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ELECTROCATALYSIS OF CATHODIC OXYGEN REDUCTION BY METAL PHTHALOCYANINES *

PART II. COBALT PHTHALOCYANINE AS ELECTROCATALYST: A MECHANISM OF OXYGEN REDUCTION

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ABSTRACT

On the basis of a detailed description of the kinetics of oxygen reduction in alkaline solution on cobalt phthalocyanine film electrodes, a mechanism of the electrocatalysis of this reaction is proposed. The main features of this mechanism are those of a redox catalysis scheme, where the central metal atom of the electrocatalyst releases an electron to the adsorbed reactant (O_2 and, at high overpotential, HO_2^-), which is subsequently further reduced to products (HO_2^- and OH^- respectively). The influence of the redox state of the electrocatalyst is explained in terms of a tentative description of the difference of the interaction of the electrocatalytic site with the respective depolarizers O_2 and HO_2^-.

The proposed model gives a satisfactory explanation of the observed kinetics of the reactions involved, as well as the observed correlations between electrocatalytic activity and properties such as phthalocyanine redox potentials.

INTRODUCTION

The nature of the interaction between metal porphyrins and oxygen has been investigated widely in recent years, since their applicability as oxygen reduction electrocatalysts was recognized [1]. In Part I [2] we have shown that cobaltphthalocyanine (CoPc) in alkaline solution catalyses only the reduction of oxygen to hydrogen peroxide, i.e. in H_2/O_2 fuel cells with CoPc oxygen electrodes only some 50% of the theoretically available power can be utilized. Apart from the disastrous consequences of the build-up of H_2O_2 in the cell, this will be a good enough reason to abandon the idea of CoPc as a oxygen reduction electrocatalyst.

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* Part of thesis, Metal phthalocyanines as electrocatalysts for cathodic oxygen reduction, by F. van den Brink, Eindhoven, 1981.
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We will show in a forthcoming part of this series that on iron phthalocyanine (FePc) electrodes, oxygen is completely reduced to water, in a direct reaction, so that the application of FePc as oxygen electrodes may be a feasible proposition. Then, however, the question remains as to what constitutes the vast difference between the, chemically very similar, compounds FePc and CoPc. To answer this question, it is necessary to have a reliable description of the kinetics and mechanism of oxygen reduction on both electrocatalysts. In this paper we will explain our kinetic results obtained for CoPc electrodes [2] in terms of a detailed mechanism, which gives an insight into the interaction between oxygen and the electrocatalyst molecule.

SUMMARY OF KINETIC RESULTS

In Part I [2] we have given an accurate description of the kinetics of oxygen reduction on cobalt phthalocyanine film electrodes in alkaline solution. This description, based mainly upon experiments with rotating ring disc electrodes and surface characterization by in situ methods such as cyclic voltammetry and ac impedance spectrometry, reveals the following fundamentals:

1. On cobalt phthalocyanine (CoPc), oxygen is at low cathodic overpotential ($E_{\text{RHE}} > 0.3 \text{ V}$), exclusively reduced to hydrogen peroxide. Only at higher overpotential does some further reduction of $\text{H}_2\text{O}_2$ to $\text{H}_2\text{O}$ occur, while the direct reduction of $\text{O}_2$ to $\text{H}_2\text{O}$ does not occur at all. Furthermore, no chemical decomposition of $\text{H}_2\text{O}_2$ is detected, so the scheme of $\text{O}_2$ reduction reduces to Fig. 1.

2. $\frac{d\eta}{d \log k_2} = -40 \text{ mV}$ in the vicinity of $E_{\text{RHE}} = 800 \text{ mV}$; below $800 \text{ mV}$ the slope decreases gradually, to reach $-\infty$ at $450 \text{ mV}$. The slope $\frac{d\eta}{d \log k_3}$ is ca. $-180 \text{ mV}$. The order in oxygen of reaction (2) is one.

3. In the reduction, no $\text{O}–\text{O}$ bonds are broken.

4. Surface processes on the CoPc film are detected at $480 \text{ mV}$ vs. RHE, both in the absence and presence of oxygen, and at $800 \text{ mV}$ vs. RHE only when oxygen is present. All surface phthalocyanine molecules participate in these processes.

INTERACTION OF OXYGEN WITH CoPc

The above observations can be partly explained by the assumption that electrocatalysis of oxygen reduction takes place by end-on adsorption of oxygen on the central Co-atom of CoPc, leading to activation of the oxygen molecule. That the central metal atom should be the electrocatalytic site follows, for example, from the correlation between the redox potential of the metal and the electrocatalytic activity.
in a series of metal porphyrins and phthalocyanines [3]. This will be treated in more
detail below.

The assumption of end-on adsorption is corroborated by the observation that the
oxygen–oxygen bond is not ruptured in the reduction \( \text{O}_2 \rightarrow \text{H}_2\text{O}_2 \), by MO consider-
ations [4,5] and by the analogy with oxygen binding by natural porphyrins and their
synthetic model compounds (e.g. picket fence porphines [6]), which have been shown
to bind oxygen end-on.

The beginning of an explanation for the observed phenomena was originally given
by Beck [7,8], who proposed a mechanism which he called “redox catalysis”. In this
mechanism the redox reaction of the central metal atom plays a crucial role. On the
basis of similar ideas, we will first propose a detailed mechanism and its accompany-
ing kinetic equation for the reduction of oxygen to hydrogen peroxide on CoPc.
Further, we will attempt to give a mechanistic description for the reduction of
hydrogen peroxide to water.

