JOURNAL OF CATALYSIS 28, 8-19 (1973)

Mechanism of the Electrocatalytic Reduction of Oxygen on Metal Chelates*

H. ALT,** H. BINDER, AND G. SANDSTEDE

Battelle-Institut e.V., Frankfurt (Main), Germany

Received February 2, 1972

N_4 complexes (tetraarylporphyrins, dibenzotetraazaannulenes, phthalocyanines), N_2O_2 complexes (Pfeiffer complexes), and N_2S_2 complexes [diacetyldi(thiophenylhydrazones)] have been studied with respect to their catalytic activity for the electroreduction of oxygen in acid electrolyte. Activity has been found with the N_4 complexes, of which the phthalocyanines are already known as catalysts. Unfortunately we found these metal chelates not to be completely stable when supported by active carbon or carbon black. Especially the phthalocyanines readily disintegrate in acid, but also the dibenzotetraazaannulenes lose their activity within several days of operation. Only certain tetraarylporphyrins were still active after 300 hr. The N_2S_2 and N_2O_2 (monomeric and polymeric) complexes did not show any activity at all although the Pfeiffer complexes are known as reversible oxygen carriers. In contrast to these complexes, the N_4 complexes used are not only macrocyclic but also have a conjugated π-electron system, which seems to be a prerequisite for the activation of the oxygen molecule. The mechanism of the activation of the O_2 molecule has been explained on the basis of simple MO considerations, which also provide an explanation for the order of activity of central metal ions—Co > Fe > Ni—and for the effect of the support and of substituents of the ligand on the activity and the stability of the chelate.

INTRODUCTION

Metal chelates play an important role in nature as active groups of enzyme catalysts. Such catalysts also are responsible for the functioning of the respiratory chain, in which the biological oxidation of combined hydrogen and oxygen proceeds according to an electrochemical mechanism. Cytochromes serve here as oxygen activators and redox systems. They have derivatives of porphyrin as active groups. These porphyrin derivatives are only stable at medium pH values. Therefore we investigated derivatives of the acid-stable tetraphenylporphyrin as catalyst candidates for the cathodic reduction of oxygen in acid electrolyte. Metal phthalocyanines are known to be electrocatalytically active in oxygen reduction. Jasinski (*1*) used Co-phthalocyanine in alkaline electrolyte; Jahnke (*2*), Jahnke and Schönborn (*3*) discovered the catalytic activity of phthalocyanine–carbon support combinations for the electroreduction of oxygen in acid electrolyte. The phthalocyanines consist of a ring system similar to the basic porphyrin structure. There is, however, an important difference: the nitrogen bridges of the phthalocyanines do not allow substitution, so that the activity and stability cannot be influenced by electron shifting. Unfortunately, the monomeric and oligomeric (polymeric) metal phthalocyanine on the support decomposed gradually when suspended in acid electrolyte (*4*), which resulted in a complete loss of catalytic activity of the catalyst.

In addition to the tetraarylporphyrins

---

* Paper presented by G. Sandstede: Meet. Int. Soc. Electrochemistry, Dubrovnik, Sept. 1971.

** Now Farbwerke Hoechst AG, Frankfurt (Main) Hoechst.

(*5*) and phthalocyanines we investigated further metal chelates in order to determine the effect of the structure on the catalytic activity. Among these were the metal dibenzotetraazaannulenes (*6*, *7*). Beck (*8*) and Haecker *et al.* (*9*) have also reported on this complex recently. Not only the type of coordination—N_4, N_2O_2, etc., but also the chemical modification of the ligand is important for the activity of the metal chelate (*4*, *10*).

Furthermore, the type of the central metal ion determines the catalytic character of the chelate (*4*, *7*), as has been found by Jasinski (*1*), Jahnke and Schönborn (*3*), Savy (*11*) and Kozawa *et al.* (*12*) in the case of the phthalocyanines. There is also a strong influence of the nature of the support on the activity of the chelate. This has been shown by Jahnke (*2*) for the phthalocyanines, and has also been observed by us for all the active chelates investigated.

It is obvious that all the factors indicated above have a great influence on the activation of the oxygen molecule by the central metal ion of the chelate. We want to go a step further and explain the effect of electronic structure on the catalytic activity of the metal chelate on theoretical grounds, using the results of MO calculations of metalloporphyrins (*13*).

EXPERIMENTAL METHODS

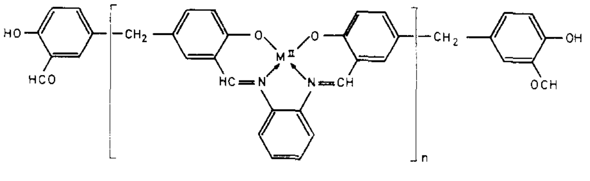
Metal Chelates

Bissalicylaldehyde-*o*-phenylenediamine, a representative of the Pfeiffer complexes, was synthesized by condensation of salicylaldehyde with *o*-phenylenediamine in ethanol (*14*). Pfeiffer complexes containing other diamines were prepared as well. Moreover, a polymeric complex was synthesized by combining a dialdehyde with a methylene group, see Fig. 1.

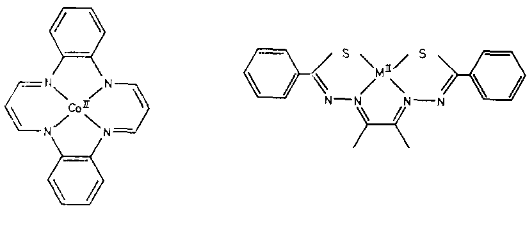
Diacetyl-di(thiophenylhydrazone), abbreviated DADT (Fig. 1), was obtained by condensation of diacetyl with thiobenzohydrazide in ethanol (*15*).

