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Metal Complexes of Phthalocyanine and $\alpha,\beta,\gamma,\delta$-Tetraphenyl Porphyrin as Heterogeneous Catalysts in Oxidative Dehydrogenation. Correlation between Catalytic Activity and Redox Potential

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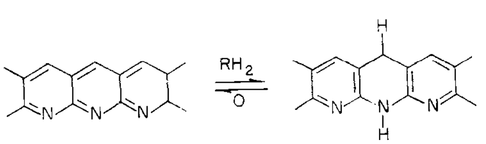
The catalytic activity of tetraphenyl porphyrin and phthalocyanine complexes for the heterogeneous dehydrogenation of cyclohexadiene in the gas phase, using nitrobenzene as the oxidizing agent, was measured. A general correlation of catalytic activity with polarographically measured first oxidation potentials was found. By controlled potential electrolysis, coulometry and EPR measurements, the mode of oxidation of these complexes in solution was ascertained. The first oxidation of Fe^{2+} and Co^{2+} tetraphenyl porphyrin appeared to be at the central metal atom, while the Zn^{2+} and Cu^{2+} complexes gave ligand oxidation. For the Ni^{2+} complex the potentials for central metal atom oxidation and ligand oxidation were very close together. Therefore, these complexes were capable of two kinds of redox processes, either valency change of the central metal atom (Fe^{2+}, Co^{2+}) or ligand oxidation/reduction (Cu^{2+}, Zn^{2+}) or both (Ni^{2+}). By comparing these principles with results obtained earlier on the catalytic activity of these complexes for cumene oxidation, this difference in redox mechanism could be correlated with the catalytic activity of the complexes in question.

INTRODUCTION

In previous publications (*1*) we reported that annellated aromatic molecules, polymers as well as monomers, may serve as catalysts for oxidative dehydrogenation. It was shown that these systems tend to take up hydrogen, which may be removed again by oxidation, thus opening the way for an oxidation/reduction cycle as shown for pyrolyzed polyacrylonitrile:

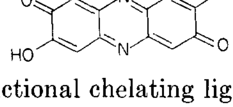


(1)

If, instead of pyrolyzed polyacrylonitrile, a polymer is used which contains benzoquinone groups (*2*), hydrogen transfer occurs to a much greater extent, but higher temperatures are necessary for reoxidizing the catalyst.

These results suggest that a correlation may exist between the redox potential of the cycling system and its catalytic activity. Quantitative verification of this suggestion is difficult to obtain, however, because of the intractable nature of these polymers.

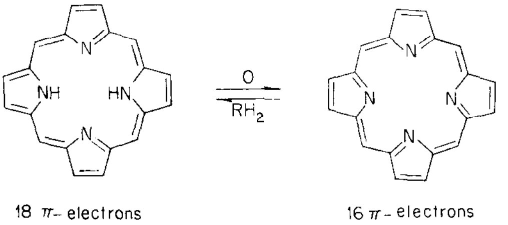
The same difficulty persists when the field is extended into that of metallo-organic polymers. The quinone group containing monomer 2,6-dihydroxy-3,7-diketo phenazine



(2)

is a bifunctional chelating ligand and forms polymers with many metal ions. The catalytic activity of these polymers for oxidative dehydrogenation could be shown to be dependent on the metal ion used. As complexation with metal ions is known to change the redox potential of a quinone, these results also suggest that some correlation between redox potential and catalytic activity should exist.

For a more quantitative verification, however, the materials have to be soluble so that redox potentials could be measured with some accuracy. Therefore, we decided to study the catalytic activity of complexes of phthalocyanine (Phc) and tetraphenyl porphyrin (TPP) for this reaction. Both form thermostable complexes with many metal ions, are soluble in certain organic solvents and can be considered capable of the same kind of redox cycle as was pictured in scheme (1):



(3)

The 16 π-electron system is very unstable and tends to be reduced again into the 18 π-electron system by taking up electrons or hydrogen atoms. Therefore, one might expect catalytic activity when an oxidizing agent and a hydrogen donor would be passed simultaneously over the catalyst.

