

The**SPEX**

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Speaker

Catalysis and the Organometallic Chemistry of the Transition Metals

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1. Introduction

To most of us the word "catalysis" triggers misty memories of a definition learned in high school: "A catalyst is an agent which speeds up a chemical reaction without affecting its chemical equilibrium." Almost certainly the definition was accompanied by the example of manganese dioxide catalyzing the decomposition of potassium chlorate to produce oxygen. After more than a half a century, this lack of appreciation of the role of catalysis persists to the present day. Most scientists are simply unaware of its industrial impact. Yet catalysts have become increasingly salient in every part of the chemical industry, from the largest scale operations — the giant oil refineries and the plastic manufacturers — down to the household quantities of chemicals dispensed in tubes for purposes as diverse as adhesives and cosmetics. Essential as catalysis is to the chemical industry, in another area it assumes even greater importance: life itself. Here catalysts are ubiquitous, their intricate, incessant, interwoven activity hidden beyond human skills and comprehension. Long ago, evolution recognized the potential of catalysis by making enzymes — nature's catalysts — essential to all life processes.

To explain catalysis, we need to delve into all of chemistry. For a catalyst may be as simple as an acid or a base, or as complex as an enzyme. The subject is relevant to inorganic, organic and biochemistry along with physical chemistry to unlock explanations.

This article will focus on an area of catalysis remarkable for its recent spectacular growth: catalysis by transition metal complexes. Its goal is to provide a general application of the subject for a reader with no special knowledge other than that of basic chemistry. To this end, I develop the subject gradually by first discussing the practical applications of catalysis (Catalyst Applications) before considering the phenomenon in general

terms (What is Catalysis?). I then examine one area of chemistry, the (Organometallic Chemistry of the Transition Metals.) It provides the background for understanding the specific area of catalysis, my primary concern. I then discuss a few early developments in transition metal catalysis (Early Ideas), followed by a glance at how these ideas are being modified today (Recent Developments). Finally, I consider present and future prospects for catalysis.

2. Catalyst Applications

A heterogeneous catalyst is one that is immiscible with the liquid or gaseous reaction mixture. It has an advantage (easy separation) and a disadvantage (the reaction can occur only on the limited surface of the catalyst). Forty years ago, the important industrial applications were mostly heterogeneous: iron catalysts to synthesize ammonia from atmospheric nitrogen; nickel catalysts to convert liquid oils into margarines by hydrogenation; cracking and reforming catalysts to improve the yield and octane rating of gasoline from crude oil.

By contrast with a heterogeneous catalyst, a homogeneous catalyst is one that is dissolved in the reactants. Homogeneous catalysts have their advantages and disadvantages, too. Dispersed throughout the reaction mixture, they are efficient and rapid-acting. The entire catalyst is operational, not the surface alone. Dozens are available commercially from several qualified manufacturers. In sharp contrast, heterogeneous catalysts are customarily manufactured by depositing a coating on a substrate relying on a proprietary technique. How the coating is applied, as well as the physical properties of the substrate, markedly affect the activity, the specificity, the lifetime and the poison tolerance of the catalyst. The major disadvantage of homogeneous catalysts is the difficulty of removing it once a reaction is complete. The chemist often resorts to a

final selective distillation for the purpose.

Catalysts are essentially practical things and, to be meaningful, our discussion bases distinctions on significant differences rather than strict definitions. Thus, heterogeneous catalysts come in many varieties; they usually consist of certain metals or metal oxides which catalyze reactions in the vapor state at high temperature. And, although the term "homogeneous catalysis" covers any soluble catalyst including acids and bases, I will limit the discussion to organometallic catalysts, i.e. homogeneous catalysts containing transition metal complexes that catalyze an organic reaction in the liquid phase by forming organometallic intermediates. The last forty years have seen a steady growth in the discovery and introduction of such homogeneous catalysts for industrial processes. It is illustrated in Table 1.

Enzymes comprise a third category of catalysts. Although these may be regarded as homogeneous catalysts — they usually perform while in solution — they are unique due to their origin in life processes. They are all proteins but may incorporate certain metals such as iron, copper, zinc and molybdenum.