**Reduction of oxygen to hydrogen peroxide**

The essential step of the “redox catalysis” mechanism is the adsorption of oxygen
at the electrocatalytic site, which is assumed to occur preferentially on the reduced
metal atom according to

\[
\text{MPc} + e^- \rightarrow \text{MPc}^- \quad (1)
\]

followed by an adsorption step

\[
\text{MPc}^- + \text{O}_2 \rightarrow \text{MPc}-\text{O}_2^- \quad (2)
\]

where the charge transfer in the activated complex \( \text{MPc}^-\text{O}_2^- \) may be only partial.

The activated oxygen, which has at least some superoxo-character, is reduced
further in the next step to hydrogen peroxide,

\[
\text{MPc}^-\text{O}_2^- + \text{H}_2\text{O} + e^- \rightarrow \text{MPc} + \text{HO}_2^- + \text{OH}^- \quad (3)
\]

and the oxidized electrocatalyst is recycled.

Mechanisms like this are, in the electrochemical literature, usually treated with
the concept of a *rate-determining step* (rds, which is much slower than the other
steps, so that these are in virtual equilibrium). However, such a concept imposes
rather extreme conditions on the relative rates of the steps involved. For example,
for the sequence (1)–(3) it can be shown that the ratios of the rate constant of the
rds to those of the other steps should be less than \( 10^{-3} \) for the “rds” to be truly rate
determining. Therefore, it is better to derive the rate equation using the *steady-state*
method.

For the sequence (1)–(3) this gives

\[
-i_2/2F = k_1 \left[ (\text{MPc}) \exp(-\alpha_1 f \eta_1) - (\text{MPc}^-) \exp(1 - \alpha_1) f \eta_1 \right]

= k_2 [\text{O}_2^-] (\text{MPc}^-) - k_2 (\text{MPc}^-\text{O}_2^-)

= k_3 (\text{MPc}^-\text{O}_2^-) \exp - \alpha_3 f \eta_3 \quad (4)
\]
Here, $i_2$ is the current due to the reaction $O_2 \rightarrow H_2O_2$, $k_i$ is the rate constant for the $i^{th}$ reaction, $\alpha_i$ its transfer coefficient and $\eta_i$ is defined here as $(E - E^o_i)$. The surface concentrations, denoted by (~), can be eliminated from eqn. (4) and expressed as fractions of their sum $s$, the total number of sites. The overall rate can then be written

$$-i_1/2F = k_2s [O_2]/\left((1 + \exp f\eta_1) (1 + (k_{-2}/k_{2}^o) \exp \alpha_3 f\eta_3) \right) + (k_2 [O_2]/k_{2}^o) \exp \alpha_1 f\eta_1 + (k_2 [O_2]/k_{3}^o) \exp \alpha_3 f\eta_3$$

$$\text{(5)}$$

When $k_1 \ll k_2 [O_2]$, $k_3$, and for intermediate coverage eqn. (5) reduces to

$$-i_2/2F = k_1^o s \exp -\alpha_1 f\eta_1$$

predicting a Tafel slope of $-60/\alpha_1 = -120$ mV for $\alpha_1 = 0.5$, and zeroth order in [O$_2$]—so eqn. (6) clearly does not explain our results.

When $k_2 [O_2]$, $k_{-2} \ll k_1^o$, $k_3^o$, the rate equation can be written as

$$-i_2/2F = k_3^o s/(1 + \exp f\eta_1)$$

$$\text{(7)}$$

In this case the correct order in oxygen, viz. one, is predicted, but the Tafel slope will be $-60$ mV for $\eta_1 \gg 0$ and $\infty$ for $\eta_1 \ll 0$—it will never be $-40$ mV, irrespective of the value of $\alpha_1$, so step (2) is not the rds over the entire potential range. However, for high overpotential (low $E$), the infinite Tafel slope indicates that there step (2) can be the rds.

When $k_3 \ll k_1^o$, $k_2 [O_2]$, eqn. (5) becomes

$$-i_2/2F = k_2 [O_2]/k_{-2}^o s \exp -\alpha_3 f\eta_3/(1 + \exp f\eta_1 + k_{-2}^o \exp f\eta_3)$$

$$\text{(8)}$$

which again predicts first-order dependence on oxygen concentration, and Tafel slopes of $-60/(1 + \alpha_3) = -40$ mV for $\eta_1 \gg 0$ and $-60/\alpha_3 = -120$ mV for $\eta_1 \ll 0$ **. Therefore, we may suppose that for low overpotential, where the observed Tafel slope of $-40$ mV is predicted by eqn. (8), step (3) is the rds.

Of course, other schemes than those similar to (1)-(3) could be considered, which involve no surface reduction step (1). Several of those would give the same potential dependence of the Tafel slope. On the other hand, only a redox catalysis mechanism will be able to explain other experimental observations, such as the correlation of electrocatalytic activity and redox potential [3] (see below).

However, there are two problems with rate eqn. (5). The first is that, although it explains the observed behaviour at low and high overpotential, no values for the rate parameters $k_{-2}/k_1^o$, $k_2/k_3^o$ and $k_{-2}/k_3^o$ could be found which explain the intermediate potential range. However, as will be shown later, the behaviour in this potential range can be attributed to the simultaneous occurrence of a second sequence of reactions in parallel to reactions (1)-(3).

* Note: the roman $k$'s used here should not be confused with the overall rate constants $k_1^o$ and $k_3^o$ for the reductions $O_2 \rightarrow H_2O_2$ and $H_2O_2 \rightarrow H_2O$ [2].

