Inorganica Chimica Acta, 19 (1976) 129–132

Reduction Potentials of Some Metal Phthalocyanines

D. W. CLACK,* N. S. HUSH** and I. S. WOOLSEY
Department of Inorganic Chemistry, University of Bristol, Bristol, U.K.
Received December 18, 1975

The reduction potentials of a number of metal phthalocyanine complexes have been measured at a dropping mercury electrode in dimethylformamide. For the divalent transition metal phthalocyanines manganese to copper inclusive, and for free base phthalocyanine, all of which were too insoluble to be examined by conventional polarographic methods, the reduction potentials have been measured by generating their soluble mono-negative ions by controlled potential electrolysis, and measuring the subsequent reductions and oxidation back to the neutral complex. The results of the investigation are discussed in the light of previous spectroscopic work with a view to correlating the electrode processes with either ligand or metal reductions.

Introduction

In view of their natural importance in photosynthesis and as oxygen carriers, and their use as pigments and in catalytic oxidation, metal porphyrin and phthalocyanine complexes, together with related 'model' macrocyclic systems, continue to be a field of current interest. Their redox behaviour is still not fully understood. Polarographic studies for a number of metal porphyrins have shown that it is possible to form anionic species where up to four electrons may be added to the porphyrin molecule.[1,2] In general reduction occurs by electron addition to a vacant orbital of the ring system and the disproportionation energies for a given ion charge have been found to be almost constant. The relative magnitude of these energies have been explained in terms of successive electron addition to the e_g–π^* ligand orbital.[3] However, when the central metal ion is transitional, partially filled or vacant *d* orbitals are available for electron uptake and there is therefore the possibility that reduction of the metal may occur. Indeed, it is now well established that the first reduction step for the Co(II) phthalocyanine complex involves addition to an orbital which is essentially metal in character.[2,4–7] Reduction potential data for some tetrasulphonated phthalocyanines in DMSO have been reported, but although these complexes have the advantage of being considerably more soluble in aprotic solvents than the unsulphonated compounds, only two or three reduction steps could be observed due to the presence of Na^+ counter ions.[5] On the other hand, higher reduction products of metal phthalocyanines have been isolated as crystalline solids by chemical reduction using sodium or radical anions.[8,9] Assignments of the electronic structures of these ions were made on the basis of magnetic susceptibility measurements. In addition both electron spin resonance[10,11] and electronic spectra[4] have been used in an attempt to rationalise the behaviour of metal phthalocyanines towards reduction. Polarographic data for the unsubstituted metal phthalocyanines have not previously been reported presumably because of the very low solubility of the majority of these compounds in solvents such as dimethylformamide or dimethylsulphoxide. In this paper we present such results with a view to assigning the electronic structures of phthalocyanine anions.

Experimental

Polarographic measurements on the phthalocyanines of Mg, Zn, AlCl and $(Pr_4N)_2$(Pr = *n*-propyl), which were sufficiently soluble to be studied by conventional methods, were made using the same apparatus employed for the measurements on the metal porphyrins.[1] For the complexes which were too insoluble to be studied in this manner, the corresponding mono-anion was generated by controlled potential electrolysis under nitrogen at potentials 0.2 to 0.3 volts more negative than the first reduction potential of the complex. The current–potential curves for these anions were then determined in the same way as for the soluble phthalocyanines with the dropping mercury electrode incorporated into the electrolytic cell (Figure 1). In order to check the validity of this method the current–potential curves of the soluble metal phthalocyanines were also measured in this way. Identical polarograms were obtained for the neutral and mono-anions of these complexes with

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Present address: * Dept. of Inorg. Chem., University College, Cardiff, CF11XL (all correspondence to this address). ** Dept. of Theoretical Chemistry, University of Sydney, New South Wales, Australia.

