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Catalysis of a Symmetry Restricted Reaction by Transition Metal Complexes. The Importance of the Ligand

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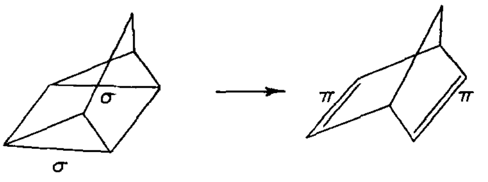
The valence isomerization of quadricyclene to norbornadiene is catalyzed by certain transition metal complexes of phthalocyanine and tetraphenyl porphyrin. To explore the dependence of catalytic activity on the number of *d*-electrons in the metal ion, complexes having a number of *d*-electrons from 5 to 10 were studied. Most of the d^6, d^7, and d^8 ions were active whereas the d^9 and d^{10} ions were inactive. The influence of the stereochemistry of the ligand was studied using cobalt (II) complexes with certain quadridentate Schiff bases whose stereochemistry could be changed by small modifications in structure. Square planarity of the complex appeared to be a condition for catalytic activity. The catalytic reaction could be inhibited by the addition of pyridine bases. 4-Picoline was more effective than pyridine, but 2-picoline did not poison the reaction at all. These results could be explained within the framework of existing theories dealing with this form of catalysis.

INTRODUCTION

It has been shown that certain classes of organic reactions that would ordinarily be expected to occur on the basis of favorable relative thermodynamic stability of reagents and products, do, in fact, exhibit considerable energies of activation. These are caused by a difference in orbital symmetry between the reagents and the products (*1*, *2*). It has also been shown that these reactions may be catalyzed dramatically by certain transition metal complexes (*3*, *4*) and a theoretical explanation for this form of catalysis has been attempted (*5*).

One of the best examples is the valence isomerization of quadricyclene to norbornadiene:†



This reaction involves the breakage of two σ-bonds in a cyclobutane ring and the formation of two π-bonds in a direction perpendicular to that of the original σ-bonds. It takes place thermally with a half time of 14 hr at 140°C, but occurs almost explosively at room temperature (*3*) in the presence of catalytic quantities of di-μ-chloro-bis[π-methallyl]dipalladium(II), dichloro(bicyclo[2.2.1] hepta-2.5-diene) platinum(II) or di-μ-chloro-bis(bicyclo[2.2.1] hepta-2.5-diene) dirhodium(I). Silver(I) and copper(I) salts have been shown to be active in breaking a σ-bond in the cyclobutene ring, by which a butadiene structure is formed (*4*). Recently the reaction of exo-tricyclo[$3.2.1.0^{2.4}$] oct-6-ene has been described, in one case with $Rh_2(CO)_4Cl_2$, as the catalyst (*6*), and the other with tris(triphenyl phosphine) rhodium(I) chloride (*7*). Both catalysts, being compounds of rhodium(I), gave a different pattern of reaction products and, therefore, the ligand is seen to play as an important role in this type of catalysis as it does in other forms

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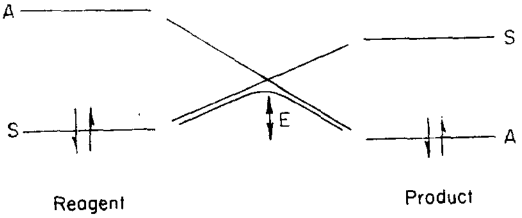
[†] IUPAC designation: tetracyclo[$3.2.0.0^{2.7}.0^{4.6}$] heptane and bicyclo[2.2.1] hepta-2.5-diene.

of catalysis by metallo-organic complexes.

This paper describes how it is possible to throw some light on the influence of the ligand in this type of catalysis. To understand the results we would like to summarize in a simple way the selection rules that govern the energy of activation, and the explanation that has been given for the catalytic effect of a transition metal ion.