The catalytic activity of phthalocyanine complexes has been studied before, covering a wide range of reactions such as the decomposition of H_2O_2 (*3*), H_2/D_2 exchange (*4*), the decomposition of hydrazine (*3*), and that of formic acid (*5*). The catalysis of oxidation of hydrocarbons and decomposition of the hydroperoxide formed was studied in detail (*6*) and is relevant to our work as discussed below. The catalytic activity of porphyrins has been less studied, but they are known to be active in many enzymes.

In our previous work we used cyclohexene as the hydrogen donor and air as the oxidant. In order to be able to work at lower temperatures we chose the diolefin cyclohexadiene-1,4, and instead of oxygen we used a milder oxidizing agent, nitrobenzene.

EXPERIMENTAL METHODS

Materials

Phthalocyanine and its complexes. All were prepared and characterized as described in Ref. (*7*).

Tetraphenyl porphyrin. As described in Ref. (*8*).

Tetraphenyl porphyrin complexes. All complexes were prepared as described in Ref. (*9*), except for the Ni complex which was synthesized according to Ref. (*10*).

Cyclohexadiene. To a 10% solution of benzene in liquid ammonia, a fourfold molar excess of Li chips was added and the solution was stirred until the Li had gone into solution. An amount of anhydrous methanol equivalent to that of the Li metal was added dropwise under stirring. The ammonia was allowed to evaporate at room temperature and the remaining solution was extracted with dilute HCl, until all the LiOH had been removed. Fractional distillation of the organic layer gave a 70% yield of chromatographically pure cyclohexadiene-1,4.

Analysis

Cyclohexadiene, benzene, aniline, and nitrobenzene were separated by gas chromatography over a column of silicone gum 15% on acid washed chromosorb 30–60 mesh. The temperature was programmed from 50 to 250° at 15°/min.

Catalytic Measurements

The complexes were heated in a vertical Pyrex tube and the cyclohexadiene/nitrobenzene mixture was introduced at the top by means of a syringe pump of variable speed. Samples of the effluent were taken at regular intervals with a microsyringe and introduced directly into the gas chromatograph. After completion of the reaction, the catalyst was dissolved in a proper solvent and the solution was studied for decomposition products by spectroscopy. Only those experiments where the catalyst was recovered unchanged were considered meaningful.

Cyclic Voltammetry

The solvents were purified by passing them over a column of alumina adsorbent, immediately before use. The electrolyte in all cases was tetrabutylammonium perchlorate in a 0.1 *M* concentration. The working electrode was a Beckman platinum disc electrode (Beckman No. 39273) and the auxiliary electrode, a piece of 0.5-mm diameter Pt wire. The saturated aqueous calomel electrode was separated from the solution by a fritted glass disc and a Luggin capillary. Cyclic potential sweeps were generated by a Hewlett-Packard 3300A function generator in conjunction with a Wenking 66TS10 potentiostat. Sweeps ranged from 1 to 150 V/min.

Controlled Potential Coulometry

The working electrode was made of Pt mesh. The auxiliary and reference electrodes were as before. They were separated from the solution by salt-bridges of a saturated solution of tetraethylammonium perchlorate in acetonitrile. The current was integrated using a voltage-to-frequency converter with an electronic counter (*11*). Electrolysis was stopped after the current had decreased to 1% of its initial value, which never took more than 15 min.

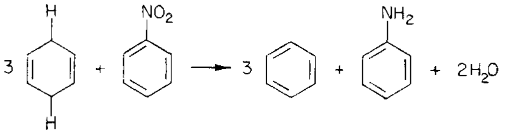
Electron Paramagnetic Resonance (EPR) Measurements

The solution obtained after electrolysis was transferred into a flat quartz cell for measurements at room temperature and into quartz ampoules of 2-mm internal diameter for measurements at liquid nitrogen temperature. The measurements were performed on a Varian V4502-15 EPR spectrometer.

RESULTS

Catalytic Measurements

The stoichiometric reaction between cyclohexadiene and nitrobenzene is as follows:



(4)

As cyclohexadiene tends to dehydrogenate spontaneously under certain conditions, experiments were only considered to be meaningful when benzene and aniline were formed in the ratio of 3:1.

The purely organic ligands phthalocyanine and tetraphenyl porphyrin were not active under our standard conditions. Although their first oxidation potentials were in the same region as those for the Cu^{2+} and Ni^{2+} complexes, which are slightly active, it can be seen from cyclic voltammetry that their oxidation products tend to decompose irreversibly, which is the probable reason for their inactivity. Their metal complexes exhibited varying activities, however, and results are summarized in Table 1, where the metal ions are arranged according to *d*-electron configuration.