Enzymes are difficult to isolate and even more difficult to synthesize, but this has not posed a detriment to their application. In the fermentation of such food products as alcohol, vinegar and cheeses, enzymes are simply added as components in the living cells that contain them. Enzymes also play a lead role in the synthesis of more sophisticated products such as L-amino acids and antibiotics.

There is an increase in complexity in catalysts progressing from heterogeneous to organometallic (homogeneous) to enzyme. With this complexity comes enhancement in the selectivity of the reactions they catalyze. For example, no heterogeneous catalysts are known that distinguish between optical isomers to

promote an asymmetric synthesis. Occasionally, organometallic catalysts do so, usually by the addition of an optically active ligand which can coordinate to the metal. Asymmetric synthesis, is, however, a normal function of enzymes.

Parallel to the complexity of the catalyst has been our understanding and exploitation of them. Heterogeneous catalysts were the first to be exploited on an industrial scale while the development of organometallic catalysts has occurred only within the last forty or so years. Major commercialization of enzymes probably lies in the distant future.

With increasing complexity, disadvantages as well as advantages emerge. Easiest to separate and work with are the heterogeneous catalysts. They are more stable at higher temperatures than the homogeneous organometallic catalysts which generally decompose above 200°C. Enzymes are further limited, to the upper temperature of life processes.

Offsetting their temperature limitations, however, are the outstanding catalytic activities of enzymes. Although unsuitable above around 40°, they catalyze reactions at extremely high rates. Where a rate can be measured for the corresponding uncatalyzed reaction, the applicable enzyme can produce a rate increase of up to a startling 10^{12} . Since the rate of a chemical reaction increases by a factor of 2 to 3 for every 10° rise in temperature, a rate increase of 10^{12} is equivalent to a temperature increase of 300 to 400°.

But raising the temperature is not a viable substitute for enzymes. The number of alternative reactions that can occur, and their ability to compete successfully with the desired reaction generally increases rapidly with temperature. Selectivity is soon lost even if the reactants and products themselves are stable at higher temperatures. The temperature restrictions necessary for enzyme and organometallic catalysis insure high selectivity.

3. What is Catalysis?

To chemists, the word "catalyst" conjures up any substance that hastens a chemical reaction. Usually, they have in mind an elixir which, in only trace amount, enables a chemical process to be run at lower temperatures and under more controlled conditions than otherwise. An *ideal* catalyst is one that is not consumed in the chemical reaction and so can be totally reclaimed at the end.

How can catalysts cause such large effects and yet be recovered unchanged?

TABLE 1

Date	Catalyst	Process	Substrate	Product
1940-50	$\text{Co}_2(\text{CO})_8$	Hydroformylation	Olefins	Aldehydes
	Co salts	Oxidation	Cyclohexane	Cyclohexanone
	Li	Polymerization	Butadiene	Polymers
1950-60	Ti and Cr alkyls	Polymerization	Ethylene	Polyethylene (high density)
	Pd salts	Oxidation	Ethylene	Acetaldehyde
	Co/Mn salts	Oxidation	p-Xylene	Terephthalic acid
	AlEt_3	Oligomerization	Ethylene	α -Olefins
	Pt salts	Hydrosilylation	Olefins	Silicon-Carbon bonded products
1960-70	W compounds	Metathesis	Olefins	Olefins (see text)
	Ni complexes	Hydrocyanation	Butadiene	Adiponitrile
	Co complexes	Carbonylation	Methanol	Acetic acid
	Pd salts	Oxidation	Ethylene	Vinyl acetate
	Mo compounds	Epoxidation	Olefins	Epoxides
	1970-80	Rhodium complexes	Carbonylation	Methanol
Ni complexes + Mo/W complexes		Oligomerization + Metatheses	Ethylene	α -Olefins
Rh complexes		Hydroformylation	Olefins	Aldehydes
Rh complexes		Hydrogenation	α -Amino-acrylic acids	Chiral amino acids

It sounds as though we are getting something for nothing, contrary to the laws of common sense as well as science. It is therefore not surprising that chemists sometimes refer to their favorite catalyst as "magic X". Clearly a warning is necessary for the superstitious. Thus the student is reminded that catalysts cannot contravene the laws of thermodynamics in the definition of a catalyst: "An agent which speeds up a chemical reaction *without affecting the chemical equilibrium.*" What a catalyst does is to accelerate the rate at which equilibrium is attained. It does this by lowering the activation energy between reactants and end products, i.e., it speeds up the kinetics of the reaction.