The complexes referred to above contain ligands with three chelate bridges. The complexes described below consist of a macrocyclic ligand; the fourth bridge is closed as well. In addition, the ligand has a closed conjugated π-electron system.

The free ligand dihydrodibenzotetraazaannulene (DBTA), Fig. 1, was synthesized from propargylaldehyde and *o*-phenylene diamine (*16*), the metal complexes then by reaction of the metal acetate with the free ligand. The iron complex which has not yet been described was equally obtained from the pure ligand and Fe(III) acetate. It might be useful to mention two difficulties with the synthesis of the dibenzo-



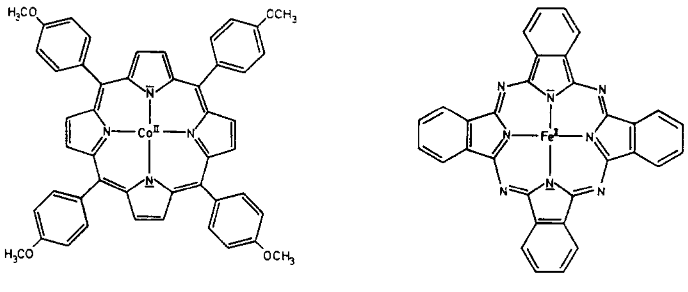
Pfeiffer complex



Co^{II} DBTA

M^{II} DADT

FIG. 1. Metal chelates with the ligand of polymeric Pfeiffer complex, of dibenzotetraazaannulene, and of diacetyldi(thiobenzhydrazone).



Co^{II} TMPP

Fe^{II} Phc

FIG. 2. Co(II)-$\alpha,\beta,\gamma,\delta$-tetra($p$-methoxyphenyl)porphyrin (Co^{II}TMPP) and Fe(II)phthalocyanine (Fe^{II}Phc).

tetraazaannulene Fe(III) hydroxide: No product was obtained in solvents like acetic acid because of thermal destruction of the ligand during heating; therefore dimethyl formamide was used as the solvent. Incomplete reaction was observed by using propargylaldehyde, *o*-phenylenediamine and Fe(II) acetate in an open reaction vessel without prior isolation of the free ligand. The analysis of these products showed that they consisted of 50% complex and 50% free ligand in contrast to the preparation method mentioned above.

α, β, γ, δ-tetraarylporphyrins (Fig. 2) were readily prepared by refluxing the aromatic aldehyde and pyrrole in propionic acid (*17*). Phthalocyanines (Phc) (Fig. 2) were prepared from phthalodinitrile in the conventional manner (*18*). A polymeric product was also synthesized by interaction of pyromellitic dianhydride with urea (*3*).

Catalysts

The metal chelate was dissolved in a solvent, and the support was suspended in the solution. Then the metal chelate was precipitated on the support by addition of water. The porphyrins were dissolved in dioxane, the Phc and DBTA complexes in concentrated sulfuric acid. Polymeric Pfeiffer complexes, which are only sparingly soluble, were boiled in tetrahydrofuran together with the support. DADT was adsorbed on the support from a solution in methylene chloride.

The metal chelate was applied in an amount of up to 10%. The active carbon (Norit BRX) we mainly used as support has a fairly high electrical conductivity and a large surface area. Besides active carbon, also carbon black was used.

Measuring Method

The electrocatalytic activity of the catalyst powder was measured in suspension (suspension electrode) using the method of Podwjaskin and Shlygin (*19*), Held and Gerischer (*20*). In this method the catalyst is suspended by vigorous stirring and tossed against a gold gauze, which serves as the working electrode, see Fig. 3. A similar setup was used by Jahnke (*2*). While whirling about in the electrolyte through which oxygen is bubbled, the catalyst particle adsorbs oxygen, thus attaining a rest potential which is characteristic of the catalyst–oxygen interaction. During contact with the gold gauze the catalyst particle takes up electrons until the potential of the gold electrode is reached provided that the time of contact is sufficient. Generally speaking, the reduction of oxygen (electrochemical charge transfer reaction) can take place directly after adsorption on the catalyst particle and during contact time with the gold gauze.

The gold gauze (50 mesh/cm^2) was rolled into a cylinder with an area of 80 cm^2, which surrounded the stirrer. Dilute sulfuric acid solution (400 ml) was used. An autogenous hydrogen reference electrode (*21*) was connected to the half cell by an electrolyte bridge. The method allows

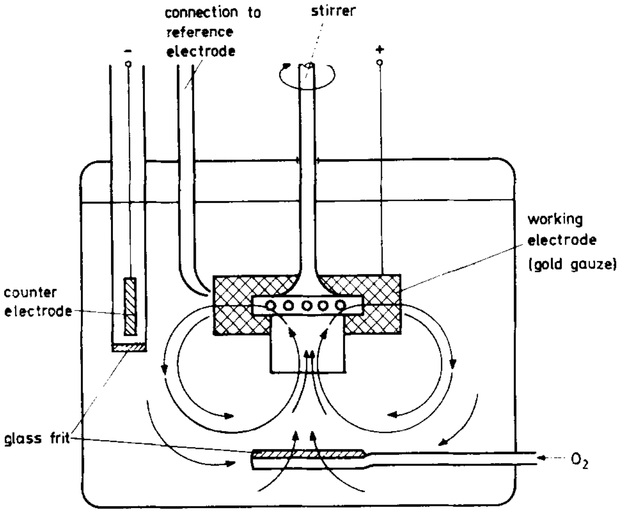


FIG. 3. Diagrammatic view of the electrochemical measuring cell for catalyst suspensions.

the measurement of current–voltage curves with suspended catalysts. It is, however, not possible to draw quantitative conclusions on the stationary reaction taking place on solid catalyst electrodes. Nevertheless, the method can be used for a quick evaluation of the activity of the catalyst, and is also suitable for the comparison of catalysts.

