

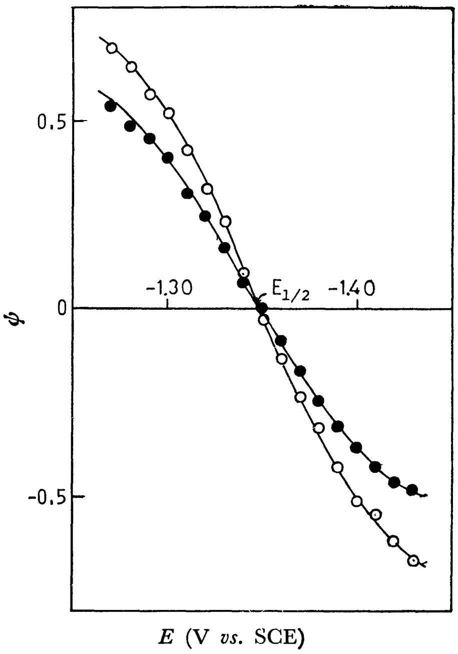

Fig. 2. $\Psi - E_{DC}$ curves of the first step of MPDM in DMF containing 0.5 M TEAP at 25 °C. Radio frequency: ○: 0.1 MHz, ●: 1.0 MHz.

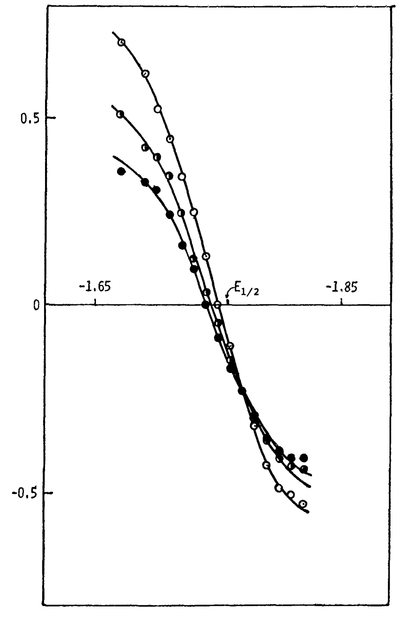

Fig. 3. $\phi - E_{DC}$ curves of the second step of MPDM in DMF containing 0.5 M TEAP at 25 °C. Radio frequency: ⊙: 0.1 MHz; ◑: 0.5 MHz; ●: 1.0 MHz.

$$P = \exp\left[\frac{nF}{RT}(E_{DC} - E_{1/2})\right], \qquad (4)$$

$\omega = 2\pi f$, f is the frequency of the applied RF voltage, and $D = (D_R)^{\alpha_m}(D_O)^{1-\alpha_m}$, D_R and D_O are the diffusion coefficients of R and O, respectively. When the rectification voltages were measured at several frequencies, all ϕ–E_{DC} curves intersect at a single point having the ordinate and abscissa given by

$$\phi = (2\alpha_m - 1), \qquad (5)$$

and

$$\tanh\left[\frac{nF}{2RT}(E_{\mathrm{DC}}-E_{1/2})\right]=(2\alpha_{\mathrm{m}}-1)\,. \qquad (6)$$

respectively. Thus we can calculate the parameter α_{m} in two ways from the coordinates of the intersection point. As predicted from the theory, the experimental curves in Fig. 2 and Fig. 3 exhibit single intersection point in each case. From their coordinates one calculates $\alpha_{\mathrm{m}}=0.5$(abscissa) and $\alpha_{\mathrm{m}}=0.5$(ordinate) for the first step, and $\alpha_{\mathrm{m}}=0.38$(abscissa) and $\alpha_{\mathrm{m}}=0.37$(ordinate) for the second step. Two values of α_{m} calculated from the coordinates agreed to within ± 0.02 for all compounds studied here.