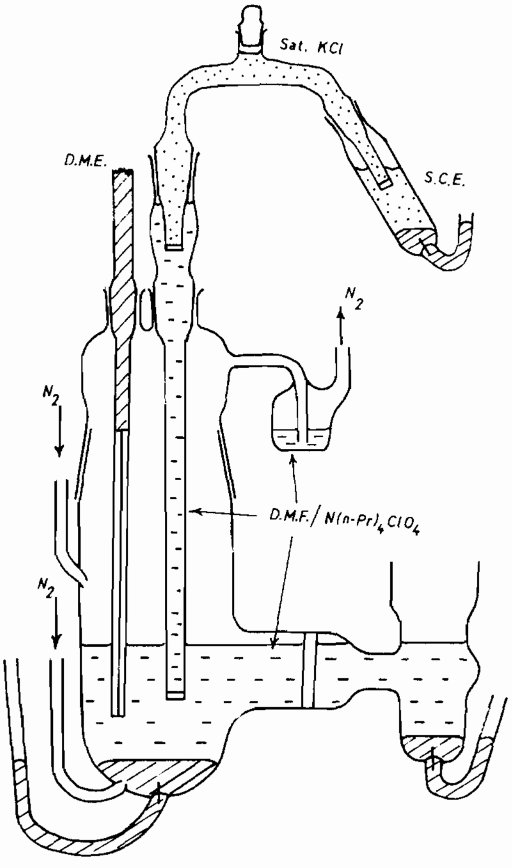

Figure 1. Electrolytic cell for polarographic measurements.

the oxidation step of the anion occurring at the same potential as the first reduction step of the neutral molecule.

Materials

Manganese and zinc phthalocyanines were prepared by published methods.[12,13] The other phthalocyanines were kindly donated by Imperial Chemical Industries, Manchester. All the metal phthalocyanines were purified by controlled vacuum sublimation under nitrogen. Dimethylformamide was used as polarographic solvent with $(Pr_4N)ClO_4$ as supporting electrolyte. Their purification has been described elsewhere.[1] $(Pr_4N)_2$ phthalocyanine was generated in solution by addition of anhydrous Pr_4NOH to a suspension of phthalocyanine free base in dimethylformamide.

Results and Discussion

The half-wave potentials for successive steps are given in the Table I. Four steps were observed for all complexes studied with the exception of cobalt phthalocyanine which showed five reduction stages. Typical current–potential curves of a soluble (Zn) and an insoluble (Cu) metal phthalocyanine are shown in Figure 2. For the soluble metal phthalocyanines the pattern of the half-wave reduction potentials follows very closely that observed previously[1] for metal porphyrins. Each complex exhibited four reduction waves with the slopes of the E *vs.* log(i_l–i)/i plots indicative of diffusion controlled processes. Small departures from

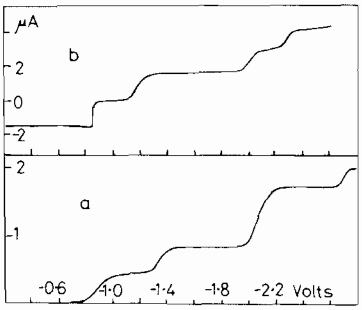

Figure 2. Current–potential curves for a) Zinc phthalocyanine, b) Copper phthalocyanine.

TABLE I. Polarographic Data.

Phthalocyanine	$E_{1/2}(-1)$	$E_{1/2}(-2)$	$E_{1/2}(-3)$	$E_{1/2}(-4)$	$E_{1/2}(-5)$
H_2Pc	–0.66[a]	–1.06	–1.93	–2.23	–
$[N(nPr)_4]_2Pc$	–1.24	–1.55	–1.95	–2.23	–
MgPc	–0.91	–1.39	–2.14	–2.58	–
AlPcCl	–0.53	–0.98	–1.42	–1.98	–
ZnPc	–0.89	–1.33	–2.06	–2.68	–
CuPc	–0.84[a]	–1.18	–2.01	–2.28	–
NiPc	–0.85[a]	–1.23	–2.01	–2.35	–
CoPc	–0.37	–1.40	–1.80	–2.08	–2.46
FePc	–[b]	–1.56	–2.05	–2.25	–
MnPc	–[b]	–1.50	–2.20	–2.75	–

[a] Very sharp wave, which shifts to more negative potentials with increasing concentration of phthalocyanine. $E_{1/2}(-1)$ for concentration $3 \times 10^{-4} M$. [b] See text. All half wave potentials referred to S.C.E.