The measurements were carried out potentiodynamically (linear voltage sweep) at a sweep rate of 40 mV/min. At a sweep rate as small as this, the current–voltage curves obtained are nearly stationary. The curves depicted in the figures were taken after cycling approximately 10 times between 400 and 800 mV in order to obtain a temporarily almost constant curve. The activity of all the catalysts investigated then decreased slowly in the course of several hours. This slow decrease seems to be due primarily to the measuring technique employed (because it was also found with pure carbon), but in part may well be a true decrease in catalytic activity, as can be inferred from measurements with polyethylene-bonded electrodes (see section "Results").

RESULTS

The activity of pure carbon black for the reduction of oxygen in dilute sulfuric acid is very small. The current measured in suspension with 50 mg carbon black at a potential of 500 mV was only a few milliamperes. With active carbon a current of up to 10 mA was measured.

The use of Pfeiffer complexes did not raise the low activity within the limits of reproducibility of 10 to 30%. Neither monomeric nor polymeric Pfeiffer complexes with Fe, Co, Ni as central atom were found to improve the activity of active carbon or carbon black.

The results obtained with $Fe^{II}DADT$ and $Cu^{II}DADT$ were likewise negative.

The three macrocyclic complexes, on the other hand, showed a more or less strong activity for the reduction of oxygen. The activity of CoTMPP—cathodic current at a constant potential—was measured as a function of the coating (Fig. 4). Even if the carbon is coated with only 5% by weight of CoTMPP, the activity almost reaches its maximum value.

The active carbon used has a specific surface area of 1500 m^2/g of which, however, only about 100 m^2/g is occupied by pores of a diameter $\geqslant 25$ Å (our own measurements) and thus is easily accessible to the TMPP molecule. The catalyst was used in a quantity of 50 mg, and contained 47.5 mg active carbon and 2.5 mg CoTMPP. An amount of 2.5 mg CoTMPP occupies an area of about 10 m^2 if the molecules lie one beside the other. Thus,

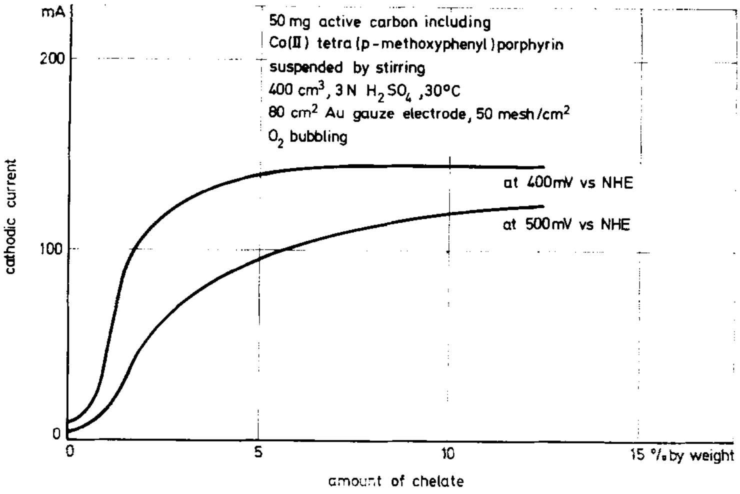


FIG. 4. Effect of the amount of chelate on the activity of the catalyst for the electroreduction of oxygen.

even a coating of only 5% by weight must form a multilayer on the carbon surface. It may be assumed that in addition to the pores $\geqslant 25$ Å in diameter there is a substantial number of slit pores which, though of smaller size, will be covered by catalyst molecules. Nevertheless, the carbon surface accessible to the catalyst is covered at more than 100%, as can be inferred from the activities measured for a smaller chelate content of the catalyst.

Figure 5 illustrates the activities of the three macrocyclic chelates. The most active chelate is CoDBTA, but the order changes after an extended period of operation. It should be noted that DBTA and TMPP are monomers, whereas Phc is a polymer. Monomeric Phc exhibits a very low electrocatalytic activity. The increased activity of polymeric Phc has been attributed by Jahnke (*2*) to its semiconductor properties. The measurements with TMPP now have shown that even a perfect nonconductor may be an active electrocatalyst. CoTMPP is capable to a limited extent of acting as a catalyst even without a support, whereas even polymeric FePhc is a very weak catalyst in this case.