** Throughout this section we will assume that $\alpha = 0.5$. 
The second problem is much more serious, since it is linked with the values chosen for $E_1^\circ$ and $E_3^\circ$. The surface process occurring at ca. 800 mV only in the presence of oxygen must obviously be connected with reaction (3)—so $E_3^\circ \approx 800$ mV. However, the other surface process, at 480 mV, is surely not reaction (1). First, eqn. (5) predicts that the Tafel slope be between $-40$ and $-60$ mV, as long as $E > 480$ mV; we have observed, on the other hand, that the Tafel slope is already near infinity for potentials below ca. 700 mV. Therefore, $E_1^\circ$ should be near 800 mV. Hence, the surface process found at 800 mV is due to both reactions (1) and (3).

Further, it is a well-known fact that cobalt porfines in general and cobalt phthalocyanine in particular form $O_2$-adducts [9], especially in alkaline aqueous solutions, the most probable structure of these adducts being Co(III)$-O_2^-$. Thus, we conclude from our kinetic measurements that the formal couple Mpc/Mpc$^-$, used hitherto, is in fact the couple (Co(III)Pc)$^+$/Co(II)Pc and that its standard potential lies between, say, 750 and 850 mV. This value should be contrasted with the standard potential of the hexa-aquo Co(III)/Co(II) couple, 2.66 V vs. RHE—so it appears that the ligand environment of Co in a CoPc solid film in alkaline solution shifts the redox potential by some 1.85 V in the cathodic direction. This shift has been postulated on the grounds of our kinetic evidence, but we have not been able to prove, from independent sources, that the reduction indeed occurs at the indicated potential. Unfortunately, neither is such a proof provided in the available literature. There are, however, a number of indications that the reduction of (Co(III)Pc)$^+$ may indeed occur at ca. 0.8 V vs. RHE. First, in any solvent the Co-atom is surrounded by four nitrogen ligands in a square planar configuration, with the Co more or less in the plane of the nitrogens. This case can only be studied in non-aqueous solutions (ref. 10 and refs. therein). For the Co(III)Pc/Co(II)Pc couple, the average value of the literature data for the standard potential is ca. 0.60 V vs. an aqueous saturated calomel electrode, i.e. ca. 1.67 V vs. RHE at pH = 14.

For similar compounds, such as tetraphenyl- (1.37 V), etio- (1.35 V) and deuteroporphyrin (1.33 V), somewhat lower values are found [11]. Therefore, $N_4$-chelation decreases the standard potential by at least 1 V. Further, the 4-coordination by Pc leaves the possibility of 5- or 6-coordination by axial ligands. These axial ligands are known to have a profound influence on both the redox properties [12,13] and the ligand exchange rates [9,14] of the complex. In this context especially the basicity and the $\pi$-acceptor strength of the axial ligands seem to be important [9,13]. By changing the ligand, differences in the M(III)/M(II) redox potentials of up to 1 V can be brought about.

In the case of solid films, in aqueous alkaline solution, there are a number of candidates for the role of axial ligands. First, there are the meso nitrogen atoms of underlying phthalocyanine molecules (which are absent in porphyrins). These can act as ligands if the film has a rigid layered, roofing-tile structure, which to some extent limits their capability to act as axial ligands. Further, especially near the surface there is an abundance of $H_2O$, $OH^-$ and $O_2$, all of which are known to be able to interact with metal phthalocyanines [9]. Therefore, there is a certain similarity between the surface region of solid Pc films and solubilized phthalocyanines. For
the latter, redox potentials ascribed to the M(III)/M(II) transition have been reported. For tetrasulphonated CoPc irreversibly adsorbed on pyrolytic graphite
\( E = 0.8 \text{ V vs. SCE in } 0.05 \text{ M } \text{H}_2\text{SO}_4 \) is given [15], corresponding to 1.1 V vs. RHE at pH = 14, assuming that the standard potential shifts by \(-60 \text{ mV/pH unit. In this case, no pH-dependence was reported, but in the case of an irreversibly adsorbed solubilized cobalt porphyrin [16] a redox process has been detected at } 1.08 \text{ V vs. RHE at pH = 14, showing this pH-dependence. Furthermore, it was shown that, upon addition of imidazole, the redox potential shifts 0.25 V in the cathodic direction. Therefore, the redox processes involved are in fact\)

\[ \text{Co(III)Pc-OH} + \text{H}_2\text{O} + e^- \rightleftharpoons \text{Co(II)Pc-H}_2\text{O} + \text{OH}^- \]

and

\[ (\text{Co(III)Pc-Im})^+ + e^- \rightleftharpoons (\text{Co(II)Pc-Im}) \]

respectively (Im stands for imidazole).

Finally, for non-solubilized phthalocyanines some values of the redox potential in concentrated (85% and 96%) sulphuric acid have been reported, i.e. in the presence of \( \text{H}_2\text{O} \) in a protic medium [7]. Although a direct comparison is hampered by the problem of the definition of pH in this medium, the values reported (0.52–0.56 V vs. aqueous SCE) do not disagree with our findings.

Therefore, the value found in the present communication for the redox potential of the Co(III)Pc/Co(II)Pc couple, which was inferred from our kinetic results, may be regarded as a reasonable one in view of the available literature data.