An appreciable energy of activation is due to the fact that in the quadricyclene → norbornadiene conversion the highest occupied molecular orbitals of reagent and product have different symmetry properties as do the lowest empty molecular orbitals. If we indicate the two symmetry properties by the letters S and A, the appreciable energy of activation associated with symmetry properties can be explained as follows:



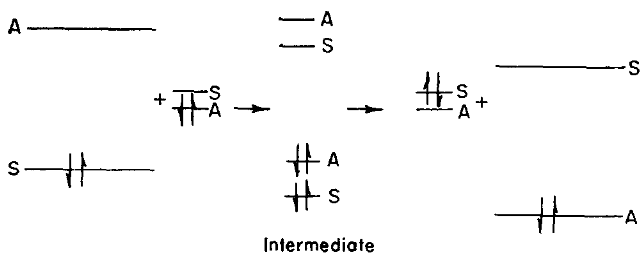
Although the molecular orbitals in the product are at a lower energy level, electrons are forbidden to go from an S-orbital into an A-orbital. The curved line indicates approximately what energetic pathway the electrons must pursue and we see that the energy of activation E is caused only by the difference in symmetry.

If the reagent complexes with a metal ion having orbitals of the same symmetries, we may get the following pathway for the electrons:

After the reagent has complexed with the metal ion, it leaves the complex shell as the thermodynamically more stable product with the result that electrons have moved from the metal A-orbital into the metal S-orbital, which is a small energetic transformation in the case pictured. If we accept this picture, some conditions for the electronic configuration of the catalytically active ion have to be met. In the case of the cyclobutane → diolefin conversion the metal orbitals of A-symmetry are the d_{zx} and p_x orbitals, and of S-symmetry are the d_{zy} and p_y orbitals. For the metal ion to be catalytically active, its A-orbital has to be filled and its S-orbital has to be empty; furthermore, the energy separation between them must be small compared to the energy difference between product and reagent, otherwise the energy gained in the total chemical reaction has to be spent in promoting electrons from the metal A to the metal S-orbital. Therefore, in the d^8 Rh(I), Pd(II), and Pt(II) complexes, either the d_{zy} orbital has to be empty or the higher unoccupied p-shell has to be close enough in energy to the occupied d-shell. In the d^{10} Cu(I) and Ag(I) complexes, all the d-orbitals are filled and we need the cooperation of the empty higher p-shell in any case.

We see here by simple theoretical considerations that the ligand will have a crucial effect on the catalytic activity of the complex in the way it splits up the metal orbitals.

In the results described below, quadridentate chelating ligands were used to insure a minimum of change in the stereochemistry of the complex when moving from one metal ion to the other. The other ap-



Reagent + metal ion → complex → metal ion + product proach was to make gradual small changes in a ligand, which changed the stereochemistry of the complex in a known way and to see how this influenced the catalytic activity.

EXPERIMENTAL METHODS

Materials

Phthalocyanine complexes. All complexes used were prepared and characterized as described in Ref. (*8*).

Tetraphenyl porphyrin complexes. The ligand was prepared according to Ref. (*9*). Most of the other complexes used were prepared as described in Ref. (*10*), except for the nickel complex, which was prepared according to Ref. (*11*).

N,N′-Bis(salicylidene) polymethylenediamine complexes. The synthesis of the ligands and the cobalt complexes has been described in Ref. (*12*).

N,N′-ethylene(salicylideneiminato) cobalt(II). The ligand was prepared according to Ref. (*12*). The metal complexes; by the addition of a solution of 0.02 mole of the acetate in 25 ml of water to a solution of 0.02 mole of the ligand in 100 ml of methanol and boiling at reflux in a nitrogen atmosphere for 10 min.

Bis(N-phenyl salicylaldiminato) cobalt (II). This was prepared according to Ref. (*13*) using aniline instead of *m*-toluidine.

Quadricyclene. Norbornadiene (100 g) was passed over a column of activated alumina and eluted with 900 ml of *n*-pentane. The solution was saturated with 4,4′-bis(dimethylamino)-benzophenone. This solution was irradiated at 0°C for 50 hr with a 450-W Hanovia medium pressure mercury lamp using Pyrex equipment. The conversion was 88%. Distillation at atmospheric pressure using a spinning band column gave a yield of 70 g of pure quadricyclene.