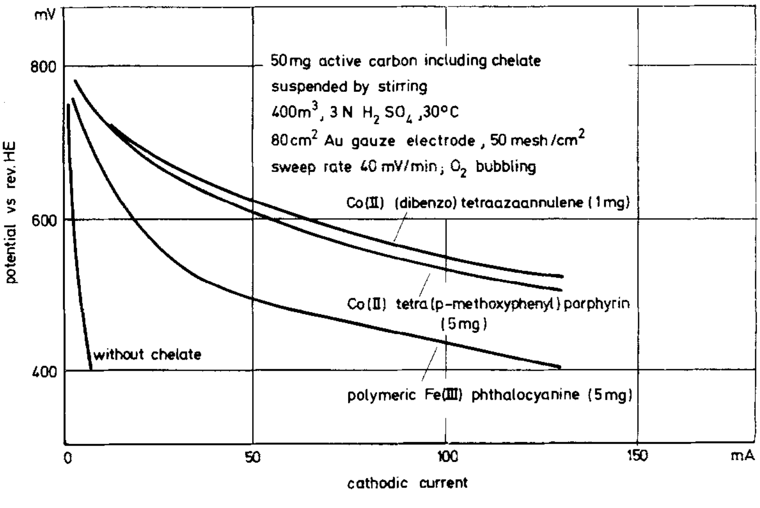


FIG. 5. Potentiodynamic current-voltage curves for oxygen reduction at metal chelate catalysts.

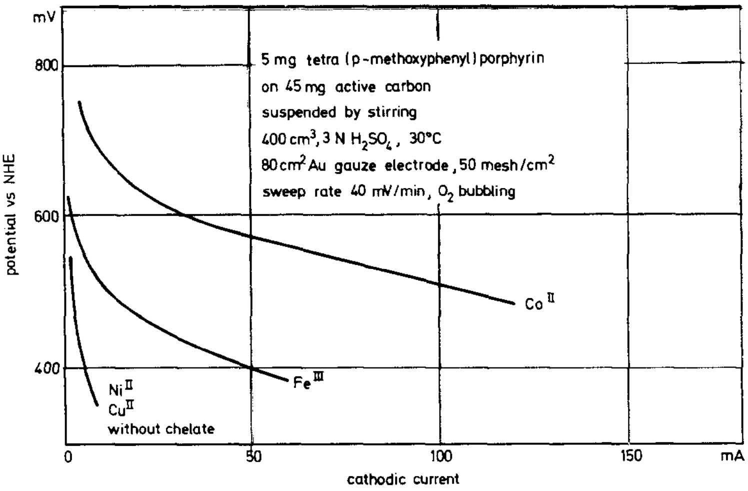


FIG. 6. Potentiodynamic current–voltage curves for oxygen reduction at metal porphyrin catalysts.

The effect of the central atom is shown in Figs. 6 and 7. The activity decreases in the following order:

TMPP: $Co^{II} > Fe^{III} > Ni^{II} \approx Cu^{II} \approx 0$,
DBTA: $Co^{II} > Fe^{III} > Ni^{II} \approx Cu^{II} > 0$.

A similar order was found for Phc (*3*, *11*, *12*) but Phc contains Fe^{II} in place of Fe^{III}, and Fe^{II}Phc is more active than Co^{II}Phc. Jahnke's (*2*) observation that the activity of Phc depends critically on the type of support has been confirmed by our measurements, but the degrees of dependence which we determined for the individual types of carbon are slightly different; see Fig. 8. A dependence of the activity on the type of support has also been observed for CoTMPP; investigations on the effect of the electronic properties of the support and the basicity of its surface are under way. Figure 9 shows that thermal treatment of the catalyst improves the activity considerably.

Of particular importance for the activity of tetraarylporphyrin is the type of substituent linked to the phenyl in *p*-posi-

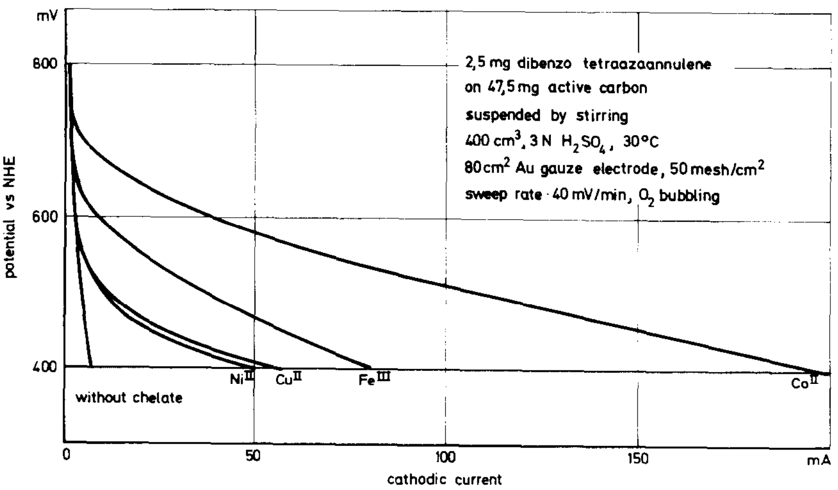


FIG. 7. Potentiodynamic current–voltage curves for oxygen reduction at metal dibenzotetraazaannulene catalysts.