After α was determined in this way, k_{sm} was calculated by either one of the following two methods: 1) when α_{m} is between 0.4, and 0.6, k_{sm} was estimated from the $\phi_{0.1}/\phi_{1.0}$ ratios at several E_{DC}'s, where $\phi_{0.1}$ and $\phi_{1.0}$ are the ϕ values measured at 0.1 and 1.0 MHz, respectively, or 2) when α is larger than 0.6 or smaller than 0.4, k_{sm} was calculated from the values of E_{DC} at $\phi=0$ for each frequency. Such calculations will give several values of k_{sm} for each charge transfer step and these values are expected to be constant if such a simple theory is applicable to the analysis of the present results. Thus we obtained, for example, for the first step of MPDM, $k_{\mathrm{sm}}=3.8$(calculated from $\phi_{0.1}/\phi_{1.0}$ at $p=4$), 3.9 ($p=2$), 3.6($p=1/2$), or 3.7 cm/s ($P=1/4$), and for the second step, $k_{\mathrm{sm}}=1.14$(calculated from E_{DC} at $\phi=0$ ofr 0.1 MHz), 1.45 (0.5 MHz) or 1.44 cm/s (1 MHz). Namely, the values of k_{sm} were reasonably constant for each step (within $\pm 10\%$). The variance of k_{sm}'s for other compounds studied here was also of the same order of magnitude as that of MPDM. The polarographic results and the kinetic parameters of porphyrins and metalloporphyrins examined in this study are summarized in Table 1.

Discussion

As described previously,[4] the first and second steps of Ni(II)-PPDM, Cu(II)-PPDM and Zn(II)-PPDM as well as PPDM and MPDM are believed to be successive additions of one electron to the porphyrin ring of the complexes. The second step of Mn(III)Cl-H_2O-PPDM is supposed also to be an addition of one electron to the porphyrin ring of Mn(II)-complex. The third wave of Mn(III)-complex is not sufficiently reproducible to give reliable kinetic data. The first step of Co(II)-complex, being assigned[4] to one-electron addition to metal-centered orbital, was complicated by specific adsorption, so that significant kinetic data were not observed.

The kinetic data are characterized as follows. For all compounds studied, the measured rate constants of the first reduction step ($R+e=R^{-}$), $k_{\mathrm{sm}}(1)$, are larger than that of the second reduction step($R^{-}+e=R^{2-}$), $k_{\mathrm{sm}}(2)$. The measured transfer coefficients of the first step, $\alpha_{\mathrm{m}}(1)$, are close to 0.5, and those of the second step, $\alpha_{\mathrm{m}}(2)$, are between 0.3 and 0.4.

For the series of compounds, a decreasing tendency of k_{sm}'s with negative shift of half-wave potentials was found, with a few exceptions. The kinetic parameters given in Table 1 are apparent values uncorrected for double layer effects, but calculation showed that this tendency was significant after the double layer correction(see Table 2). As stated in previous paper,[4] the negative shift of the reduction potentials in the series may be correlated with the order of increasing negative charge in the porphyrin ring,[11] that is, with an increase in the non-uniformity of charge distribution in the depolarizer molecule. Similar correlation of the rate constants with molecular structures was first found for a series of nitro-compounds by Peover and Powell,[12] who attributed this phenomenon to the non-uniform distribution of charge in the anion radicals derived from the nitro-compounds. Similar experimental results for substituted nitrobenzenes were confirmed also by the present authors.[13] Therefore, it is likely that the change of rate constants for the series of porphyrin compounds would again be interpreted in terms of Marcus-Hush's theory, *i.e.*, by the difference in the electrostatic solvent reorganization energy, as proposed by Peover and Powell. It is noted, however, that the decreasing of the rate constants with the negative shift of half-wave potentials is less pronounced in the case of the porphyrin compounds than the nitro-compounds. This would be due to the difference in electrostatic solvation energy, which arises from the difference in molecular size between the porphyrin compounds and

TABLE 1. POLAROGRAPHIC RESULTS AND KINETIC PARAMETERS OF PORPHYRINS AND METALLOPORPHYRINS IN DMF CONTAINING 0.5 M TEAP AT 25 °C

Compound	$-E_{1/2}$ (1) (V *vs.* SCE)	k_{sm} (1) (cm/s)	α_{m} (1)	$-E_{1/2}$ (2) (V *vs.* SCE)	k_{sm} (2) (cm/s)	α_{m} (2)
PPDM	1.25	5.6	0.50	1.61	1.7	0.30
MPDM	1.35	3.8	0.50	1.75	1.34	0.38
Ni(III)-PPDM	1.28	5.1	0.55	1.84	0.76	0.32
Cu(II)-PPDM	1.33	4.1	0.50	1.76	0.85	0.30
Zn(II)-PPDM	1.47	3.8	0.43	1.80	0.68	0.28
Co(II)-PPDM	0.96	—	—	2.00	0.64	0.4
Mn(III)Cl·H_2O-PPDM	1.46[a)]	3.4	0.48	1.93[b)]	—	—

a) The second reduction step of Mn(III)-complex. b) The third reduction step of Mn(III)-complex.