Analysis

Quadricyclene and norbornadiene were conveniently separated by gas chromatography on a 12-ft × ⅛-in. column of silicone-gum QF.1, 20% on 60–80 mesh chromosorb W AW/DMCS. The temperature was programmed from 50–150° at 15°/min; and the injection port was heated not higher than 100°C.

Kinetic Measurements

Quadricyclene and catalyst were dissolved in $CDCl_3$ at 0°C and brought into the cavity of a Varian A56/60 NMR spectrometer held at 35°C. The first order decomposition of the quadricyclene could be followed by integration of the multiplet at $\delta = 1.4$ ppm.

The Vapor-Phase Catalytic Reaction

The catalyst was heated in a vertical Pyrex tube to 150°C in a nitrogen stream (20 ml/min) and the quadricyclene was introduced at the top of the tube by means of a Sage syringe pump. The liquid feed rate was 1.6 ml/hr. Samples of drops coming out of the tube were taken with a microsyringe and injected directly into the gas chromatograph.

Preparation of Supported Liquid-Phase Catalysts (14)

Monsanto's Arochlor 5460 (1 g; this material is a chlorinated biphenyl) and metal complex (10 mg) was dissolved in 5 ml of chloroform. After the solution had become homogeneous (if not, more chloroform or a different solvent had to be used), 5 g of Carborundum SAHT 99, sintered alumina support (⅛ × ⅛-in. pellets) was added and the chloroform evaporated by heating while the flask was vigorously shaken under nitrogen. In such a way, the metal complex remained as a solution in the Arochlor within the pores of the catalyst carrier.

RESULTS

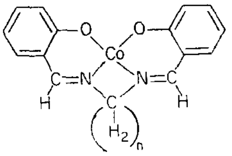
The quadridentate ligands used in this study were phthalocyanine, tetraphenyl porphyrin and some Schiff bases. The phthalocyanine, tetraphenyl porphyrin and *N,N′*-ethylene(salicylideneiminato) complexes are square planar and were used for studying the effects of changing the metal ion. Schiff bases made from salicylaldehyde and other amines were used for studying the effect of gradually changing ligand structure with the same metal ion.

As phthalocyanine complexes in general are not appreciably soluble in the more common solvents, it was difficult to study their catalytic activities in a homogeneous medium. Therefore the technique of supported liquid-phase catalysts was used (*14*). In this technique the catalyst, dissolved in a high boiling liquid, is dispersed within a porous inert carrier and the reagent is passed over the composite catalyst in the vapor phase at elevated temperature. Because of the high temperature solubility, difficulties are less likely to occur.

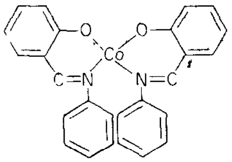
Supported Liquid-Phase Catalysis

Changes of metal ion. Under the conditions chosen for these experiments reactions gave either 100% conversion or did not occur at all. Only in a few cases was less than 100% conversion found. Thus, the approach taken was to determine whether a certain metal complex was catalytically active or not. However, this did not give information about the relative activities of the different complexes. Bivalent metal ions with a number of d-electrons ranging from 5 to 10 were studied as far as they were accessible as a soluble square planar structure. Table 1 gives the results. We see that d^6, d^7, and d^8 ions are mostly active. None of the d^9 and d^{10} ions are active. Manganese phthalocyanine is the only accessible bivalent square planar d^5-complex and it is inactive. Fe(III) tetraphenyl porphyrin acetate which is also d^5 is inactive but it is not bivalent and therefore does not strictly belong in the series. The inactivity of nickel phthalocyanine might be caused by the insolubility of this material.

Change in the ligand structure. N,N'-Bis(salicylidene) polymethylene diamino cobalt(II) complexes have the following structure:



The complex with $n = 2$ is square planar and is catalytically active as shown in Table 1. With $n > 2$ deviations from square planarity occur as can be concluded from magnetic susceptibility measurements (*15*) and with $n = 5$ and 6 the optical spectrum is very much like that of bis(N-phenylsalicylaldiminato) cobalt(II), which is a bidentate complex and which is tetrahedral (*15*):



How these different properties correlate with catalytic activity is shown in Table 2.