The course of a chemical reaction is like a journey to take a person from village R to village P that is separated by a mountain range S (Fig 1). Choosing the uncatalyzed path the person must scale the mountain. The catalytic path, entailing less energy, would take him via a less energetic route such as R-S'-P'. Hardly a sorcerer, the discoverer of the latter route would nonetheless have been hailed for finding a more expedient route than the strenuous RSP. Phrased more scientifically, the X coordinate in Fig 1 represents the free-energy change while Y represents the reaction coordinate for the conversion of reactants R to products P. Should the catalytic route involve stable but short-lived intermediates such as P', the activation

energy for the slowest step in the catalytic path (S'-P') would need to be less than that for the uncatalyzed path (S-R).

Although ideally a catalyst is not consumed in a reaction, it obviously takes part in the reaction. This is explainable if the catalyst undergoes a series of chemical interactions winding up in its regeneration.

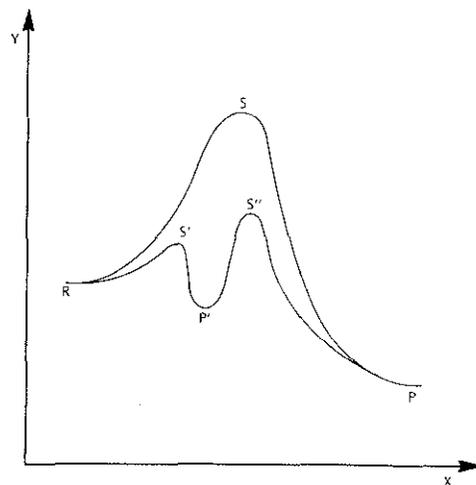


Fig 1

A chemical reaction going from reactants R to products P may proceed via the high energy but uncatalyzed path R-S-P or via the low energy path RS'P'S''P which is catalyzed. The X coordinate represents energy and Y is the reaction coordinate.

derivatives of the transition metals were assumed to be unstable. The few exceptions to this generalization, such as Zeise's salt, $K[PtCl_3(C_2H_4)] \cdot H_2O$, were regarded as mere curiosities.

In the last few decades, however, a plethora of stable organo-transition metal complexes has been discovered and their chemistry detailed in research journals. An idea of the rapid growth in the subject can be judged from the expansion of the *Journal of Organometallic Chemistry* from one volume of about 500 pages per year in the mid '60s to about twenty such volumes per year in the mid '70s. This growth is attributable predominantly to the transition metals.

Causes for the unexpected stability found for so many organotransition metal complexes are complex and inter-related. Their stability can be explained on the basis of either thermodynamics or kinetics. By the latter I am referring to compounds which, although thermodynamically unstable, decompose immeasurably slowly due to a high activation energy. It is appropriate to call this characteristic "metastability." Whether thermodynamics or kinetics is responsible for the stability of any given complex is not always clear. The stability of Ferrocene is believed to be based on "resonance," the same type of stabilization found in aromatic hydrocarbons. Without question, this is a thermodynamic stability. Important examples of "metastability" are the so-called "inert" complexes which pose a large energy barrier to the exchange of ligands. "Labile" complexes, on the other hand, are those with a low activation energy for ligand exchange. Examples of inert complexes are those with 0, 3, or 6 "d" electrons. Complexes of Cr^{3+} (3 electrons) and Co^{3+} (6 electrons) are prime examples. Complexes in which the metals have other numbers of d electrons are generally labile except for the transition metals of the third period (e.g. Os, Ir, Pt) which are all somewhat more inert than the corresponding first and second row metals. Inert complexes generally make poor catalysts since most catalytic reactions require that at least one of the reacting molecules be attached to the metal at some time. Occasionally the whole reaction occurs within the coordination sphere of the metal. In such cases it is essential that the metal catalyst form complexes which are labile. Complexes of Rh^+ are labile and excellent catalysts. Being more inert, corresponding complexes of Ir^+ are poorer catalysts. Since the two metals reside in the same group of the periodic table, they are isoelectronic and have a similar chemistry except that reactions of iridium often are slower. This makes

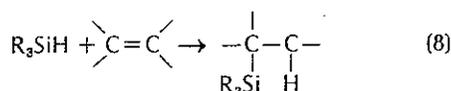
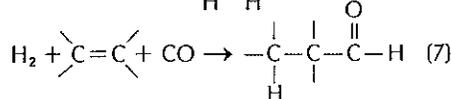
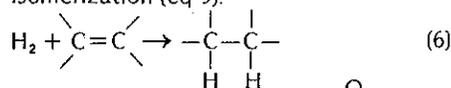
them easier to study, and these studies are frequently undertaken for the insight they provide into reactions catalyzed by rhodium.

