

Heterogeneous and Homogeneous Catalysis by Substituted Cobalt Tetraphenylporphyrins, and Correlations with IR Spectra

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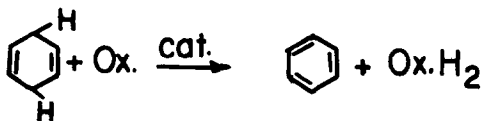
Received January 30, 1973; revised September 19, 1973

The catalytic activity of Cobalt tetraphenyl-porphyrin is measured as a function of substituents on the phenyl ring. The model reaction is the oxidative dehydrogenation of cyclohexadiene-1,4, using nitrobenzene as the oxidant. Catalytic activity is measured heterogeneously as well as homogeneously under the same conditions of temperature and pressure. Infrared frequencies of a specific metal-dependent deformation absorption are measured in solution as well as the solid phase.

A smooth correlation is shown to exist between catalytic activity, homogeneous as well as heterogeneous, and infrared frequency, measured in solution. No such correlation exists with I.R. frequency measured in the solid state. This is explained by conformation differences of the tetraphenyl porphyrin molecule in solution and in the solid state. The causes of the similarities in catalytic behavior between the homogeneous and the heterogeneous system are discussed.

INTRODUCTION

In the past, we have reported that there exist correlations between the catalytic activities of metallo-porphyrins for a redox reaction and their physical properties. The reaction in question was the oxidative dehydrogenation of cyclohexadiene-1,4 using nitrobenzene or air as the oxidant (Ox):



Scheme I

Correlations were shown to exist between catalytic activity and the redox potential of the catalyst, with nitrobenzene (1) as well as air (2) as the oxidant.

The rate determining step in Scheme I was shown by us to be the electron transfer from catalyst to oxidant (nitrobenzene or oxygen), which may be total (radical ion formation) (1) or partial (charge transfer com-

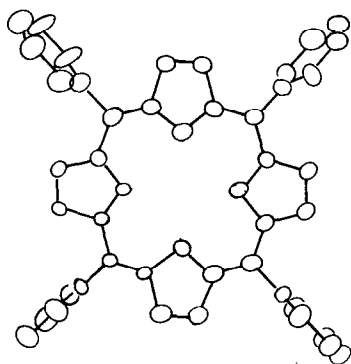
plex formation) (3). In the case of the cobalt complex, it was further shown that it is the central metal ion that transfers the electron, and not the ligand (4).

With these complexes, it is possible to modify the electron density at the central metal atom (and with it the catalytic activity) by substituents on the periphery of the π -electron-system.

For phthalocyanine complexes, we could show that fluorine substitution has a dramatic influence on catalytic activity, which could be correlated with the equilibrium constant of charge-transfer complex formation between catalyst and oxidant or catalyst and hydrogen donor (3).

Contrary to the phthalocyanines, the tetraphenylporphyrin molecule is not planar and the phenyl rings make an angle of near to 90° with the rest of the molecule (Scheme II).

One would expect, therefore, that resonative influences of substituents on the phenyl groups are not relayed to the center of the molecule, where the metal atom is situated. On the other hand, it has been sug-



Scheme II

gested on the basis of spectral and surface tension measurements (5, 6) that in the dissolved state the phenyl groups are more coplanar than in the solid state. Furthermore, it has been shown by NMR techniques that, in Ru-tetraphenylporphyrin, the phenyl group starts to rotate in solution at about 100°C (7). Therefore, it might be that in solution resonant influences are felt more than in the solid state.

On the other hand, studies have been performed on the infrared spectra of metalloporphyrins showing that the ligand deformation absorption in the 920–1000 cm^{-1} region is metal-dependent. The infrared stability order followed the order of stability of the metalloporphyrins as derived from consideration of replacement reactions, dissociation reactions and various electronic spectral data (8–10). By measuring this infrared frequency, one can obtain an indication of how the stability of the cobalt-ligand bond changes as a function of substituents on the phenyl ring, and this can be done in solution as well as in the solid state.

The metallo-tetraphenyl porphyrins, because of their solubility in organic solvents, afford the possibility of measuring catalytic activities of the solid as well as its solution. We report here measurements of infrared absorptions of substituted porphyrins in the solid state as well as in solution, which are compared with their catalytic activities in the solid state (heterogeneous catalysis) as well as in the dissolved phase (homogeneous catalysis).

EXPERIMENTAL

Syntheses

H_2 (tetrakis *p*- OCH_3)*T.P.P.*, H_2 (tetrakis *p*- NO_2)*T.P.P.* and H_2 (tetrakis *p*- CH_3)*T.P.P.* were synthesized from pyrrole and the corresponding *p*-substituted benzaldehyde, according to the method of Martell (11).

H_2 *T.P.P.* was synthesized from pyrrole and benzaldehyde in propionic acid according to the modified method of Adler (12).