The magnetic susceptibility values show that going from $n = 2$ to $n = 3$ already

TABLE 1

CATALYTIC ACTIVITY FOR THE ISOMERIZATION OF QUADRICYCLENE TO NORBORNADIENE, USING SQUARE PLANAR COMPLEXES OF BIVALENT METAL IONS AS SUPPORTED LIQUID-PHASE CATALYSTS[a]

	Electron structure:	d^5	d^6	d^7	d^8		d^9		d^{10}
Ligand	Metal ion:	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Pt^{2+}	Cu^{2+}	Ag^{2+}	Zn^{2+}
Phthalocyanine		−	+	+	−	+[b]	−	−	−
Tetraphenyl porphyrin				+	+		−	−	−
N,N'-Ethylene (salicylideneiminato)				+	−		−		−

[a] Ten mg of complex in 1 g of Arochlor 5460 on 5 g of SAHT 99. $T = 150°C$; N_2 stream of 20 ml/min; Liquid feed of quadricylene 1.6 ml/hr.

[b] Solvent: hexamethyl phosphoramide instead of Arochlor; + = 100% reaction; − = no reaction.

TABLE 2
CONVERSION OF QUADRICYCLENE TO NORBORNADIENE USING DIFFERENT COBALT(II) COMPLEXES AS SUPPORTED LIQUID-PHASE CATALYSTS[a]

Ligand	Conversion to norbornadiene %	Magnetic susceptibility μ_{eff} BM (*15*)	Spectral evidence for tetrahedral configuration (*15*)
N,*N*′-Bis(salicylidene)(CH$_2$)$_2$ diamino	100	2.28	
(CH$_2$)$_3$ diamino	50	4.50	
(CH$_2$)$_4$ diamino	0	4.37	
(CH$_2$)$_5$ diamino	0	4.26	+
(CH$_2$)$_6$ diamino	0	4.23	+
Bis(*N*-phenylsalicylaldiminato)	0	4.34	+

[a] Ten mg of complex in 1 g of Arochlor 5464 on 5 g of SAHT 99; $T = 150°C$; N_2 stream of 20 ml/min; liquid feed of quadricyclene 1.6 ml/hr.

converts a low spin complex to a high spin one and we have to assume that the ligands around the cobalt are tilted out of plane. According to the spectral evidence, only at $n = 5$ are they tilted out of plane enough to resemble a tetrahedral configuration. The complex with $n = 3$ shows a weak activity* (the only case where we found less than 100% conversion), but from $n = 4$ on, the activity is zero. Therefore, tilting the ligands out of plane makes the cobalt complex inactive for this reaction.

For more quantitative measurements of catalytic activity we have to work in a homogeneous medium. This is described in the next section.

Homogeneous catalysis. Only a few of the complexes mentioned in Tables 1 and 2 were sufficiently soluble to measure their catalytic activities in a homogeneous medium. In Table 3 the activities of three of them are compared. The cobalt tetraphenyl porphyrin (CoTPP) was so active that the chloroform started to boil, because of the heat of reaction; and its catalytic activity was appreciably higher than that of the square planar Schiff base.

From the present results, it is sufficiently clear that square planarity is a condition for catalytic activity. To find out whether the reaction takes place at the free octahedral sites of these complexes, an attempt was made to inhibit the catalytic activity by the addition of pyridine bases which are known to coordinate at the octahedral sites of metallo-porphyrins (*16*). Figure 1 shows how the addition of these bases influences the half time of reaction when Co–tetraphenyl porphyrin is used as the catalyst.

TABLE 3
COMPARISON OF CATALYTIC ACTIVITIES FOR THE CONVERSION OF QUADRICYCLENE TO NORBORNADIENE IN CHLOROFORM SOLUTION[a]

Complex	Catalytic activity
Cobalt tetraphenyl porphyrin	Vigorous decomposition
N,*N*′-Ethylene(salicylideneiminato) cobalt(II)	$t_{\frac{1}{2}} = 21$ min
Bis(*N*-phenylsalicylaldiminato) cobalt(II)	No trace of decomposition after 6 hr

[a] One ml of CHCl$_3$; 3 mmoles of quadricyclene; 0.01 mmole of catalyst; $T = 35°C$.