The numbers in Table 1 require some

TABLE 1

CONVERSION INTO BENZENE (% OF CYCLOHEXADIENE) OBTAINED BY PASSING A NITROBENZENE–CYCLOHEXADIENE MIXTURE OVER COMPLEXES OF PHTHALOCYANINE[a] AND TETRAPHENYL PORPHYRIN[b] WITH BIVALENT TRANSITION METALS[c,d]

Electronic configuration	Metal ion	Ligand Phc	Ligand TPP	Metal ion	Ligand Phc
d^5	Mn	20			
d^6	Fe	12		Ru	36
d^7	Co	6.2	18		
d^8	Ni	1.4	4	Pd	5
d^9	Cu	1.5	4.3		
d^{10}	Zn	2.6	6		

[a] Hourly liquid space velocity (moles cyclohexadiene/mole of catalyst/hr) = 1.28.

[b] Hourly liquid space velocity (moles cyclohexadiene/mole catalyst/hour) = 2.13.

[c] $T = 250°C$.

[d] Mole ratio cyclohexadiene/nitrobenzene = 4.

explanation. When the reaction was started, conversions into benzene and aniline increased slowly with time until a constant value was reached, which stayed constant for hours at a time. This value was recorded in Table 1. Conversions were reproducible for different synthetic batches of catalyst and were independent of crystal size. This is in accordance with our experience in general, using organic materials as heterogeneous catalysts, that activity is not dependent on surface area the way it is for inorganic catalysts, and presumably more than the surface layers participate in the reaction.

We see that for the first-row transition elements conversions decrease from d^5 to d^8 and increase somewhat from d^8 to d^{10}. The Ru and Pd phthalocyanines are both more active than their first-row counterparts and the d^8 Pd complex is less active than the d^6 Ruthenium one.

Cyclic Voltammetry

Most of the complexes of Table 1 were sufficiently soluble to allow measurement of their redox potentials. The method of cyclic voltammetry measures the current generated when the potential on a stationary Pt electrode is changed at a certain rate in a cyclic manner. Because the frequency of the cycles can be changed between wide limits, this method can give information about the stability of the product generated by the electrochemical reaction in Table 2 the first oxidation potentials are recorded for most of the complexes reported in Table 1. All oxidation processes recorded were reversible and the stability of the oxidation products could be verified by EPR measurements and coulometry. The trend in the potentials is opposite to that of the catalytic activities; potentials increase from d^5 to d^8 and decrease after that.

TABLE 2

First Oxidation Potentials of Phthalocyanine[a] and Tetraphenyl Porphyrin[b] Complexes of Bivalent Transition Metals in Volts Versus Saturated Aqueous Calomel Electrode[c]

Electronic configuration	Metal ion	Ligand Phc	Ligand TPP	Metal ion	Ligand Phc
d^5	Mn	−0.11			
d^6	Fe	+0.16	−0.32	Ru	+0.06
d^7	Co	+0.77	+0.52		
d^8	Ni	+1.1	+1.01	Pd	+1.1
d^9	Cu	+1.0	+0.99		
d^{10}	Zn	+0.68	+0.78		

[a] Solvent 1-chloronaphthalene.

[b] Solvent benzonitrile.

[c] TPP complexes: 10^{-3} M; Phc complexes: filtered, saturated solutions; electrolyte: Bu_4NClO_4 0.1 M.

[d] Solvent hexamethyl phosphoramide.

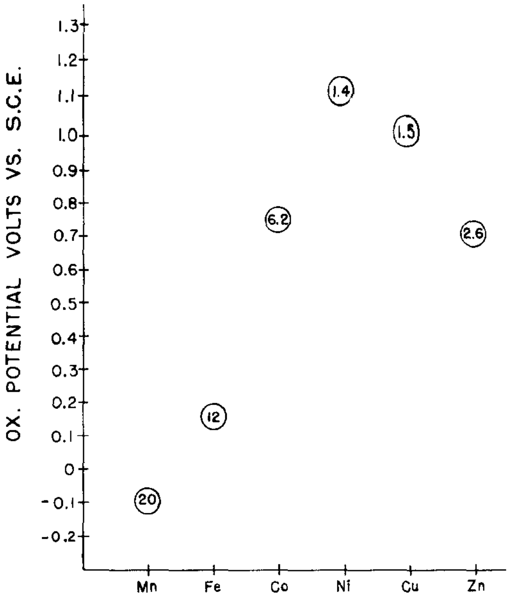


Fig. 1. Catalytic activities of phthalocyanine complexes as a function of atomic number and oxidation potential: Numbers in circles indicate conversion into benzene under standard conditions (Table 1).