reversibility were apparent for chloro-aluminium phthalocyanine where the waves were slightly drawn out and the third and fourth stages had rather ill-defined limiting currents. The differences in successive half-wave reduction potentials for these complexes, except for $(Pr_4N)_2$ phthalocyanine, are very similar and the reduction processes are evidently the same for these molecules. The values parallel those of similar metal porphyrins with ${}^1\Delta^2$ $E_{1/2} \sim 0.4$ volts, ${}^2\Delta^3$ $E_{1/2} \sim 0.7$ volts and ${}^3\Delta^4$ $E_{1/2} \sim 0.4$ volts. Although the waves were reversible for $(Pr_4N)_2$ phthalocyanine ${}^2\Delta^3$ $E_{1/2}$ is significantly smaller than for the other soluble metal phthalocyanines, however the pattern is almost identical to that observed for the corresponding porphyrin complex. The first reduction step for this complex occurs at −1.24 volts which is therefore the most negative of all the phthalocyanines studied. This may be explained in terms of a loosely associated $(Pr_4N^+)_2Pc^{2-}$ species (Pc = phthalocyanine) so that reduction is effectively occurring to an already negatively charged ion. On the other hand the reduction potential of −0.53 volts for AlClPc is the most positive for all complexes where electron addition to the ring takes place, and may be attributed to the higher formal positive charge on the metal in this case.

In view of the fact that reduction of the central metal ion is extremely unlikely for these closed shell complexes, and impossible for $(Pt_4N)_2$ Pc, the reduction processes within these systems are assigned to stepwise electron addition to the phthalocyanine ring e_g level. Both theoretical considerations[3] and electronic[4] and magnetic circular dichroism[14] spectra, together with previous results for metal porphyrins, support this conclusion. It is evident from figure 2a that the reduction wave at about −2.0 volts is significantly larger than that expected for a one-electron process. This behaviour was also observed on occasions with other metal phthalocyanines and also with porphyrins and is believed to be due to the presence of impurities which resulted from either hydrolysis of the dimethylformamide or decomposition of the metal phthalocyanines during sublimation.

The complexes of Cu, Ni and H_2 were all studied as solutions of their mono-anions, formed by one-electron reduction, on account of the insolubility of the neutral molecules. Figure 2b typifies the polarograms for these complexes, which show three reversible one-electron reduction waves and a single one-electron oxidation step corresponding to the formation of the neutral complex. The pattern of reduction is very similar to that of magnesium phthalocyanine and on this basis is characteristic of ligand reduction only. The reduction potentials are in good agreement with those obtained for the corresponding tetrasulphonated phthalocyanines[5] where only three of the possible four reductions were observed. The effect of tetrasulphonate substitution is simply to shift all the reductions by about 0.1 volt to more positive potentials. Similarly, replacement of the hydrogen in free base phthalocyanine by a divalent metal such as Zn or Cu results in a raising of the energy of the e_g level by about 0.2 eV. Similar changes were also observed for corresponding porphyrin complexes.[1]

A comparison of these results with spectroscopic data[4] for these ions reveals two interesting points. Chemical reduction of the copper and free base phthalocyanines with sodium in tetrahydrofuran results in the gradual replacement of the central metal ion or protons by sodium ions. Thus only the mono- and di-negative ions of copper phthalocyanine and none of those of free base phthalocyanine have been characterised. However, the polarographic results clearly show that it is possible to form all four anions of both these complexes. Moreover, electron spin resonance and electronic spectra of electrochemically generated mono- and di-anions of tetrasulphonated copper phthalocyanine have also shown that both reductions occur by addition to the phthalocyanine ring system.[5] Thus, the di-ion shows an e.s.r. spectrum consistent with a Cu(II)–d^9 square planar geometry, the two extra electrons being paired in the e_g orbital. However, the single narrow resonance line observed for chemical reduction of the unsubstituted complex at the di-ion stage has been interpreted in terms of the electronic configuration $b_{1g}{}^2$(metal) $b_{1u}{}^1$(ring).[10] It was suggested that this arrangement occurred because of a lowering of the energy of the b_{1u} orbital in the sulphonated molecule. The present polarographic results show that this is not the case. It is possible that the narrow resonance at $g = 2.002$ is due to a paramagnetic reduced species of disodium phthalocyanine which is known[4] to be a product of the chemical reduction of copper phthalocyanine with sodium.