The most important contribution to the stability of organo-transition metal complexes results from the presence of T-bonding ligands such as carbon monoxide, olefins, and tertiary phosphines. Based solely on thermodynamic data in the literature, the conventional transition metal-carbon σ -bond appears to be weak (60 kcal/mole). Since both metal-metal and carbon-carbon bonds are stronger, one might expect an organometallic compound to be unstable and, therefore, readily undergo an exothermic dissociation reaction. On the contrary, many organometallics turn out to be highly stable, indicating that factors other than metal-carbon σ -bond strengths are responsible.

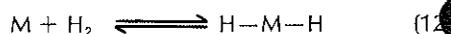
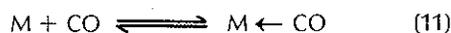
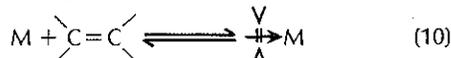
"Back-bonding" appears to be the mechanism responsible. The electronegativity of both carbon and many of the transition metals is similar. Hence, highly covalent bonds should form between the metal and carbon. In low oxidation state compounds (such as zero valent metal complexes) the electron density on the metal is very high when compared with the more commonly encountered positive metal ions. This high electron density can be delocalized — relieved — however, by back-bonding in which electron density from the metal is donated to vacant antibonding orbitals on the carbon atom in a ligand such as ethylene. This mechanism serves simultaneously to reduce electron density on the metal and weaken the C-C bond, while at the same time appreciably strengthens the metal-carbon bond. Many catalytic reactions involve olefins and carbon monoxide as reactants, examples of which are discussed in the next section. To the extent that olefins and carbon monoxide are involved as ligands in these reactions, the catalytic intermediates are partially stabilized. However, further catalyst stabilization frequently necessitates the addition of other stabilizing ligands, particularly tertiary phosphines. Here an optimal catalytic activity is sought for a certain ratio of phosphine to metal. Excess phosphine is harmful since it can also compete with reactant molecules like carbon monoxide or olefin for coordination sites on the metal catalyst. Further optimization of catalytic activity can also result from variation of the basicity and/or the steric hindrance of the phosphine. Thus, phosphines are widely applied to "fine tune" many catalytic reactions.

5. Early Ideas

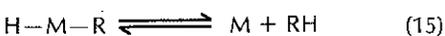
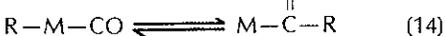
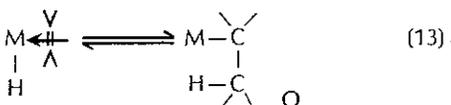
To provide a feeling for transition metal catalysts, I will now develop a few of the ideas which provided unifying concepts in the early '60s for important catalytic reactions of olefins. Although I have limited myself to four examples, the basic ideas are generally applicable to many other processes. They are: olefin hydrogenation (eq 6), hydroformylation (eq 7), hydrosilylation (eq 8), and isomerization (eq 9).



For these reactions to be catalyzed by metals one expects some form of association between one or more of the reacting molecules and the catalysts. In fact such reactions are known for each of the molecules involved:



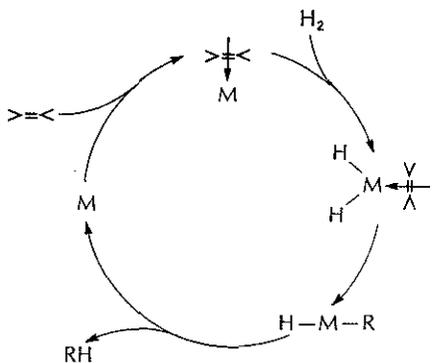
(M represents a transition metal complex in which the additional ligands have been omitted for the sake of clarity). In the first two examples the bond in each molecule is weakened by coordination while in the last example the bond is completely broken. Reactions 6-9 belong in the realm of organic chemistry while, more recently, reactions 10-12 were recognized to fall in the realm of organometallic chemistry. Additional important reactions that have been established in the latter area are the following:



Reaction 13 depicts the addition of a metal hydrogen bond across an olefin bond to form a metal alkyl symbolized by M-R in reactions 14 and 15. In reaction 15, a four-centered process results in a cis addition to the double

bond. A similar type of reaction is involved in 14. Reactions 15 and 16 are product-forming reactions which regenerate catalyst and are therefore similar to the reverse of 12. They are called reductive eliminations to contrast them with reactions such as 12 which are termed oxidative additions. These terms refer to the change in the formal oxidation number of the metal which increases by two units in reaction 12 and decreases by two units in 15 and 16.

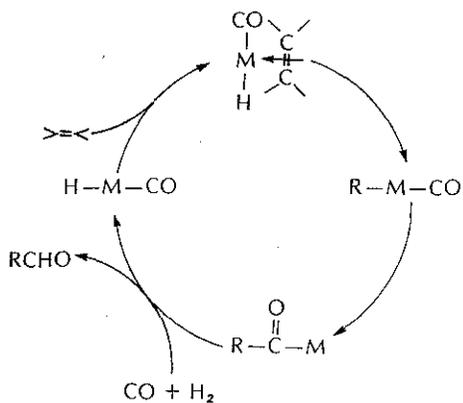
A highly simplified catalytic cycle explaining olefin hydrogenation may be constructed from the basic ingredients represented by 10, 12, 13, and 15 (Scheme 1).



Scheme 1 — Hydrogenation

A catalytic cycle for the addition of hydrogen to an olefin by a metal catalyst M to give a hydrocarbon (RH).

A similar catalytic cycle can be constructed to explain hydroformylation from eqs 10, 11, 12, 13, 14, and 16:



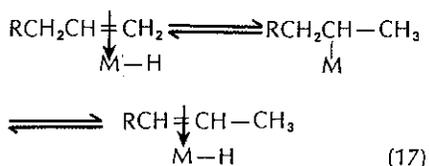
Scheme 2 — Hydroformylation

A catalytic cycle for the addition of carbon monoxide and hydrogen to an olefin to give an aldehyde (RCHO).

Two main factors account for the catalytic effect in Schemes 1 and 2.

- the reacting molecules are brought together by interaction with the catalyst;
- these interactions facilitate subsequent steps either by weakening multiple bonds as in 10 and 11 or actually severing single bonds as in 12.

Olefin isomerization which frequently accompanies hydrogenations and hydroformylations is conveniently explained by the reversibility of eq 13. Thus:

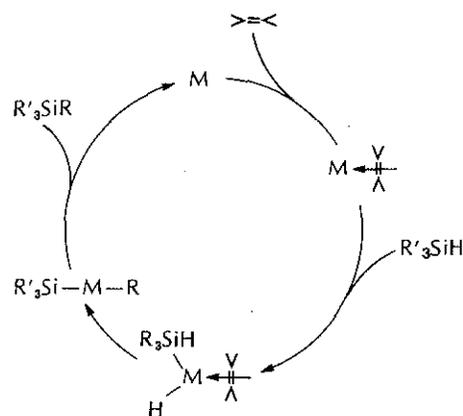


Mechanisms similar to the above were proposed to explain some catalytic hydrogenations and hydroformylations in the early '60s. They were unusual because the reactions were all postulated to occur between species coordinated to the metal catalyst. Here the term "coordination catalysis" is appropriate, since all of the reaction steps occur within the coordination sphere of the metal. At the time I was employed by General Electric, whose Silicones Product Department had a considerable commercial stake in the hydrosilylation reaction 8. After hearing a talk on the subject, I discussed the possible mechanism of the catalysis with John Harrod, a colleague sharing my interest. We decided that the catalyst, chloroplatinic acid, once it was reduced by the silicon hydride to the divalent state, possessed all appropriate chemistry for a coordination catalysis. Thus, Pt^{II} was known to undergo reactions similar to 10 and 12 if stabilized by appropriate ligands, and it seemed reasonable that it should react with silicon hydrides in a reaction 18 similar to 12.