---

11) M. Zerner and M. Gouterman, *Theoret. Chim. Acta*, **4**, 44 (1966).

12) M. E. Peover and J. S. Powell, *J. Electroanal. Chem.*. **20**, 427 (1969).

13) T. Kakutani, M. Senda, and H. Kinoshita, "International Congress on Analytical Chemistry, Kyoto, 1972", Abstract, p. 301.

TABLE 2. COMPARISON OF THE MEASURED RATE CONSTANTS AND THE FRUMKIN CORRECTION FACTORS FOR DOUBLE LAYER EFFECTS

Compound	k_{sm} (1)/k_{sm} (2)	$-\phi_0$ (1) mV	$-\phi_0$ (2) mV	$f[\phi_0 (1)]$	$f[\phi_0 (2)]$	$f[\phi_0' (1)]$	$f[\phi_0' (2)]$
PPDM	3.29	95	106	6.36	214	2.64	15.0
Ni(II)-PPDM	6.71	96	110	7.85	299	2.94	16.8
Cu(II)-PPDM	4.82	98	109	6.75	250	2.69	15.8
MPDM	2.83	98	109	6.75	350	2.69	18.7
Zn(II)-PPDM	5.59	101	110	5.42	239	2.34	15.3

the nitro-compound.

Results in Table 1 show that the measured rate constants of the negative ion reductions are about an order of magnitude smaller than those of the neutral molecule reductions. The measured rate constant, k_{sm}, is related to the true rate constant, k_s, by[14]

$$k_s = k_{sm} \exp\left[-(\alpha_m n - z)\frac{F}{RT}\phi\right],$$

where ϕ is the potential at the pre-electrode site relative to the solution and z is the charge on the oxidized from. Table 2 shows the potential values of the outer Helmholtz plane at the half-wave optentials of the first and second steps, $\phi_0(1)$ nad $\phi_0(2)$, being calculated from Gouy-Chapman theory on the assumption that no specific adsorption of the supporting electrolyte ions occurs. Also shown are some calculated values of Frumkin correction factor, $f[\phi]=\exp[-(\alpha_m n-z)F\phi/RT]$; $f[\phi_0(1)]$ and $f[\phi_0(2)]$ are calculated on the assumption that the pre-electrode site is the outer Helmholtz plane, whereas $f[\phi_0'(1)]$ and $f[\phi_0'(2)]$ are calculated on the assumption that it is located 2 Å out of the outer Helmholtz plane, where the ϕ_0' potentials are about 50 per cent of ϕ_0. It will be reasonable to suppose that the pre-electrode sites are much the same for the anion reduction at the neutral molecule reduction. Accordingly, if we admit the prediction[15] of about the same true rate constants for anion reduction as the neutral molecule reduction, we may conclude that the pre-electrode site is likely located about 2 Å or further out of the outer Helmholtz plane. Similar results have also been obtained for aromatic compounds by Peover.[15] However, the measured transfer coefficients of the anion reductions are significantly different from those of the neutral molecule reductions, suggesting that the charge transfer mechanisms are very different for these two reductions. It is noted that the presence of homogeneous chemical reaction following the charge transfer predicts an increase of the measured transfer coefficient.[8] Stronger repulsive effect (Levich correction)[8] for the form also predicts an increase in the measured transfer coefficient. These arguments lead to another supposition that the true rate constants are not necessarily the same for the anion reduction as the neutral molecule reduction. Theories of Marcus[16] and Hush[17] seem to predict that the electrostatic solvent reoganization energy may depend upon the transfer coefficient. As to the location of pre-electrode site, closer approach to the electrode surface may be understandable by imagining the reacting depolarizers at the size with their porphyrin ring planes parallel to the electrode surface. Conclusive interpretation can not be given at present. Further study is in progress.

This work was partly supported by a grant from the Ministry of Education, to which the authors' thanks are due.

---

[14] R. Delahay, "Advances in Electrochemistry and Electrochemical Engineering," Vol. 1, ed. by P. Delahay, Interscience Publishers, New York (1961), p. 233.

[15] M. E. Peover, "Reactions of Molecules at Electrode," ed. by N. S. Hush, John Wiley & Sons, Inc., London (1970), p. 259.

[16] R. A. Marcus, *J. Chem. Phys.*, **43**, 679 (1965).

[17] N. S. Hush, *Trans. Faraday Soc.*, **57**, 557 (1961).