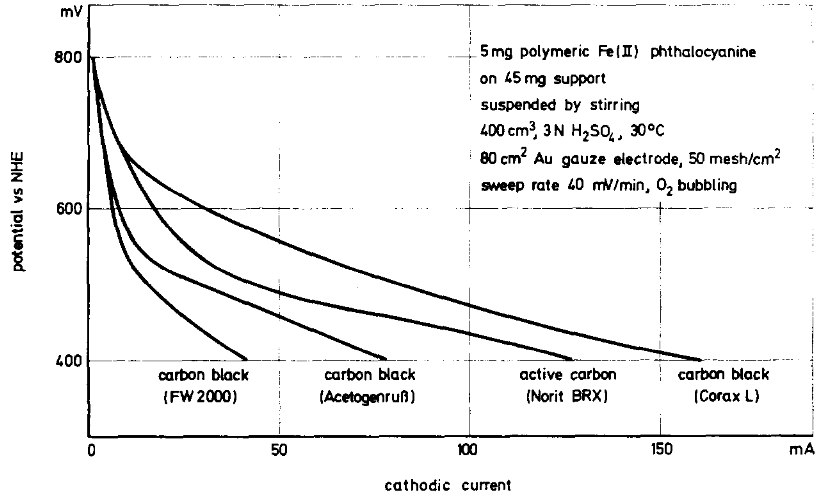
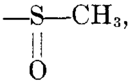
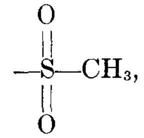


FIG. 8. Potentiodynamic current–voltage curves for oxygen reduction at Fe(II)phthalocyanine on various carbon supports.

tion (Fig. 10). Electron donor groups raise the activity in the following order:

$OCH_3 >$  $> SCH_3 > H.$

Although the methylmercapto group is the strongest donor, its effect is only small. This is probably due to oxidation of the sulfur so that the substituent is present in the form of methylsulfinyl,  $-\underset{\underset{O}{\|}}{S}-CH_3$, or methylsulfonyl,  $-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-CH_3$, which rather have electron acceptor properties. In order to test the long-term stability of the cata-

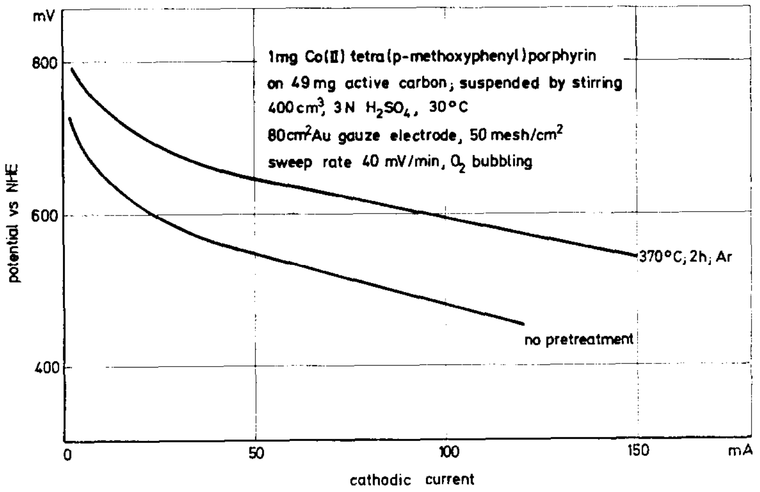


FIG. 9. Potentiodynamic current-voltage curves for oxygen reduction, effect of pretreatment on the activity of the chelate catalyst.

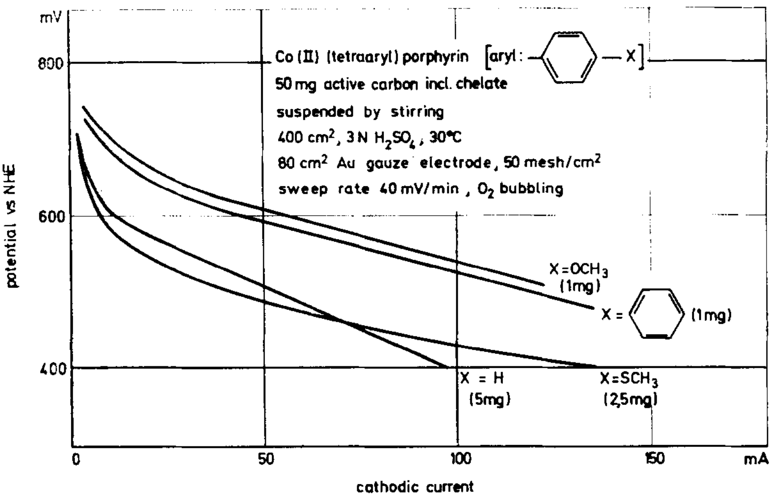


FIG. 10. Potentiodynamic current–voltage curves for oxygen reduction at Co(II)(tetraaryl)porphyrins; effect of the ligand in *p*-position.

lyst, we conducted investigations with polyethylene-bonded electrodes. Figure 11 shows that the activity of an electrode containing CoTMPP coated carbon is about five times that of an electrode containing active carbon alone. The pressure was adjusted such that only a very small quantity of oxygen bubbled from the electrode at the side of the electrolyte. The potential was first up to 50 mV above the curve of Fig. 11 but rapidly decreased within a few hours. Subsequently, it decreased only slightly, but even after several hundred hours a further decrease of up to 5 mV/day was still observed.

Electrodes with CoDBTA or polymeric FePhc completely lost their activity after a few days; the potential was even smaller than that obtained with active carbon alone. The low activity of CoDBTA may possibly be attributed in part to oxidative linkage of two complex molecules to the

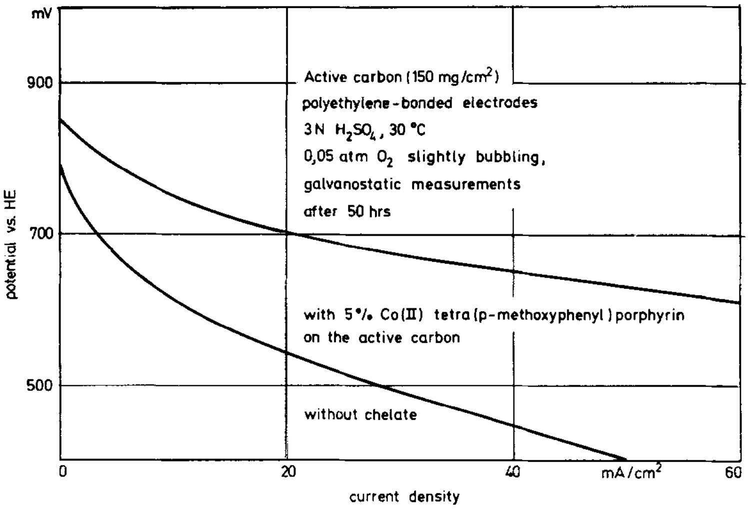


FIG. 11. Galvanostatic current–voltage curves for the reduction of oxygen at porous bonded electrodes.