H_2 (tetrakis 4-pyridine) *T.P.P.* was synthesized from pyrrole and 4-pyridine carboxaldehyde according to G. B. Fleischer (13).

H_2 (tetrakis pentafluoro) *T.P.P.* was synthesized from pyrrole and pentafluorobenzaldehyde, according to Longo (14).

H_2 (tetrakis 3-pyridine) *T.P.P.* was synthesized by reacting pyrrole and 3-pyridine carboxaldehyde in propionic acid, followed by chromatographic separation on Kiesel gel in chloroform solution.

H_2 (tetrakis *m*- NO_2) *T.P.P.* was synthesized by reacting pyrrole and *m*-nitro benzaldehyde in a mixture of 1/25 chloroacetic acid-benzene. Separation was carried out chromatographically on Kiesel gel in chloroform solution.

H_2 (tetrakis *p*- $N(CH_3)_2$) *T.P.P.* was prepared by reacting pyrrole, *p*-dimethyl-amino benzaldehyde and zinc acetate in pyridine solution in ampoules at 170°C. After hydro-

lyzing the Zn^{II} (tetrakis *p*- $N(CH_3)_2$) *T.P.P.*

to the metal-free complex, using 10*N* HCl, purification was carried out on Kiesel gel in $CHCl_3$ -ether solution.

H_2 (tetrakis *p*- OH) *T.P.P.* was prepared by reacting pyrrole and *p*-hydroxy-benzaldehyde in propionic acid and was purified by Soxhlet extractions with ether.

H_2 (tetrakis *p*- $\bar{O}Na^+$) *T.P.P.* was prepared by potentiometric titration of H_2 (tetrakis

p-OH) T.P.P., with a standard solution of NaOH.

Co^{II} complexes of all the above metal-free (substituted) T.P.P. were prepared by reacting Co^{II} acetate with the porphyrin ligands in either pyridine or acetic acid solutions. After adding chloroform or benzene, the mixture was treated repeatedly with distilled water until all the pyridine (or acetic acid) and Co^{II} were removed.

More detailed descriptions will be given in a separate article dealing with the synthesis of these porphyrin compounds.

Heterogeneous Catalysis

The details of this technique have been described previously (1). A mixture of nitrobenzene and cyclohexadiene-1,4 is passed by means of a syringe pump into a vertical pyrex reactor, where it is vaporized and passes over the catalyst in the gaseous phase. The catalyst consists of several grams of the solid metallo-organic material. We have indicated in the past (15) that, with the materials in question, surface area is not to be relied upon for measuring specific catalytic activities, and that it is better to calculate activity per mole of catalyst.

The products benzene and aniline are separated by gas chromatography, using a silicon gum column, and conversion into both are used for computing the catalytic activity. Conversions can be measured this way with a reproducibility of 0.1%.

Homogeneous Catalysis

The technique known as "supported liquid phase catalysis" was used (16). The catalytic material (10 mg) is dissolved in 5 ml of chloroform, together with 1 g of a high boiling solvent (Arochlor 5460, a chlorinated biphenyl plasticizer, which is not volatile under our reaction conditions). To this solution, 5 g of a catalyst support is added (SAHT 99, a low-surface sintered alumina, surface area 2.6 m²/g, pore size distribution between 0.03 and 10 μ m, obtained from the Carborundum Company, Latrobe, Pa.). The chloroform is evaporated under vigorous agitation, and the catalytic material remains dissolved in the Arochlor within the pores of the support.

This system is heated under argon to the same temperature as used with the solid phase catalysts and the reaction performed under exactly the same conditions. It is assumed that the reaction occurs in the homogeneous solution of the catalytic material and it is remarkable that 10 mg of material is capable of giving about the same conversions as several grams of solid catalyst. Also in this case, catalytic activity was computed as conversion per mole of catalyst.

Although the diffusion of reactants into the solution and of products out of the solution, is certainly a factor determining the reaction velocity, it may be assumed to be approximately equal for all catalysts concerned, because the difference in velocity caused by the substituents is comparatively small.

Infrared Measurements

All I.R. spectra were measured on a Perkin Elmer 125 instrument, which allows for measuring these frequencies with an accuracy of ± 1 cm⁻¹. The solid phase spectra were measured on material dispersed in hexachlorobutadiene, while solution spectra were measured as CH₂Cl₂ solutions in 1/2 cm cells.

RESULTS

In Table 1, the characteristic infrared frequencies are given in the solid as well as the dissolved phase. They are arranged in order of descending electron donating power of the substituents according to the Hammett-Taft scale. Dimethylamino is the most electron-donating substituent and pentafluoro the most electron-attracting one.

We see that the frequencies, which are measured in solution, decrease gradually with decreasing electron-donating power of the substituents. The frequencies measured in the solid phase do not show this gradual dependence, but show a maximum with the p-methyl substituent and the non-substituted phenyl.

