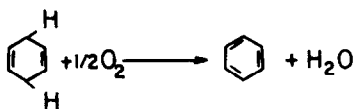


## NOTES

## A Comparison Between the Chemical and Electrochemical Catalysis by Tetraphenylporphyrin and Phthalocyanine Complexes

In the past we have studied the catalytic activity of tetraphenylporphyrin and phthalocyanine complexes for the oxidative dehydrogenation of cyclohexadiene-1,4 in a heterogeneous system. If oxygen is the oxidant, this reaction can also be considered as a chemically catalyzed reduction of molecular oxygen to water:



These complexes have also been studied as catalysts for the electrochemical reduction of molecular oxygen, which is of importance for fuel cell technology:



Both reactions are similar. In the chemical system protons as well as electrons are supplied by the donor cyclohexadiene, while in the electrochemical system, the protons are supplied by the electrolyte solution and the electrons via the electrode.

It is the purpose of this note to compare catalytic activities for the two systems and to draw conclusions about the extent to which the mechanisms are identical.

In the chemical system with nitrobenzene as the oxidant, it has been found that catalytic activity is dependent on the central metal ion in the complex (1) and can be correlated with the oxidation potentials of the catalyst (2). The oxidation potentials

of these complexes can be modified by substituents on the periphery of the molecule, and substituent effects have been studied for the phthalocyanines as well as for the tetraphenylporphyrins. Electron attracting fluorine substituents greatly influenced the catalytic activity of phthalocyanine complexes in such a way that progressive fluorination of iron and cobalt phthalocyanine caused a decrease in activity, followed by a strong increase at higher degrees of fluorination (3). This was explained by a change in mechanism, whereby the catalyst starts to act as an electron-acceptor instead of an electron-donor at high degrees of fluorination. The donor/acceptor properties were followed by studying charge transfer spectra in solution, whereby correlations were found between catalytic activity and the equilibrium constant of charge transfer complex formation.

For tetraphenylporphyrin complexes, it was found that electron donating substituents on the phenyl group cause a moderate increase in rate (4).

With molecular oxygen as the oxidant, catalytic activity also correlated with the oxidation potentials of the catalysts, except for the copper complexes, which were more active than could be accounted for on the basis of their oxidation potential (5).

Many of these phenomena could also be found for the electrochemical reduction of oxygen, catalyzed by these complexes. Cobalt phthalocyanine appeared to be a good catalyst in basic solution (6). In

TABLE 1  
OVERPOTENTIALS (mV) OF OXYGEN REDUCTION  
AT 1  $\mu$ A CURRENT FOR CARBON BLACK  
ELECTRODES AT DIFFERENT pH VALUES

pH:	14	6	0
Overpotential	-320	-560	-640

acidic solution the activity of the phthalocyanines followed their oxidation potentials in that



and chlorine substituents, which are electron attracting, caused a decrease in electrocatalytic activity (7). A more quantitative study at much lower currents could confirm most of these effects, which were also measured in approximately neutral solutions (8). With tetraphenylporphyrin complexes it could be shown that electron donating substituents caused an increase in catalytic activity and that in acidic solution the cobalt complex is more active than the iron complex (9). The electrocatalytic activity of iron phthalocyanine has been studied in detail (10, 11) under different conditions of pH and it was found to be almost as active as platinum. Part of the catalytic activity was ascribed to a chemical decomposition of intermediately formed hydrogen peroxide which was chemically

catalyzed by the complex (catalase activity).

In the present study catalytic electrodes were prepared by mixing carbon black, on which the catalyst was precipitated 10% by weight, with a Teflon emulsion and painting the paste obtained on a 100 mesh metal gauze. By heating at 250°C for 1 hr in an argon stream, good hydrophobic electrodes were obtained. Oxygen was passed over the electrode, which was in contact with the electrolyte solution, and current/voltage plots were measured potentiostatically as well as galvanostatically. The linear part of the plot was extrapolated to a current value of 1  $\mu$ A and from the potential value obtained at this current, the overpotential could be calculated.

Table 1 shows the overpotentials obtained when carbon black is studied without a catalyst. These are the catalytic effects of the catalyst carrier, which have to be subtracted from the values found for carbon black impregnated with catalyst. Results obtained with several complexes at three different pH values are given in Table 2. We see that for the phthalocyanine complexes, the same order prevails as has been noted previously, viz, Fe > Co > Cu.