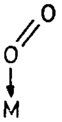
central atoms (*16*), which may occur during preparation of the electrode.

All three substances are known to be resistant to acids. We found, however, that this is not the case if they are adsorbed on a support. About 4% of the Fe in FePhc is found in the electrolyte after 3 days if the substance is stored in 3 *N* H_2SO_4 at room temperature. At 80°C the quantity is increased to about 20%. The Co and Fe complexes of TMPP were somewhat more stable; the Ni and Cu complexes were found to be completely stable, but these are not active. Co-tetra(*p*-diphenyl)porphyrin was the only active substance that proved to be completely stable at room temperature.

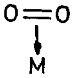
The Pfeiffer complexes, both monomeric and polymeric, were slightly soluble in 3 *N* H_2SO_4 and decomposed in part.

Interpretation of the Oxygen Activation

Pfeiffer complexes are known to bind oxygen reversibly. From magnetic and iR measurements (*22*) it may be concluded that the O_2 molecule is linked to the central atom at an angle to the perpendicular: edge-on.



edge-on



side-on

A position exactly in the direction of the perpendicular can be excluded according to these measurements, whereas Vaska complexes—bis[bis(diphenylphosphino)ethane] M^I-hexafluorophosphate—involve the side-on position, as can be inferred from X-ray measurements (*23*). The bond that binds the O_2 molecule to the complex is in both cases a donor bond formed either by σ-electrons (Pfeiffer complexes) or by π-electrons (Vaska complexes). In Vaska complexes the bond between the O_2 molecule and the complex becomes increasingly irreversible as the electron density of the central atom rises, i.e., if Co is replaced by Rh or Ir. The O–O bond length is then increased. Hemin, an Fe-porphyrin derivative, binds O_2 completely reversibly (*24*); MO calculations suggest an edge-on position of the adsorbed oxygen molecule. The adsorption of O_2 by monomeric CoPhc is likewise reversible, as has been shown by ESR measurements (*25*). Yamamoto and Kwan (*26*) recently conducted ESR measurements with Co-tetraphenylporphyrin. The molecule has a characteristic ESR signal caused by Co^{II}. If O_2 is added, the signal vanishes and a new one appears, which is probably due to the paramagnetic O_2. Upon removal of the O_2 the original signal is regained. In the presence of benzimidazole or other bases the adsorption of O_2 is not reversible. The ESR signal vanishes irreversibly, and a new one does not appear.

Since the macrocyclic ligand is arranged around the central atom in a square plane, the two axial positions are empty. One is then occupied by O_2. The other may be occupied by an additional ligand, e.g., benzimidazole or the solid support. This, however, will have an effect on the bond strength of the O_2, which can be explained as follows.

The five *d*-orbitals of the free transition metal ion are degenerate, i.e., they have the same energy. The orbitals will, however, be split into e_g and t_{2g} orbitals if the ion is in the center of a symmetric octahedral complex, as is known from ligand field theory (*27*). If the symmetric field of the six identical ligands is perturbed axially, there will be a shift in the position of the energy levels: one or two levels (e.g., d_{xy}) will be shifted to a higher position, and the d_{z^2} level will be shifted to a much lower position so that even an inversion may occur. The position of the levels depends on the field strength of the two axial ligands and that of the planar ligand. Consequently, the bond strength of the oxygen molecule will be influenced by the other four or five ligands.

The effect of the macrocyclic ligands, the support, and additional ligands on the oxygen–chelate interaction has thus been interpreted qualitatively, but we may still go one step further.

From the π-complexes of ethylene it is known (*28*) that substituents are linked

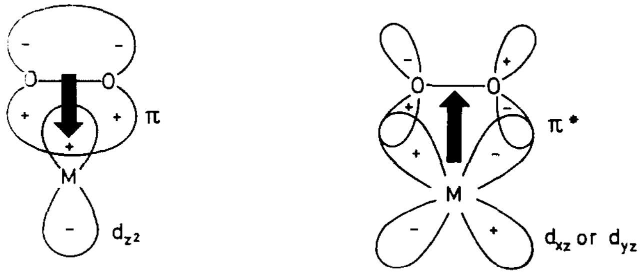


FIG. 12. Electron donation and back donation in oxygen-complexed transition metal bonding.

to the complex by the π-electrons of the double bond of the ethylene molecule and that there are antibonding orbitals which give rise to retrodative bonding or back-bonding. The antibonding orbitals are occupied by electrons of the other molecule or its central atom. Such an interaction is also possible with O_2. Figure 12 shows that the d_{z^2} orbital of the metal ion is most likely to bind the oxygen molecule because it has the proper symmetry for the required overlapping. Back-bonding with the antibonding π^* orbitals of the oxygen molecule is only possible if the d_{xz} or d_{yz} orbitals of the metal ion are occupied. Only these d-orbitals have the proper symmetry. The p_x and p_y orbitals would also be suitable with respect to their symmetry, but their energy level would probably be too high.