In Table 2, the catalytic results are given for the oxidative dehydrogenation of cyclohexadiene-1,4 with nitrobenzene as the oxidant. In order to be able to compare the results of the heterogeneously catalyzed reaction with those of the homogeneous ca-

TABLE 1
CHARACTERISTIC INFRARED FREQUENCIES FOR
SUBSTITUTED COBALT TETRAPHENYLPORPHYRINS
IN cm^{-1}

T.P.P. Substituent	Dissolved Phase	Solid Phase
$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{p-N} \\ \diagup \\ \text{CH}_3 \end{array}$	997	996
p-OH	998	991
p-ONa	998	991
p-OCH ₃	996	993
p-CH ₃	993	1002
H	991	1000
3-Pyridine	987	992
4-Pyridine	988	992
3-NO ₂	985	994
4-NO ₂	984	994
Pentafluoro	980	985

talysis, conversions into benzene and aniline, calculated per mole of catalyst, were taken as unity for the non-substituted catalyst in both phases. The other numbers in Table 2 are the relative activities, compared to the

TABLE 2
RELATIVE CATALYTIC ACTIVITIES OF SUBSTITUTED
COBALT TETRAPHENYLPORPHYRINS IN
DISSOLVED AND SOLID PHASES

T.P.P. Substituent	Dissolved phase ^{a,b} (Homogeneous Catalysis)	Solid phase ^{a,b} (Heterogeneous Catalysis)
$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{p-N} \\ \diagup \\ \text{CH}_3 \end{array}$	1.44	
p-OH	1.54	1.38
p-ONa	1.70	1.54
p-OCH ₃	1.18	1.12
p-CH ₃	1.44	1.08
H	1.00	1.00
4-Pyridine	0.94	0.98
3-NO ₂	0.88	0.92
4-NO ₂	0.82	0.88
Pentafluoro	0.80	

^a Temperature, 230°C.

^b Molar ratio $\text{C}_6\text{H}_6/\phi\text{NO}_2 = 4/1$.

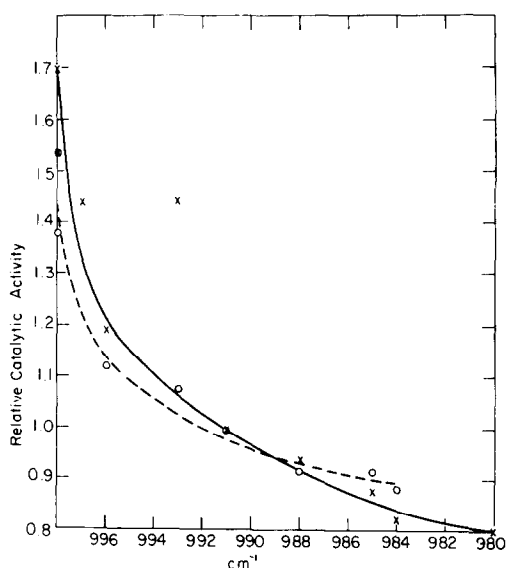


FIG. 1. Catalytic activity as a function of liquid phase infrared absorption frequency. O, heterogeneous catalysis; X, homogeneous catalysis.

non-substituted catalyst under identical conditions.

The differences in catalytic activity caused by the substituents are small. However, even changing the central metal atom in the non-substituted tetraphenylporphyrin does not cause much greater changes, and these, nevertheless, can be directly connected with changes in redox potential (*1*). Therefore, here also, although the changes are small, they are reproducible and are to be considered as significant differences in catalytic activity.

In Fig. 1, catalytic activities in both phases are given as a function of the infrared frequency measured in the liquid phase, and in Fig. 2, the same activities are plotted as a function of the infrared frequency, measured in the solid phase. Both for homogeneous and heterogeneous catalysts, there is seen to be a correlation between the activities and infrared frequencies measured in solution. No correlation whatsoever exists with the frequencies measured in the solid phase.

DISCUSSION

The use of Co-porphyrins in the study of heterogeneous catalysis has certain advantages. Most heterogeneous catalysts have a

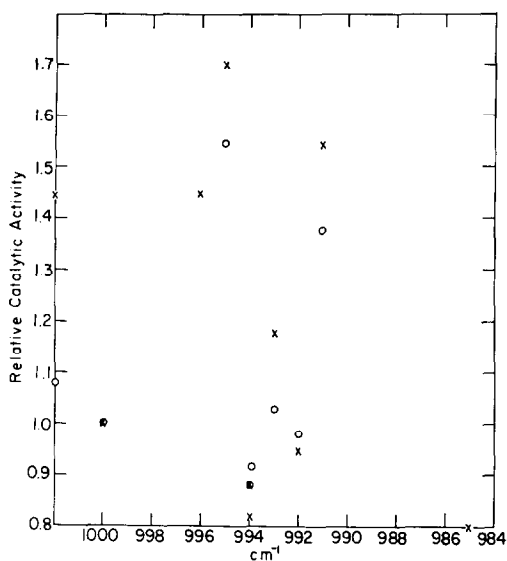


FIG. 2. Catalytic activity as a function of solid phase infrared absorption frequency. ○, heterogeneous catalysis; ×, homogeneous catalysis.

range of catalytic sites that are not identical. In Co-porphyrin, on the other hand, the sites are identical and can be defined as a Co^{2+} -ion, surrounded by a geometrically fixed ligand with a certain π -electron density.