For the tetraphenylporphyrins, the cobalt complex is more active than the iron

TABLE 2  
OVERPOTENTIALS (mV) OF OXYGEN REDUCTION AT 1  $\mu$ A CURRENT AND NET CATALYTIC EFFECTS  
FOR IMPREGNATED CARBON BLACK ELECTRODES AT DIFFERENT pH VALUES

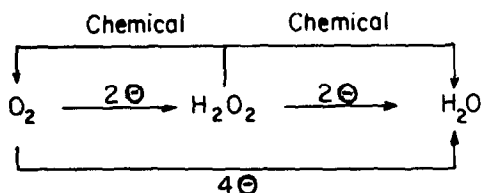
Metal ion	Ligand: pH:	Tetraphenylporphyrin			Phthalocyanine		
		14	6	0	14	6	0
Fe <sup>2+</sup>	Overpotential				-270	-380	-460
	Difference with carbon black				50	180	180
Fe <sup>3+</sup>	Overpotential	-300	-460	-600	-260	-390	-460
	Difference with carbon black	20	100	40	60	170	180
Co <sup>2+</sup>	Overpotential	-280	-460	-500	-330	-450	-540
	Difference with carbon black	40	100	140	-10	110	100
Cu <sup>2+</sup>	Overpotential	-320	-520	-600	-340	-510	-600
	Difference with carbon black	0	40	40	-20	50	40

complex in acidic solution. At higher values of pH, however, both show about equal activity. The results for  $\text{Fe}^{3+}$ - and  $\text{Fe}^{2+}$ -phthalocyanine are practically identical.

Although it has been reported that electron donating substituents on Co-tetraphenylporphyrin do improve catalytic activity in acidic solution (9), we could not detect this effect, and neither a *p*-methoxy nor a *p*-nitro substituent changed the activity of Co-tetraphenylporphyrin to a significant degree under any condition of pH.

The influence of fluorination of the phthalocyanine complexes, which was considerable in the chemical reaction, is shown in Table 3 for cobalt and iron phthalocyanine. With the iron complex we find effects which are similar to those reported for the chemical reaction. With increasing fluorination, overpotentials increase (catalytic activity decreases), but decrease again with subsequent fluorination. The electrocatalytic effect of the cobalt complex, on the other hand, is not influenced by fluorination.

The importance of hydrogen peroxide as an intermediate in oxygen reduction has been discussed (10) and it has been argued that the reduction can go stepwise, whereby hydrogen peroxide is formed in a two electron reduction and is either reduced in a subsequent electrochemical step, or is decomposed chemically with subsequent formation of oxygen and water. The other alternative is a direct four electron electrochemical reduction of oxygen to water:



Some information about the two step mechanism can be obtained by studying the electrochemical reduction of hydrogen peroxide in the absence of oxygen. This was done for all our catalysts.

Current/voltage plots were measured with electrolytes containing 3% of hydro-

gen peroxide, while argon, instead of oxygen, streamed over the electrode, all other reaction conditions being equal to those prevailing in the oxygen reduction measurements. The results obtained with the cobalt and copper complexes were identical to those obtained with carbon black alone. However, the iron complexes caused an increase in current at low potentials. This can be due either to a catalysis of the electrochemical reduction of hydrogen peroxide, or to a chemically catalyzed decomposition of hydrogen peroxide, whereby oxygen is formed, which is reduced in step 1. The second possibility is the more probable one, because of the known catalase activity of iron complexes of this kind (12). It is of special importance that iron phthalocyanine, as well as iron hexadecafluorophthalocyanine, showed this effect in acidic solution, while the tetrafluoro complex did not, which is again the same trend as found in the chemical and electrochemical reductions.

We can now list points of agreement and disagreement between the results of chemical and electrochemical catalysis.

1. In both systems the catalytic activity of the phthalocyanine complexes correlates with their oxidation potential when the central metal atom is changed. The tetraphenylporphyrin complexes show a less satisfactory correlation in this respect.

2. Catalytic activity of the phthalocyanine complexes is lowered by electron attracting substituents. Electron donating substituents are reported to increase the activity of tetraphenylporphyrin complexes in both systems, but we could not verify this for the electrocatalysis. The influence of fluorination is the same in both systems as far as iron phthalocyanine is concerned, but not for the cobalt complex.

3. The cobalt and copper complexes do not catalyze the electrochemical reduction of hydrogen peroxide any more than carbon black. The effect found for the iron complexes can be due to an electrochemical as well as a chemical reason, and fluorination shows the same trend as found for the chemical and electrochemical reductions.