Zerner and Gouterman (*13*) calculated the position of the d-orbitals of the transition metal ion in porphyrin complexes, using MO theory. They found that the d_{xz} and d_{yz} orbitals have the same energy and are closely below the d_{z^2} orbital. The qualitative MO energy level diagram for porphyrin complexes and the ground state occupancy schemes for different central metal ions are shown in Fig. 13. The d_{z^2} orbital is empty in the case of Fe(II) and Fe(III), and singly occupied in the case of Co(II). With Ni(II) the d_{z^2} orbital is completely filled.

The dependence of the electrocatalytic

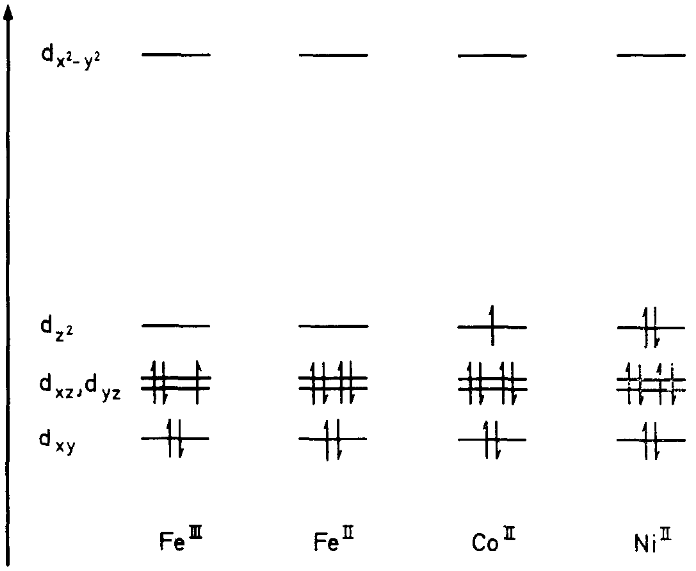


FIG. 13. d-Electron configuration of the central metal ion of porphyrin chelates (diagrammatic view).

activity of the porphyrin complexes on the nature of the central metal ion can be rationalized on the basis of the occupancy schemes if the following assumptions are made:

i. Electrocatalysis takes place during the first step of cathodic oxygen reduction, i.e., the two-electron reduction of oxygen to hydrogen peroxide. This assumption is supported by a polarographic study of oxygen reduction in the presence of phthalocyanine complexes (*29*).

ii. The reduction of oxygen is favored by a partial electron transfer from the metal ion to the antibonding π^* orbitals of the oxygen molecule in the porphyrin–oxygen complex. Therefore, strong back-bonding in the chelate–oxygen bond is assumed to be a prerequisite for the activation of the oxygen molecule.

iii. Back-bonding is favored by filled $d_{xz,yz}$ orbitals and vacant d_{z^2} orbitals. The role of the d_{z^2} orbital can be explained as follows: Back-bonding requires bonding, i.e., interaction of filled oxygen orbitals with the vacant d_{z^2} orbital of the metal. This interaction tends to lower the energy of the antibonding π^* orbitals of oxygen and to raise the energy of the $d_{xz,yz}$ orbitals. Thus, the back-bonding interaction between these orbitals is increased.

With Co(II), Fe(II) and Fe(III) the above-mentioned conditions for strong back-bonding are satisfied and catalytic activity is predicted, whereas with Ni(II) and Cu(II) poor or no catalytic activity is expected. These conclusions are in agreement with the experimental results obtained with porphyrin complexes, phthalocyanine chelates, and dibenzotetrazaannulene complexes (see Figs. 6 and 7).

The influence of the support and other ligands or substituents on the electrocatalytic activity can also be understood in terms of their effect on the back-bonding from the chelate to the oxygen molecule. The assumption of strong back-bonding is supported in the case of CoTMPP by ESR measurements (*30*). In this work the influence of additional ligands on the chelate oxygen interaction has been demonstrated as well.

Pfeiffer complexes and other nonmacrocyclic complexes did not display any activity for the reduction of oxygen in our measurements. This observation can be explained by the assumption that the O–O bond in the oxygen complexes of these chelates is not sufficiently activated by back-bonding. This might be due to the different energies of the highest occupied molecular orbitals in the nonconjugated nonmacrocyclic complexes. In a catalytic chemical reaction, viz, isomerization of quadricyclene, Manassen (*31*) found a similar difference in the activity of Pfeiffer complexes and square planar complexes.

The support as the fifth ligand will probably also affect the bonds between the central metal ion and the four nitrogen atoms of the macrocyclic ligand. It should therefore be possible to improve the stability of the supported complex by variation of the support and by substitution at the ligand. Investigations in this direction are under way, and we are also investigating the formation of H_2O_2 and its effect on the stability of the complex. It is conceivable that the C or N bridges between the pyrrole rings are weakened by the support, so that oxygen or hydrogen peroxide may oxidatively degrade the molecule at this site. Thus, a number of problems still have to be solved before a technologically feasible catalyst can be developed. The mechanistic concepts obtained from MO considerations have made it possible, however, to tackle the problems by a direct approach.