This leaves, however, the process at 480 mV to be explained. In Part I [2] we concluded that all surface phthalocyanine molecules contribute to this process. Therefore, it must be ascribed to a further reduction of the phthalocyanine molecules to \( \text{CoPc}^- \)—a species which has been detected spectrophotometrically in CoPc films [17]. In this species the extra electron may or may not be localized on the central metal atom, since for similar compounds [11] in non-aqueous solutions values for the standard potential of the Co(II)/Co(I) couple between 0.3 and 0.6 V are found—so the standard potential in the solid state would hardly be shifted, contrary to that of the Co(III)/Co(II) couple. This lack of influence of complexation (by axial ligands), as found for the Co(III)/Co(II) couple, would indicate that the reduction process is that of the ring structure, rather than of the central Co-atom. However, formally we will write \( (\text{Co(I)}\text{Pc})^- \). The reduced form \( \text{CoPc}^- \) is known to form \( \text{O}_2 \)-adducts which are comparable in stability to those of CoPc [9].

Now, however, we have, parallel to the sequence (1)–(3), an analogous mechanism involving adsorption of \( \text{O}_2 \) on \( \text{CoPc}^- \), which plays a role for \( E < 480 \text{ mV}; \)

\[ \text{CoPc} + e^- \overset{4}{\rightleftharpoons} \text{CoPc}^- \]

\[ \text{CoPc}^- + \text{O}_2 \overset{5}{\rightleftharpoons} \text{CoPc-} \text{O}_2^- \]

\[ \text{CoPcO}_2^- + \text{H}_2\text{O} + e^- \overset{6}{\rightleftharpoons} \text{CoPc} + \text{HO}_2^- + \text{OH}^- \]

(9) (10) (11)
For reaction 4 (eqn. 9) we can estimate the rate from the characteristic frequency found for the surface process at 480 mV, viz. \( k_4 \geq 500 \text{ s}^{-1} \) [2]. Further, for high overpotential reactions 4–6 will be the predominant route since all CoPe molecules will be in the reduced state CoPe\(^-\) for \( E < 480 \text{ mV} \). In that potential range we have found a constant value for \( k_5 \), viz. \( 3.1 \times 10^{-4} \text{ m s}^{-1} \), so there reaction 5 (eqn. 10) is clearly the rds and we can estimate a value for \( k_5 \): \( k_5 = 3.1 \times 10^{-4} \text{ m s}^{-1} \) and, with \( s = 5 \times 10^{-6} \text{ mol m}^{-2} \) [2] we find \( k_5 = 60 \text{ m}^3 \text{ mol}^{-1} \text{s}^{-1} \). Therefore, \( k_5 \ll k_4 \) and we assume reaction 4 to be in equilibrium. Further, the surface process (eqn. 1) is not detected in the frequency range of impedance measurements of \( 10^{-10} \text{ s}^{-1} \) and the Tafel slope near 800 mV is \( -40 \text{ mV} \) and surely not \( -120 \text{ mV} \), which would have been found if reaction 1 (eqn. 1) were rds. Therefore, we conclude that reaction 1 is also in equilibrium. In that case we have for the parallel sequences 1–3 and 4–6 respectively,

\[
\frac{-i_2(\text{II})}{2F} = k_2[O_2](\text{CoPc}) - k_{-2}(\text{CoPc}^- + O_2^-) = k_3^0(\text{CoPc}^+ + O_2^-) \exp -\alpha_3 f \eta_3 \tag{12}
\]

\[
\frac{-i_2(\text{I})}{2F} = k_5[O_2](\text{CoPc}^-) - k_{-5}(\text{CoPc}^- + O_2^-) = k_6^0(\text{CoPc}^- + O_2^-) \exp -\alpha_6 f \eta_6 \tag{13}
\]

while the concentrations of the various CoPe species are related by

\[
\frac{(\text{CoPe}^+)}{(\text{CoPc})} = e^{\eta_1}, \quad \frac{(\text{CoPe}^-)}{(\text{CoPc}^-)} = e^{\eta_6}
\]

\[
(\text{CoPe}^+) + (\text{CoPc}) + (\text{CoPc}^-) + (\text{CoPc}^+ + O_2^-) + (\text{CoPc}^- + O_2^-) = s \tag{14}
\]

From eqns. (12)–(15) the rate equation is derived

\[
i_2 = i_2(\text{II}) + i_2(\text{I}) \tag{16}
\]

\[
-\frac{i_2(\text{II})}{2F} = k_2[O_2]s/\left[1 + e^{\eta_1} + e^{-\eta_6}\left(1 + \frac{k_3[O_2]}{k_{-3} e^{-\alpha_3 f \eta_3}}\right)\right] \times \left[1 + \frac{k_{-2}}{k_{-3} e^{-\alpha_3 f \eta_3}}\right] + \frac{k_2[O_2]}{k_{-3} e^{-\alpha_3 f \eta_3}} \tag{17}
\]

\[
-\frac{i_2(\text{I})}{2F} = k_5[O_2]s/\left[1 + e^{\eta_6}\left(1 + e^{\eta_1} + \frac{k_2[O_2]}{k_{-2} e^{-\alpha_3 f \eta_3}}\right)\right] \times \left[1 + \frac{k_{-5}}{k_{-6} e^{-\alpha_6 f \eta_6}}\right] + \frac{k_4[O_2]}{k_{-6} e^{-\alpha_6 f \eta_6}} \tag{18}
\]

For \( \eta_4 \gg 0 \) (i.e. \( E \gg E_\text{c} = 480 \text{ mV} \) eqn. (17) reduces to eqn. (5) with \( k_1^\circ \gg k_2[O_2], k_3^\circ, \) while \( i_2(\text{I}) \ll i_2(\text{II}) \). For \( \eta_4 \ll 0 \), \( i_2(\text{II}) \to 0 \) and \( i_2(\text{I}) \gg i_2(\text{II}) \).