By chemical substitution on the ligand, the I.R. absorption frequency as well as the catalytic activity can be changed, and from Fig. 1 we see that they correlate well. The correlation, however, is not a linear one.

A change of 2 cm^{-1} from 996 to 998 cm^{-1} corresponds with an increase in catalytic activity of about 60%. On the other hand, a change of 16 cm^{-1} in the range of 980–996 corresponds with an increase in catalytic activity of only 40%. It appears that substituents that are more electron-donating than hydrogen influence catalytic activity significantly in this system without affecting the infrared frequency very much. Substituents more electron-withdrawing than hydrogen, on the other hand, influence the infrared absorption frequency without affecting catalytic activity very much. Therefore, the response to induced changes in electron density is different for catalytic activity and infrared frequency in this system.

Catalytic activity is seen to be especially

sensitive to strong electron-donating substituents, and if the purpose is to get higher catalytic activity, substituents have to be selected in this region. It is difficult to find substituents, however, that are more electron-donating than the dimethyl-amino-group, but it might be that in polymeric compounds, where the metal-ion containing π -electron systems are connected by conjugated double bonds, higher electron densities on the cobalt ion can be obtained. Alternatively, a change of the metal ion in the monomeric system can convert it into one that has a lower oxidation potential, and in that case a greater dependence of catalytic activity and I.R. absorption on electron-withdrawing substituents can be expected.

From Fig. 2 we see that no correlation can be found between catalytic activity and infrared absorption measured in the solid state. In order to understand this we have to use the approach of Thomas and Martell (8).

The effects exerted by substituents on aromatic systems are considered to be of an inductive (I) or resonative (R) nature, or a combination of the two. For resonative influences to be felt, π -orbital overlap is necessary, and the system has to be more or less planar. This does not apply to inductive effects. If we are concerned with a substituent like a methoxy-group, its R-effect is felt as electron donation and its I-effect as electron withdrawal. In planar systems, the R-effect is dominant and the methoxy group is considered to be an electron-donating substituent. However, Thomas and Martell, in their study on infrared spectra of metallo-tetraphenylporphyrins, which were measured in the solid phase, found the methoxy-group to be even more electron withdrawing than a chlorine substituent. This was explained by the non-planarity of the tetraphenylporphyrin molecule in the solid state, since the R-effect of the methoxy substituent is not measured in the center of the porphyrin molecule, and only the I-effect is found.

Our results, as given in Table 1, cover a much wider range of substituents and confirm this hypothesis. Maximum frequencies are found for the substituents hydrogen and methyl, which have the smallest electron-withdrawing I-effect as measured by the

Taft σ^* -scale. All other substituents, including those that are electron-donating in solution, absorb at a lower frequency in the solid phase. This seems to confirm that, in the solid phase, only I-effects are felt, while in solution R-effects also contribute.

There remains the question as to why the results of heterogeneous catalysis show approximately the same correlation with the infrared frequency as do those of homogeneous catalysis. This is in accordance with results we found in the past, where catalytic activity in the heterogeneous phase was compared with physical parameters of the catalyst measured in solution.

The reason might be sought in the high temperature of the reaction, since the phenyl groups oscillate enough even in the solid state to allow for a greater degree of coplanarity.

We must take into account, however, that our solid is a molecular crystal, which is held together by intermolecular forces only. Therefore, when reagents are adsorbed on its surface, there is no clear difference between adsorbent and adsorbate. We may say that the porphyrin is dissolved in the nitrobenzene layer as well as the nitrobenzene is adsorbed on the surface. In such a case, the catalytic reaction takes place in this "solution" and behaves similarly to the homogeneous case. This might also explain why conversions are dependent more on the weight of the catalyst than on surface area. This effect is now being studied.

Figure 1 reveals that the catalytic activity of the methyl-substituted porphyrin in the dissolved phase falls far out of the correlation found for all the other substituents. We have no ready explanation for this anomaly.

ACKNOWLEDGMENTS

The authors are grateful to Monsanto Co. for a grant to Dr. Bar-Ilan, and they thank Dr. A. Wolberg for many stimulating discussions.

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