It can be seen from figure 2b that oxidation of the mono-anion of copper phthalocyanine corresponds to an irreversible process and this feature was also apparent for other insoluble metal phthalocyanines. The wave is extremely steep with $E_{3/4}-E_{1/4} \sim$ 20mvolts compared with 60mvolts for a reversible wave. In addition this potential shifts to more negative values with increasing concentration of the anion, with a displacement of approximately 0.04 volts occuring over the concentration range 1×10^{-4} to $5 \times 10^{-3}\,M$. Both these effects may be attributed to the insolubility of the neutral complex produced on oxidation.

Cobalt phthalocyanine was unique in showing five separate reduction waves. The complex was studied as its mono-anion generated be electrolysis at −1.0 volts. This was much more stable to oxidation than any of the other mono-anions, which is reflected in the value of the first reduction potential of −0.37 volts. Such a positive reduction potential is consistent with reduction occurring at the central metal ion forming a cobalt-(I) species, and is in agreement with spectroscopic results.[4,16] The nature of the subsequent reduction stages is however less clear. E.s.r. spectra of the dinegative ion[11] have yielded narrow resonances close to 2.0023 which suggests the electronic configuration $a_{1g}{}^2$(metal)$e_{1g}{}^1$(ring) and this conclusion is also supported by the electronic spectrum of the di-ion in tetrahydrofuran solution.[4] In contrast electronic spectra of the first and second reduction stages of the closely related cobalt corrin show that metal reduction occurs initially but that the metal reverts to the +2 oxidation state when the di-anion is formed.[15] Electrolytic reduction of cobalt phthalocyanine tetrasulphonate has produced the corresponding cobalt(I) species as first reduction product, but further reduction was thought to involve addition to the metal giving rise to a cobalt(0) species.[5] This assignment has however been questioned.[10, 17] Unfortunately the present polarographic results do not permit an unambiguous assignment for the reduction processes of cobalt phthalocyanine. However, one inference can certainly be drawn from the available data. The successive disproportionation energies of the reaction 2(phthalocyanine)$^{n-}$ $\rightarrow$ (phthalocyanine)$^{(n-1)-}$ + (phthalocyanine)$^{(n+1)-}$ where n = 1,2 or 3 are given by the corresponding potential intervals $-{}^{n}\Delta^{n+1}\ E_{1/2}$. Averaging over the data for H_2Pc, CuPc, NiPc, AlClPc, ZnPc, MgPc where electron addition is confined to the ring e_g orbital yields

$$-{}^{1}\Delta^{2}\ E_{1/2} = 0.41 \pm 0.05$$
$$-{}^{2}\Delta^{3}\ E_{1/2} = 0.75 \pm 0.15$$
$$-{}^{3}\Delta^{4}\ E_{1/2} = 0.42 \pm 0.14$$

It therefore the subsequent reduction stages for cobalt(I) phthalocyanine correspond to stepwise filling of the ring e_g level one might expect similar values for these disproportionation energies. Table I shows that although ${}^{1}\Delta^{2}\ E_{1/2}$ for [Co(I)Pc]$^-$ is close to the average ${}^{1}\Delta^{2}\ E_{1/2}$ value, ${}^{2}\Delta^{3}\ E_{1/2}$ is considerably smaller than anticipated for such a process. In view of this it seems clear that at some stage the central cobalt reverts to its original oxidation state of +2, a situation similar to that in the cobalt corrin.

Both manganese and iron phthalocyanines were studied as their soluble mono-anions and, although three further reduction waves were always observed for each complex, in neither case was a reproducible oxidation step back to the neutral molecule apparent. Oxidation waves for [MnPc]$^-$ occurred at –1.08 and –0.78 volts on different occasions and sometimes both waves were present at the same time. The same behaviour was also found for [FePc]$^-$ with oxidation steps occurring at –1.05 volts and –0.73 volts.

If the value of –1.08 volts is taken as the first reduction potential for manganese phthalocyanine then the pattern of potential intervals follows that where addition to the ring occurs for all stages of reduction, and the results are therefore in harmony with spectroscopic data for these ions. On the other hand neither of the values –1.05 or 0.73 volts for iron phthalocyanine lead to the expected sequence for ring reduction and it may reasonably be concluded that metal reduction occurs at some stage. It would be unwise to speculate further on the nature of subsequent reduction products for these two molecules without knowing the first reduction potential.

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