Unfortunately, eqns. (16)–(18) contain too many unknown parameters to make an attempt to fit them numerically to the available data for \( k_5^\circ \) feasible. However, by trial and error we have succeeded in obtaining a reasonably accurate fit, which is
shown in Fig. 2. We conclude that eqns. (16)–(18) give a best approximation to the observed data under the following conditions:

1. Potential:
\[ E_1^o = 0.80 \text{ V}, \quad E_2^o = 0.82 \text{ V}, \quad E_4^o = 0.48 \text{ V}, \quad 0.6 \text{ V} \leq E_6^o \leq 0.8 \text{ V} \]

2. Rate parameters:
\[ \frac{k_2}{k_3^o} \leq 1, \quad \frac{k_5}{k_6^o} \leq 1 \]
\[ k_{-2}/k_3^o \approx 7, \quad 1 \leq k_{-5}/k_6^o \leq 10 \]

3. Asymptotic values:
\[ k_5 \approx 60 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}, \quad k_2 \approx 0.75 k_5 \]

The values given for \( k_2 \frac{[O_2]}{k_3} \) and \( k_5/k_6^o \) are upper limits, since any value below them gives an equally accurate fit.

To summarize, by combining our data from surface characterization with the kinetic data over the entire potential range investigated (0–0.85 V vs. RHE) we have been able to propose a detailed mechanism. Furthermore, since we have not confined ourselves to the concept of a rate-determining step, we have been able to give a fairly accurate estimate of all pertinent mechanistic parameters involved.

From the values of the standard potentials, we can calculate the equilibrium constants of the adsorption of oxygen and of the superoxide ion, \( O_2^- \), on cobalt.
phthalocyanine. From the sequence

\[
\text{CoPc}^+-\text{O}_2^- \rightleftharpoons \text{CoPc}^+ + \text{O}_2^-, \quad K_{O_2}(\text{II}) = \frac{[\text{CoPc}^+]}{[\text{CoPc}] \left[ \text{O}_2^- \right]} 
\]

\[
\text{O}_2^- + \text{H}_2\text{O} + e^- \rightleftharpoons \text{OH}^- + \text{HO}_2^-, \quad E^\circ = 0.265 \text{ V vs. NHE} 
\]

the standard potential of reaction (3) can be calculated

\[
E_3^\circ = 1.092 + 0.059 pK_{O_2}(\text{II}) \text{ V vs. RHE} \tag{19}
\]

and analogously for that of reaction 6

\[
E_6^\circ = 1.092 + 0.059 pK_{O_2}(\text{I}) \text{ V vs. RHE} \tag{20}
\]

at T = 298 K and pH = 14. From the standard potential of the overall reaction

\[
\text{O}_2 + \text{H}_2\text{O} + 2 e^- \rightleftharpoons \text{HO}_2^- + \text{OH}^-, \quad E^\circ = -0.065 \text{ V vs. NHE} 
\]

the standard potentials \(E_1\) and \(E_4\) can be expressed as functions of the \(K_{O_2}\)'s and the equilibrium constants of reactions 2 and 5

\[
K_{O_2}(\text{II}) = \frac{[\text{CoPc}^+]}{[\text{CoPc}] \left[ \text{O}_2^- \right]} 
\]

\[
K_{O_2}(\text{I}) = \frac{[\text{CoPc}^-]}{[\text{CoPc}] \left[ \text{O}_2^- \right]} 
\]

The results are

\[
E_1^\circ = 0.432 + 0.059 \left[ pK_{O_2}(\text{II}) - pK_{O_2}(\text{II}) \right] \text{ V vs. RHE} \tag{21}
\]

\[
E_4^\circ = 0.432 + 0.059 \left[ pK_{O_2}(\text{I}) - pK_{O_2}(\text{I}) \right] \text{ V vs. RHE} \tag{22}
\]

Application of eqns. (19)–(22) to our case, where

\[
E_1^\circ \approx 0.80 \text{ V} \quad E_3^\circ \approx 0.82 \text{ V} 
\]

\[
E_4^\circ \approx 0.48 \text{ V} \quad E_6^\circ \approx 0.6–0.8 \text{ V} \quad \text{vs. RHE}
\]

\[
K_{O_2}(\text{II}) \approx 2.4 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \quad K_{O_2}(\text{II}) \approx 41 \text{ m}^3 \text{ mol}^{-1}
\]

\[
K_{O_2}(\text{I}) \approx 3.4 \times 10^4 - 14 \text{ m}^3 \text{ mol}^{-1} \quad K_{O_2}(\text{I}) \approx 2.2 \times 10^5 - 89 \text{ m}^3 \text{ mol}^{-1}
\]

The large value of the \(K_{O_2}\)'s compared to that of the \(K_{O_2}\)'s gives us an indication why CoPc electrocatalyses oxygen reduction— the catalyst stabilizes the superoxide ion by the formation of a complex and thus increases its concentration.