4. Copper complexes show an exceptional

TABLE 3  
OVERPOTENTIALS (mV AT 1  $\mu$ A) OF OXYGEN REDUCTION FOR FLUORINATED IRON  
AND COBALT PHTHALOCYANINES

Metal ion:		Fe <sup>2+</sup>			Co <sup>2+</sup>		
Ligand	pH:	14	6	0	14	6	0
Phthalocyanine		-270	-380	-460	-330	-430	-560
Tetrafluorophthalocyanine		-390	-460	-620	-340	-440	-570
Hexadecafluorophthalocyanine		-250	-420	-490	-330	-430	-560

activity in the chemical system, in contrast to the electrochemical system where they show only a slight activity, compared to a total inactivity of the nickel and zinc complexes.

5. The electrocatalytic effect of Fe<sup>2+</sup>-phthalocyanine is equal to that of the Fe<sup>3+</sup> complex, which contradicts results found for the chemical system, where the Fe<sup>3+</sup> complex is much more active (13).

Point 5 favors a redox mechanism as has been suggested recently (14), where the catalyst is oxidized chemically into a higher oxidation state by the oxygen and reduced subsequently by the electrode. According to such a mechanism, a steady state of Fe<sup>2+</sup>- and Fe<sup>3+</sup>-phthalocyanine would have to be formed on the electrode, independent of which oxidation state is initially present. It would also be in agreement with the effects caused by fluorination. Moderate fluorination increases the oxidation potential of iron phthalocyanine, because of which catalytic activity decreases. On subsequent fluorination, the catalyst starts to act as an electron acceptor, which means that it is reduced at the electrode first and oxidized by the oxygen in a subsequent step. Such a change in mechanism can cause an increase in rate as has been shown for the chemical reaction (3). The effect of fluorination can also be of a chemical nature, however, in that the catalase activity of iron phthalocyanine is modified, but not its electrochemical activity. This would explain why cobalt phthalocyanine is not influenced, because it does not show catalase activity when unfluorinated. The redox mechanism can also explain the low activity of iron tetraphenylporphyrin in acidic

solution. The oxidation potential of this complex is very low in comparison with the others, and at the high potentials of the electrode in acidic solution, the concentration of the Fe<sup>2+</sup> complex would be extremely small.

Other mechanisms have been put forward where the catalyst interacts with the oxygen to form an adduct (8, 9), which is subsequently reduced at the electrode. The chemisorption of oxygen on these complexes is very low at room temperature (15), and it may be that charge transfer interactions, like the ones proposed for the chemical system, also play a role in the electrochemical reaction, when such a mechanism is active.

A redox mechanism, as well as adduct formation, ought to be dependent on substitution, especially by strongly electron attracting substituents like fluorine. Why cobalt phthalocyanine does not show this effect assuming such a mechanism, has yet to be explained. Considerable refinement of the proposed mechanisms is necessary to explain all the experimental facts, and additional comparative measurements between chemical and electrochemical activity can be of great help in this respect.

#### REFERENCES

1. MANASSEN, J., AND BAR-ILAN, A., *J. Catal.* **17**, 86 (1970).
2. WOLBERG, A., AND MANASSEN, J., *J. Amer. Chem. Soc.* **92**, 2982 (1970).
3. BAR-ILAN, A., AND MANASSEN, J., in "Proceedings of the Fifth International Congress on Catalysis" (J. W. Hightower, Ed.), p. 1149. North-Holland/Amer. Elsevier, New York, 1973.

4. BAR-ILAN, A., AND MANASSEN, J., *J. Catal.* **33**, 68 (1974).
5. BAR-ILAN, A., AND MANASSEN, J., *Intra-Sci. Chem. Rep.* **6**, 65 (1972).
6. JASINSKY, R., *J. Electrochem. Soc.* **112**, 526 (1965).
7. JAHNKE, H., AND SCHONBORN, M., *Angew. Chem., Nachr. Chem. Techn.* **18**, 319 (1970).
8. SAVY, M., ANDRO, P., BERNHARD, C., AND MAGNER, G., *Electrochim. Acta* **18**, 191 (1973).
9. ALT, H., BINDER, H., AND SANDSTEDT, G., *J. Catal.* **28**, 8 (1973).
10. KOZAWA, A., ZILIONIS, V. E., AND BRODD, R. J., *J. Electrochem. Soc.* **117**, 1470 (1970).
11. KOZAWA, A., ZILIONIS, V. E., AND BRODD, R. J., *J. Electrochem. Soc.* **118**, 1705 (1971).
12. COOK, A. H., *J. Chem. Soc.* **1938**, 1761, 1768, 1774, 1845.
13. BAR-ILAN, A., AND MANASSEN, J., unpublished data.
14. BECK, F., *Ber. Bunsenges. Phys. Chem.* **77**, 353 (1973).
15. CONTOUR, J. P., LENFANT, P., AND VIJH, A. K., *J. Catal.* **29**, 8 (1973).

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