We see that an appreciable excess of base over catalyst is needed to bring the rate of reaction to reasonable proportions, but then the dependence of rate on concentration of base is a smooth one. As shown, 4-picoline is more efficient than pyridine in inhibiting the reaction, as could be expected because of the electron donating properties of the methyl group, which makes 4-picoline a better coordinating agent than pyridine. On the other hand, 2-picoline does not inhibit the reaction in any measurable way and this can only be explained by steric

* The low catalytic activity cannot be ascribed to decomposition of the catalyst during reaction, because its activity stays constant during the run and is reproducible.

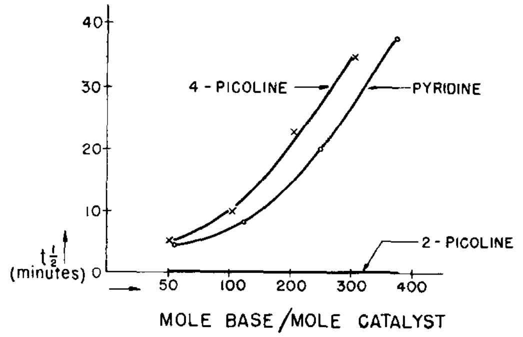


FIG. 1. Half times of the isomerization of quadricyclene into norbornadiene in $DCCl_3$ solution (1 ml), containing 3 mmole of quadricyclene; 0.01 mmole of CoTPP; and varying amount of nitrogen bases; $T = 35°C$.

hindrance. The methyl group at the 2-position does not allow coordination of the 2-picoline with the Co–porphyrin (*17*). These results clearly show that quadricyclene reacts by complexation at the octahedral positions of the square planar complex. The fact that such a great excess of pyridine base is necessary can best be explained by assuming that the equilibrium:

$$\text{CoTPP} + \text{base} \overset{K_1}{\rightleftharpoons} \text{CoTPP–base},$$

competes with the equilibrium

$$\text{CoTPP} + \text{quadricyclene} \overset{K_2}{\rightleftharpoons} \text{CoTPP–quadricyclene}.$$

The CoTPP–quadricyclene complex is the intermediate in the catalytic reaction. The ratio between K_1 and K_2 will define what concentration of base is necessary to depress the rate of the catalytic reaction sufficiently to bring it into a measurable range. In this respect we must not forget, that quadricyclene with its two cyclopropane rings might act as a bidentate.

DISCUSSION

The results can be summarized as follows: Square planarity is a condition for catalytic activity, tilting of the ligands out of plane arrests the catalytic activity and preferential coordination with pyridine bases decreases it considerably; d^6, d^7, and d^8 ions are mostly active; d^9 and d^{10} ions are not. CoTPP is much more active than the square planar Schiff Base.

In the square planar complexes in question, the d_{zy} and d_{zx} orbitals have the lowest energy among the *d*-orbitals and are certainly filled in the low spin d^6, d^7, and d^8-complexes under consideration. Therefore, our condition that the metal *A*-orbital has to be filled and its *S*-orbital empty is not fulfilled.

In the introduction we pointed out that as long as the energy separation between the filled *d*-shell and the first empty *p*-shell is small compared to the energy difference between product and reagent, we may expect catalytic activity. In such a way could be explained why Ag(I) and Cu(I) salts are active in spite of a filled *d*-shell. It is difficult to explain the exceptional activity particularly of CoTPP in this way, since the energy separation between the filled *d*-shell and the first empty *p*-shell is appreciably greater in bivalent ions than it is in monovalent ones (*18*) (in this context it is worthwhile to note that Ag(I) salts show almost no activity in the decomposition of quadricyclene). However, Fig. 2, where the energies of different metal porphyrins, as calculated by Zerner and Gouterman (*19*), are reproduced, shows that in these compounds an empty ligand orbital is situated at an energy not much higher than that of the filled *d*-orbitals. This orbital has the same symmetry properties as the degenerate d_{zy} and d_{zx} orbitals of the metal (e_g in Fig. 2). Therefore, staying within the framework of the theory, as outlined in the introduction, we may conclude that as long as the energy separation between the filled *d*-shell and this empty ligand orbital is small compared to the energy difference between norbornadiene and quadricyclene and the ligand orbital has the right symmetry, we may expect catalytic activity. Most of the experimental results may now be explained:

1. According to Fig. 2, the energy separation between the filled *d*-shell and the empty ligand orbital is smallest with cobalt, which may explain the exceptional activity of its complexes.

2. This energy separation increases drastically in the copper and Zn complexes, which explains their inactivity.

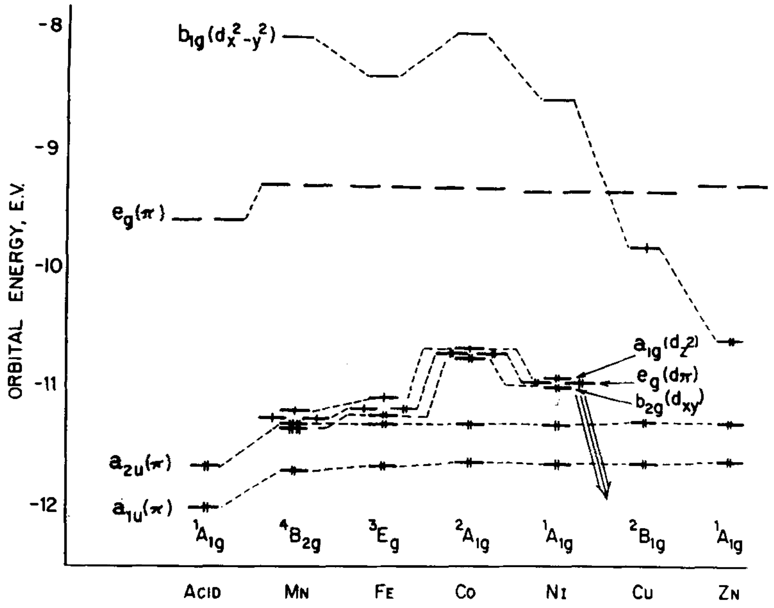


FIG. 2. Calculated energies of the top filled and lowest empty orbitals of porphyrin and its metal complexes.

3. The Schiff base ligands used in this study have a much less extended π-electron system than the porphyrins and the phthalocyanines. As soon as the ligands around the cobalt ion are tilted out of plane, symmetry properties are changed and overlap between the π-orbitals of the ligand and those of the metal is reduced, which causes the complex to be inactive as a catalyst. Therefore, the function of the square planar chelating ligands used in this study seems to be to furnish an empty orbital of the right energy and symmetry.

In a catalytic reaction of this kind we have to differentiate between two steps: (i) The complexation of quadricyclene with the metal complex; and (ii) The isomerization of quadricyclene into norbornadiene. We discussed the action of pyridine bases in terms of interference with step (i). Although the dependence of catalytic activity on d-electron number and ligand stereochemistry could also be explained in terms of complexation alone, we showed that if connected with the electronic properties, which govern step (ii), a rather consistent picture emerges.

It has been shown in this study that square planar complexes of d^6, d^7, and d^8 transition metal ions with quadridentate ligands may be effective catalysts for the symmetry restricted valence isomerization of quadricyclene to norbornadiene. The catalytic reaction occurs by coordination of the reagent at the empty octahedral sites of these complexes. This coordination might be very weak as no stable complexes of porphyrins and phthalocyanines with these kind of hydrocarbons, either olefinic or strained aliphatic, are known. Catalytic activity was extremely sensitive to the stereochemistry of the ligand and the electronic configuration of the metal ion. If it is assumed that the function of the ligand is to furnish an orbital of the right energy and symmetry, the experimental results fit within the framework of existing theories about this kind of catalysis.

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