The lower values for \(K_{O_2}(\text{I})\) and \(K_{O_2}(\text{I})\) apply when \(E_6^\circ = 0.80 \text{ V}\) is taken. Since we do not expect \(E_6^\circ\) to differ much from \(E_3^\circ\), we will henceforth use \(E_6^\circ = 0.8\), although we cannot be sure about this value. However, we have found only one peak at about 800 mV in the cyclic voltammogram of CoPc films in the presence of oxygen, and this could be associated with both reactions 3 and 6. Now we can calculate some of the rate constants. Assuming that all surface phthalocyanine molecules are active sites, we have \(s = 5 \times 10^{-6} \text{ mol m}^{-2}\), so \(k_5 = 60 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}\) and \(k_2 = 0.75 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}\). Using the \(K_{O_2}\)'s, we find \(k_{-2} = 2 \times 10^6 \text{ s}^{-1}\) and
TABLE 1
Steps involved in the reduction $\text{O}_2 \rightarrow \text{H}_2\text{O}$ on CoPc, and their characteristics inferred from observed kinetics and proposed mechanism

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $\text{Co}^{2+} \text{Pc} + e^- \rightleftharpoons \text{CoPc}$</td>
<td>$E^\theta_1 = 0.80 \text{ V}, k_1^0 \geq 10^3 \text{ s}^{-1}$; $K_{\text{O}<em>2(\text{II})} = 2.4 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$; $k_2 = 45 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k</em>{-2} = 2 \times 10^6 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>2. $\text{CoPc} + \text{O}_2 \rightleftharpoons \text{CoPc}^{+} - \text{O}_2^-$</td>
<td>$E^\theta_2 = 0.82 \text{ V}, k_2^0 = 3 \times 10^5 \text{ s}^{-1}$; $K_{\text{O}<em>2(\text{II})} = 40 \text{ m}^3 \text{ mol}^{-1}$; $E^\theta_4 = 0.48 \text{ V}, k_4^0 \geq 500 \text{ s}^{-1}$; $K</em>{\text{O}<em>2(\text{I})} = 15 \text{ m}^3 \text{ mol}^{-1}$; $k_5 = 60 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k</em>{-5} = 4 \text{ s}^{-1}$; $E^\theta_5 = (0.6-0.8) \text{ V}$, $0.4 \text{ s}^{-1} \leq k_5^0 \leq 4 \text{ s}^{-1}$; $K_{\text{O}_2(\text{E})} = 90 \text{ m}^3 \text{ mol}^{-1}$</td>
</tr>
<tr>
<td>3. $\text{CoPc}^{+} - \text{O}_2^- + \text{H}_2\text{O} + e^- \rightarrow \text{CoPc}^{+} + \text{HO}_2^- + \text{OH}^-$</td>
<td>$k_{-5} = 4 \text{ s}^{-1}$. Since $k_{-2}/k_2^0 = 7$ and $1 \leq k_{-5}/k_5^0 \leq 10$, we have $k_2^0 = 3 \times 10^5 \text{ s}^{-1}$ and $0.4 \text{ s}^{-1} \leq k_5^0 \leq 4 \text{ s}^{-1}$. The rate of reaction 1 is not known, but we know that it must be high compared to $k_2$, $k_1^0$ must be at least $10^3 \text{ s}^{-1}$. Finally, we can estimate $k_5^0 \geq 500 \text{ s}^{-1}$, from the characteristic frequency of the associated surface state capacitance. These results have been summarized in Table 1.</td>
</tr>
<tr>
<td>4. $\text{CoPc} + e^- \rightleftharpoons \text{CoPc}^-$</td>
<td>$E^\theta_5 = (0.6-0.8) \text{ V}$, $0.4 \text{ s}^{-1} \leq k_5^0 \leq 4 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>5. $\text{CoPc}^- + \text{O}_2 \rightleftharpoons \text{CoPc} - \text{O}_2^-$</td>
<td></td>
</tr>
<tr>
<td>6. $\text{CoPc}^- - \text{O}_2^- + \text{H}_2\text{O} + e^- \rightarrow \text{CoPc} + \text{HO}_2^- + \text{OH}^-$</td>
<td></td>
</tr>
</tbody>
</table>

To summarize, we have found that oxygen reduction on CoPc proceeds, dependent on potential, on both CoPc, where the metal is supposed to be in its Co(II) state, and on CoPc$, where the extra electron is most probably delocalized over the Pc-ring $\pi$-system. On both types of sites, the overall rate is mainly determined by the rate constant for the adsorption of oxygen; only for low overpotentials has the reduction of adsorbed oxygen a rate comparable to that of the desorption of oxygen. The proposed mechanism is corroborated by:

1. the fact that both CoPc and CoPc$^-$ are known to form $\text{O}_2$-adducts;
2. the presence of surface processes at $+0.80$ and $+0.48 \text{ V}$ vs. RHE;
3. the values found for the Tafel slopes at low, intermediate and high overpotential;
4. the fact that no O–O bond rupture occurs in the overall reaction.

**Reduction of hydrogen peroxide to water**

As stated in the introductory summary, hydrogen peroxide is reduced at CoPc to water only at low potentials. The availability and accuracy of the data on the overall rate constant $k_3$ for this reaction are much poorer than those on $k_2$, discussed in the previous section. For this reason we will not present a detailed mechanism for this reaction. However, using our results, we can make a few observations on the mechanism.