So, in general, it can be concluded that a lower first oxidation potential corresponds to a higher catalytic activity. To see things more in perspective catalytic activities are plotted as a function of atomic number and oxidation potential in Fig. 1 for the phthalocyanine complexes.

In addition to the general trend, we see that the Zn complex, although it is oxidized at a lower potential, is not as active as the Co complex; therefore, oxidation potential does not seem to be the only variable on which catalytic activity depends. To understand this phenomenon we have to study the oxidation mechanism in more detail.

Unfortunately, the Phc complexes are not very suitable for this kind of a study because of their low solubility. Therefore, the TPP complexes were chosen for a detailed electrochemical and EPR study and the results found seemed to apply equally well to the Phc complexes.

Electrochemical and EPR Studies

By controlled potential electrolysis it is possible to oxidize a TPP complex in solution at a fixed potential and to check whether one or more than one electron is removed. The products were reasonably stable and could be analyzed by electron paramagnetic resonance (EPR).

Removal of an electron from the central metal ion (change of valency) changed the EPR spectrum drastically. If on the other hand the electron was removed from the organic ligand, while the valency of the central metal ion did not change, a spectrum characteristic of the ion-radical species was obtained. Therefore, both processes could be clearly distinguished. The detailed results of this investigation will be published in a separate communication (*12*) and here we report only the results relevant to the catalytic measurements. In Fig. 2, they are presented graphically.

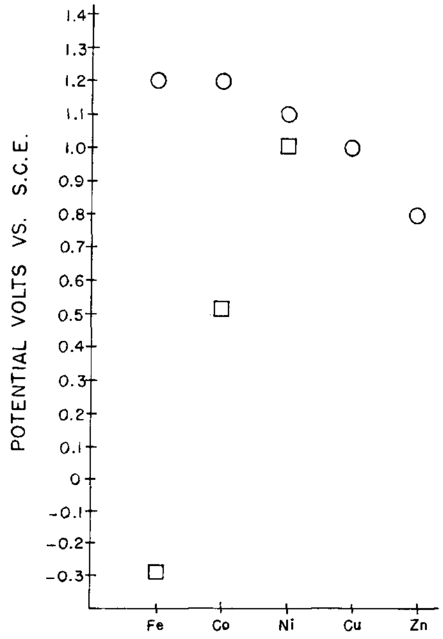


FIG. 2. Oxidation behavior as a function of potential and atomic number for TPP complexes: □ change of valency of the central metal ion; ○, removal of electron from the organic ligand.

Considering Fig. 2, we can understand why in Fig. 1 the first oxidation potentials as a function of atomic number went through a maximum. Valency change from the bivalent to the trivalent state depends linearly on atomic number for Fe^{2+}, Co^{2+}, and Ni^{2+} (actually, it can be shown that they depend linearly on the third ionization potential of the metal atom in question). The potential for ligand oxidation does not change drastically from Fe to Ni but shifts to appreciably lower values for Cu and Zn. There is a clear theoretical basis for this behavior as will be discussed elsewhere (*12*). Here, it is sufficient to note that the first oxidation potentials for Fe^{2+} and Co^{2+} TPP correspond to a valency change of the metal ion; for Cu^{2+} and Zn^{2+} TPP on the other hand, they correspond to a ligand oxidation. For the Ni complex, valency change and ligand oxidation occur at nearly the same potential.

Therefore, we can understand now, while catalytic activities decrease from Fe^{2+} to Ni^{2+} and increase again from Ni^{2+} to Zn^{2+}, this increase is not as we expected it to be on the basis of the potentials alone. The mechanism of oxidation has changed from valency change to ligand oxidation and the latter process seems to be less efficient for catalyzing our reaction.