ACKNOWLEDGMENTS

We thank Miss R. Berndt, Mrs. G. Kaufmann, Dr. W. Klöpffer, and Dr. R. Reiner for the preparation of the substances and their analyses, and Mr. W. Lindner, Dr. H. Behret, and Dr. W. H. Kuhn for their valuable assistance. The work was sponsored by the West German Ministry for Defence, Bonn, under the guidance of Dr. R. Dieberg. Permission to publish these results is gratefully acknowledged.

REFERENCES

1. JASINSKI, R., *Nature* (*London*) **201**, 1212 (1964); *J. Electrochem. Soc.* **112**, 526 (1965).

2. Jahnke, H., presented: Bunsentagung, Augsburg, May, 1968; *Abstr. Ber. Bunsenges. Phys. Chem.* **72**, 1053 (1968).

3. Jahnke, H., and Schönborn, M., "Comptes Rendus, Troisièmes Journées Internationales d'Etude des Piles à Combustible," p. 60. Presses Académiques Européennes, Bruxelles, 1969.

4. Alt, H., Binder, H., Lindner, W., and Sandstede, G., presented: Symp. From Electrocatalysis to Fuel Cells, Battelle Seattle Research Center, Seattle, WA, Dec., 1970; "Proceedings," Univ. of Washington Press, Seattle, 1971.

5. Sandstede, G., presented: 5th Symp. Direct Energy Conversion, Essen, Oct., 1970, and Colloq. Gesellschaft Deutscher Chemiker, Dortmund, Nov., 1970; abstr. *Chem.-Ing.-Tech.* **43**, 495 (1971).

6. Alt, H., Binder, H., Klempert, G., Köhling, A., Lindner, W., and Sandstede, G., presented: Symp. Electrocatalysts for Fuel Cells, Battelle-Institut, Frankfurt (Main), Mar., 1971; *Batteile-Information, Frankfurt, Engl. Ed.* **n11**, 61 (1971).

7. Alt, H., Binder, H., Lindner, W., and Sandstede, G., *J. Electroanal. Chem. Interfacial Electrochem.* **31**, App. 19 (1971).

8. Beck, F., presented: Symp. Appl. Electrochem., Vienna, Feb., 1971.

9. Haecker, W., Jahnke, H., Schönborn, M., and Zimmermann, G., presented: Symp. Electrocatalysts for Fuel Cells, Battelle-Institut, Frankfurt (Main), Mar., 1971; *Battelle-Information, Frankfurt, Engl. Ed.* **n11**, (1971).

10. Alt, H., Binder, H., Lindner, W., and Sandstede, G., presented: Bunsentagung, Hannover, May, 1971; Abstr. *Ber. Bunsenges. Phys. Chem.* **74**, (1971).

11. Savy, M., presented: Meet. Comité International de Thermodynamique et de Cinétiques Electrochimiques, Prague, Sept., 1970, Extended Abstr., p. 193.

12. Kozawa, A., Zilionis, V. E., Brodd, R. J., and Powers, R. A., "Proceedings of the Artificial Heart Program Conference, June 1969," Chap. 71, p. 849. National Heart Inst., Washington, DC, 1969; *J. Electrochem. Soc.* **117**, 1470, 1474 (1970).

13. Zerner, M., and Gouterman, M., *Theor. Chim. Acta* **4**, 44 (1966).

14. Calvin, M., Bailes, R. H., and Wilmrath, W. K., *J. Amer. Chem. Soc.* **68**, 2254, 2267 (1946).

15. Bähr, G., and Schleitzer, G., *Z. Anorg. Allg. Chem.* **280**, 175 (1955).

16. Hiller, H., Dimroth, P., and Pfitzner, H., *Justus Liebigs Ann. Chem.* **717**, 137 (1968).

17. Adler, A. D., Longo, F. R., Finarelli, J. D., Goldmacher, J., Assour, J., and Korsakoff, L., *J. Org. Chem.* **32**, 476 (1967).

18. Moser, F. H., and Thomas, A. L., "Phthalocyanine Compounds." Reinhold, New York, 1963.

19. Podwjaskin, J. A., and Shlygin, A. J., *J. Phys. Chem. (Russ.)* **31**, 1305 (1957).

20. Held, J., and Gerischer, H., *Ber. Bunsenges. Phys. Chem.* **67**, 921 (1963).

21. Binder, H., Köhling, A., and Sandstede, G., *Chem.-Ing.-Tech.* **43**, 1084 (1971).

22. Crumbliss, A. L., and Basolo, F., *J. Amer. Chem. Soc.* **92**, 55 (1970).

23. McGinnety, J. A., Payne, N. C., and Ibers, J. A., *J. Amer. Chem. Soc.* **91**, 6301 (1969).

24. Maggiora, G. M., Viale, R. O., and Ingraham, L. L., *in* "Oxidases and Related Redox Systems," (T. E. King, H. S. Mason, and M. Morrison, Eds.), Wiley, New York, 1965.

25. Ogata, Y., Marumo, K., and Kwan, T., *Chem. Pharm. Bull.* **17**, 1194 (1969).

26. Yamamoto, K., and Kwan, T., *J. Catal.* **18**, 354 (1970).

27. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry." Wiley (Interscience), London, 1967.

28. Henrici-Olivé, G., and Olivé, S., *Angew. Chem.* **83**, 121 (1971).

29. Beyer, W., and v. Sturm, F., *Angew. Chem.* **84**, 154 (1972).

30. Walker, F. A., *J. Amer. Chem. Soc.* **92**, 4235 (1970).

31. Manassen, J., *J. Catal.* **18**, 38 (1970).