The most important feature is that the reaction starts only at potentials $<0.4 \text{ V}$ vs. RHE, while the reversible potential of the couple $\text{HO}_2^- / \text{OH}^-$ is $1.69 \text{ V}$ vs. RHE.
Therefore, some reaction with a reversible potential in the range of, say, 0.4–0.6 V must play a role. One possibility would be reduction of HO_2^- to the hydroxyl radical:

\[ HO_2^- + H_2O + e^- \rightleftharpoons OH^- + 2 OH^- \quad E^\circ = 0.575 \text{ V vs. RHE} \]

This would mean a mechanism such as

\[
\begin{align*}
\text{CoPc}^- + \text{HO}_2^- + H_2O & \rightleftharpoons \text{CoPc}^-\text{OH} + 2 \text{OH}^- \\
\text{CoPc}^-\text{OH} + e^- & \rightleftharpoons \text{CoPc}^-\text{OH}^- \\
\text{CoPc}^-\text{OH}^- & \rightleftharpoons \text{CoPc}^- + \text{OH}^- \\
\text{CoPc}^- + e^- & \rightleftharpoons \text{CoPc}^- 
\end{align*}
\]

The first step of this mechanism would involve adsorption of HO_2^- on CoPc^-, which is, at 300 mV, the predominant species, and we have shown [2] that this is a fast process compared to the overall rate. Then, charge transfer followed by O–O bond breaking would have to occur, whereupon the O^-ion would be protonated very fast. Therefore, if the first step were rate determining, it would have to be because the charge transfer

\[ \text{CoPc}^- - \text{HO}_2^- \rightleftharpoons \text{CoPc}^- - \text{O}^- + \text{OH}^- \]

is slow. In that case, however, the rate, i.e. \( k_3 \), would have to be independent of electrode potential, which is not what we have observed.

The second step (eqn. 24), will be very fast in any case, since its standard potential is 2.811 V vs. RHE [18], and even if this were lowered by adsorption, the adsorption would have to be extremely strong (\( \Delta G_{ads} \approx -2.5 \text{ eV} \)) to account for the low potentials where the overall reaction occurs. Thus, the second step is ruled out as well.

The third step (eqn. 25), as the rds would again lead to a potential-independent rate. Therefore, we conclude that there the fourth step (eqn. 26) must be rds. The rate equation is in that case

\[-i_3/2F = k^0 \exp -a_4/f_4 \]

which predicts a Tafel slope \( b = -60/a_4 \) mV. To explain the observed Tafel slope \( b \approx -180 \text{ mV} \), \( a_4 \) would have to be ca. \( \frac{1}{3} \). This does not contradict our findings for oxygen reduction, since in the rate equation used there (eqn. 16), \( a_4 \) does not appear. So, \( a_4 \approx \frac{1}{3} \) is possible and could indicate that the extra electron is not localized on the central Co-ion, but is delocalized on the \( \pi \)-ring system.

The value of \( k^0_4 \) is known (see Table 1), viz. \( k^0_4 \geq 500 \text{ s}^{-1} \), so we know that the (intrinsic) rates of the reactions given in eqns. (23)–(25) should be considerably larger, i.e. > 10^3 s\(^{-1}\). In principle it is also possible that a mechanism without redox catalysis applies, i.e.

\[
\begin{align*}
\text{CoPc}^- + \text{HO}_2^- + H_2O + e^- & \rightleftharpoons \text{CoPc}^-\text{OH} + 2 \text{OH}^- \\
\text{CoPc}^-\text{OH}^- + e^- & \rightleftharpoons \text{CoPc}^- + \text{OH}^- 
\end{align*}
\]

Such a mechanism, with either of the two steps as the rds, would also give a Tafel
slope of $-60/\alpha \; \text{mV}$ as well. On the other hand, it would not take into account the fact that hydrogen peroxide is a rather strong oxidator, which is likely to oxidize CoPc$^-$. Further, in this mechanism, it is still more difficult to understand a Tafel slope of $-180 \; \text{mV}$, i.e. $\alpha = \frac{1}{2}$. However, we are not able to discriminate between the various possibilities. We therefore conclude that, although we cannot be certain, most probably reduction of hydrogen peroxide follows a mechanism where HO$_2^-$ is adsorbed on CoPc$^-$, which is followed by bond breaking. This leaves an adsorbed hydroxyl radical, which is reduced in a fast step to a hydroxyl ion. The rate-determining factor is the availability of CoPc$^-$, where the extra electron is probably delocalized in the $\pi$-system of the Pc ring.

In our opinion, a mechanism like this, with bond breaking after the first electron transfer and therefore involving a radical, is the only possibility as long as only one catalytic site is involved in the reaction. A simultaneous two-electron transfer will only be possible if HO$_2^-$ interacts with two sites simultaneously. A mechanism like this could predominate on, for example, reduced platinum, but on CoPc films the sites are separated by a distance of the order of the molecular diameter, i.e. 1.2 nm [19], so the hydrogen peroxide molecule is too small to have a two-site interaction.

DISCUSSION AND CONCLUSIONS

The mechanism for the reactions involved in oxygen reduction on CoPc can be summarized as follows.

The reduction of oxygen to hydrogen peroxide proceeds by two parallel paths, both of which involve slow adsorption of oxygen on the electrocatalytic site, followed by oxidation of the site by the adsorbed oxygen molecule. For the path which predominates in the low overpotential region, the site is the (central metal atom of the) CoPc-molecule, while the high overpotential path involves the CoPc-monoanion. On the latter species, some reduction of HO$_2^-$ also takes place, by a fast adsorption of HO$_2^-$, followed by O–O bond cleavage. Here, the rate of reduction of CoPc to CoPc$^-$ is limiting.