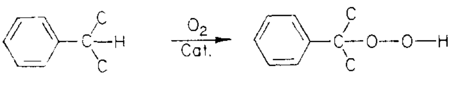
DISCUSSION

The present results showed a *general* correlation of catalytic behavior with oxidation potential and a more *detailed* dependence on the mechanism of oxidation. This problem of metal versus ligand oxidation has much wider implications, however, and exists in principle for every catalyst consisting of a metal ion surrounded by ligands, as is the case for all catalysts that are not purely metallic, but are composed of metal compounds.

Good correlation between the catalytic activity of the solid phase and physical parameters in solution could be found, since the whole catalytically active entity, a metal ion surrounded by an extended π-electron system, could be transferred into solution unchanged. The importance of these results is twofold.

1. They show that the center of catalytic activity has to be sought in the molecule, which means metal ion together with its ligand, and that solid state effects are of secondary importance. We are engaged in a study to find more information about the effects that are characteristic of the solid phase.
2. They show that a redox cycle via ligand oxidation/reduction has an impact different from that caused by a changing valency of the metal ion. This is not only restricted to the reaction described here, but actually becomes much clearer when we consider other reactions.

Hock and Kropf have studied the catalytic activity of phthalocyanine complexes for the oxidation of cumene some years ago *(6a)*:



Cumene Cumenehydroperoxide

They found that Mn^{2+}, Fe^{2+}, and Co^{2+} phthalocyanines were good catalysts for this reaction but that the hydroperoxide could not be recovered unchanged, it was broken down. The Zn^{2+} and Cu^{2+} phthalocyanines on the other hand were also catalytically active but did not break down the hydroperoxide. The Ni^{2+} compound, in their words, occupied an intermediate position in that it only broke down part of the hydroperoxide formed. This was not well understood at the time, but becomes quite clear when we consider the present results. Hydroperoxide decomposition is considered to be catalyzed by a metal ion of variable valency as follows:

$$M^{2+} + RCOOH \longrightarrow RCO^{\cdot} + OH^{-} + M^{3+}$$
$$M^{3+} + RCOOH \longrightarrow RCOO^{\cdot} + H^{+} + M^{2+}$$

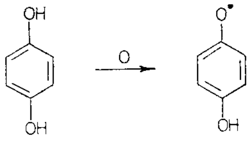
It is generally assumed that a condition for this reaction is an intermediate complex between the hydroperoxide and the metal ion *(13)*. We have seen that the Fe^{2+} and Co^{2+} complexes can give a redox cycle by way of changing valency. The square planar structure of the complex gives ample opportunity for coordination with the hydroperoxide and, therefore, the two conditions for decomposition in the latter are fulfilled. The Zn^{2+} and Cu^{2+} complexes on the other hand can give a redox cycle by way of the ligand and even when the hydroperoxide is complexed with the metal ion it does not necessarily have to be decomposed as the valency of the metal ion does not change. The Ni^{2+} complex is capable of ligand oxidation/reduction as well as valency change and therefore gives only partial hydroperoxide breakdown.

We see here a parallel with acid catalysis. There is a correlation between a thermodynamic quantity, the oxidation potential and a kinetic quantity, the catalytic activity and, as in acid catalysis where there is a difference in catalytic activity for Brønsted and Lewis acids, also in this case, a change in redox mechanism changes the catalytic activity.

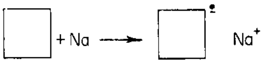
In the introduction we described the oxidation/reduction cycle as a quinone/hydroquinone reaction which is a two-electron process. The first step actually is the formation of the semiquinone:

$$\boxed{Me^{2+}} \xrightarrow{O} \boxed{Me^{3+}} \quad \text{and}$$
$$\boxed{Me^{2+}} \xrightarrow{O} \boxed{Me^{2+}}^{\pm}$$

With the metallo-organic compounds, by analogy, we can indicate two different kinds of such an intermediate:



We see here an analogy with the work described by Tamaru and co-workers (*14*) where an electron acceptor is reacted with sodium metal, which gives an intermediate, which is catalytically active for many reactions:



Therefore, by the use of organic model catalysts it has been possible to describe several well defined intermediate stages which seem to be important for the catalytic reaction and the analogy with unsaturated valencies proposed to be active on the surface of iorganic heterogeneous catalysts is obvious.

ACKNOWLEDGMENTS

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