One may wonder why the rates of adsorption of O$_2$ on CoPc and CoPc$^-$ are of the same order of magnitude and why, in connection with this, the fast adsorption step of HO$_2^-$ on both species, leads to O–O bond rupture and reduction only on the monoanion.

The indifference of the O$_2$ adsorption rate to the redox state of the electrocatalyst is a further indication that, in CoPc$^-$, the formal oxidation state of the central metal atom is Co(II) rather than Co(I) and that a reduced ring system, Pc$^-$, prevails. The extra electron on the ring system exerts only a marginal influence on the relative energies of the Co d-orbitals, which play a predominant role in the formation of the adsorption complex between CoPc and O$_2$, together with the $\pi$-orbitals of the oxygen molecule. On the other hand, in HO$_2^-$ the interacting orbitals will have much more of the nature of lone pairs, and therefore a substantially higher energy on an absolute scale. Therefore, we suppose that the more negative charge on the ring system does not produce an alteration of the relative positions of the Co d-orbitals.
(to give a change in \(\text{O}_2\) adsorption behaviour), but raises them to a level where a better match with the (high-energy) lone pairs of \(\text{HO}_2^-\) gives a more efficient interaction, i.e. not the rate of adsorption but the adsorption energy is changed. We hope to elaborate on this point in a future communication, where we will give our views on the catalytic site–depolarizer interactions in oxygen reduction on phthalocyanines.

A second point which needs clarification is that of the standard potential of the reduction process \(\text{Co(III)}\text{Pc} \leftrightarrow \text{Co(II)}\text{Pc}\). Our observations [2] that for low overpotential the Tafel slope for oxygen reduction is \(-40\) mV and for high overpotential \(-\infty\) forces us to accept that this reduction plays a role in oxygen reduction and that its standard potential is about \(0.8\) V—which is also the potential where, judging from the available literature data, we would expect it to occur. On the other hand, we have not been able to detect it in our impedance measurements. These were conducted in the frequency range between 10 and \(5000\) s\(^{-1}\), while from our kinetic results we estimate the rate constant of the reduction process to be at least \(10^3\) s\(^{-1}\)—so, we have not missed the process because the measurement frequencies were too high.

Therefore, there must be some reason why the \(\text{Co(III)}/\text{Co(II)}\) transition is not visible in the impedance spectra. Possibly this can be related to the conductivity of the \(\text{CoPc}\) film. This is seen to be rather low for high electrode potentials, while it has a maximum at about \(0.48\) V [2]. We believe that, at high potentials, conduction occurs by chains of Co-atoms, linked by oxygen molecules:

\[
\ldots-O-O-Co-O-O-Co-O-O-\ldots
\]

Such a condition mechanism would be especially effective near the film surface, since there oxygen can diffuse from the atmosphere or from the electrolyte solution into the film. On the other hand, at low potentials, we have \(\text{CoPc}^\text{−}\), where the extra electron is supposed to be delocalized in the phthalocyanine \(\pi\)-system. Such a delocalized electron is expected to increase conductivity considerably, and indeed such an increase is observed.

Now the impedance measurements were performed in deoxygenated solution. Since cathodic polarization is expected to remove oxygen from the film surface, the surface resistance of the film is increased at high potentials. Then, there will be a larger ohmic potential drop in the film surface, so that the \(\text{Co(III)}/\text{Co(II)}\) transition will virtually be shifted to much more positive potentials and will not be visible in the impedance spectrum.

On the other hand, since at low potential values conduction is mainly by the \(\pi\)-system, the conductivity will not be affected by the presence or absence of oxygen, so the \(\text{CoPc}/\text{CoPc}^\text{−}\) transition will still be visible in the impedance.

A final point which has previously been ignored is the role which is possibly played by the adsorption of \(\text{OH}^\text{−}\)-ions on the electrocatalytic sites. This is most likely to occur at \(\text{CoPc}^\text{+}\):

\[
\text{CoPc}^\text{+} + \text{OH}^\text{−} \leftrightarrow \text{CoPcOH} \quad K_{\text{OH}} = \frac{[\text{CoPcOH}]}{[\text{CoPc}^\text{+}][\text{OH}^\text{−}]}\]
This would modify our kinetic eqns. (5) and (16) by the replacement of the terms $e^{n_1}$ by $(1 + K_{OH}[OH^-]) e^{n_1}$. This does not affect the equations seriously as long as $K_{OH}[OH^-] \ll 1$. If, however, this condition does not apply, the order of the currents in $[OH^-]$ would be $-1$. Since we have not varied the $OH^-$ concentration, we are not in a position to estimate $K_{OH}$. However, an order $-1$ in $[OH^-]$ has been reported [15].

In conclusion, we can say that we have satisfactorily completed and explained the kinetic description given previously. This was accomplished by the adoption of a "redox catalysis" model, which explains all available data. The main feature of this model is, that the polarizer, which is $O_2$ over the entire potential range investigated, and $HO_2^-$ only at high overpotential, is adsorbed on the catalytic site (the central Co-atom of CoPc), which subsequently releases an electron to the adsorbed species. This is subsequently reduced to the respective products, which are desorbed, and reduction of the site completes the cycle. Such a process is found to occur both on CoPc at low overpotential, and on CoPc$^-$ at high overpotential. The difference in the electrocatalytic behaviour of the two catalyst species CoPc and CoPc$^-$ is tentatively explained with regard to their respective electronic distributions and their influence upon the nature of the catalyst-adsorbent complex.

ACKNOWLEDGEMENTS

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REFERENCES

11. R.H. Felton in ref. 9, p. 53.