These assumptions led us to the catalytic cycle shown in Scheme 3.

Since reactions such as 18 were unknown at the time, we sought them. Although we were able to obtain only inferential evidence for reaction 18 with phosphine complexes of Pt^{II}, with similar complexes of the isoelectric Ir^I we found the expected reaction 19. Reactions such as this also furnished us with a new approach to the synthesis of silicon-transition metal bonds as a bonus.



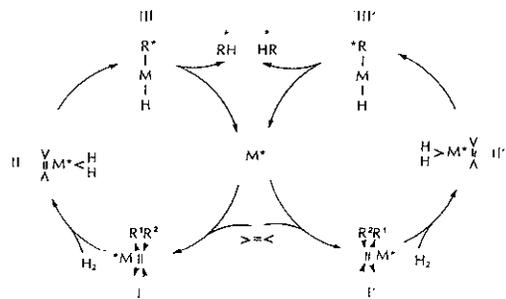
Scheme 3 — Hydrosilylation

A catalytic cycle for the addition of a silane (R₃SiH) to an olefin to give an alkyl silane (R₃SiR)



As the mechanism we proposed was largely based on circumstantial evidence, we expected that it would be modified by subsequent investigations. The fact that no better proposals have been published to date is more a tribute to the experimental difficulties involved than to the accuracy of our original suggestions.

Accurate or not, the suggestions pointed us in the right direction. The similarities we had shown between the catalysis of hydrosilylation, hydrogenation, and hydroformylation led us to examine hydroformylation catalysts for the hydrosilylation reaction. This, in turn, expanded our range of hydrosilylation catalysts to dicobalt octacarbonyl and various rhodium complexes. With these, we were able to find more conclusive evidence for the generalized mechanism represented by Scheme 3.



Scheme 4 — Asymmetric Hydrogenation

The choice of an optically active catalyst results in two parallel catalytic cycles in which the intermediate catalytic complexes have a mirror image relationship. For the production of an optically active product, one cycle must be dominant — for example when the rate of formation of I exceeds that of I' or the rate of formation of II exceeds II'.

6. Recent Developments

Many of the early ideas postulated in the previous section have undergone modification recently, particularly the role played by intermediates. For example, the coordination of an olefin to a metal ion, as in eq 10, was initially thought to result in "activation" of the olefin, opening it to attack by reagents. This idea is consistent with the theoretical picture of a metal olefin bonding. It involves not only a transfer of electron density from a filled π orbital of the olefin to a vacant d orbital on the metal but the reverse: a compensating transfer of electron density from a filled d orbital on the metal to antibonding π orbitals on the olefin. The direction of the resulting changes in electron density are crudely depicted in Fig 2. The coordinated olefin thus resembles a diradical (an excited state of the olefin) more than the normal ground state. X-ray and Raman measurements of the coordinated olefin actually show an increase in the C-C distance consistent with a weakening of the double bond.

More recently, it has been shown that with this picture there are problems involved in accounting for catalytic activation. Many catalytic reactions of coordinated olefins, such as oxidation by the Wacker process, are interpreted as imparting activation of the olefin to nucleophilic attack. Since coordination of the olefin results in compensating shifts of electron density, it is difficult to account for enhanced nucleophilic attack. Further, though the coordinated olefin may appear to resemble an excited state, it has adopted this configuration by virtue of the stabilization energy resulting from this interaction with the metal. Why should this stabilization result in catalytic activation? The situation is rather like that pictured in Fig 1 where P' represents a metal-olefin complex. It is actually more stable than the separate non-interacting metal + olefin which could be represented by R . Why should this result in an activation energy $S''-P'$ less than $S-R$? The answer, of course, must be that the formation of a metal-olefin complex opens up a new low-energy reaction pathway. Roald Hoffman has recently suggested a possible path for nucleophilic attack on a coordinated olefin. His model involves movement of the metal along the plane of the double bond towards one of the carbon atoms. This creates a site of low electron density at the other carbon atom, thus facilitating nucleophilic attack.

New ideas have arisen not only from theoretical considerations, however, but also from experimental advances. Thus, new insights into catalysis have been brought about from kinetic studies of

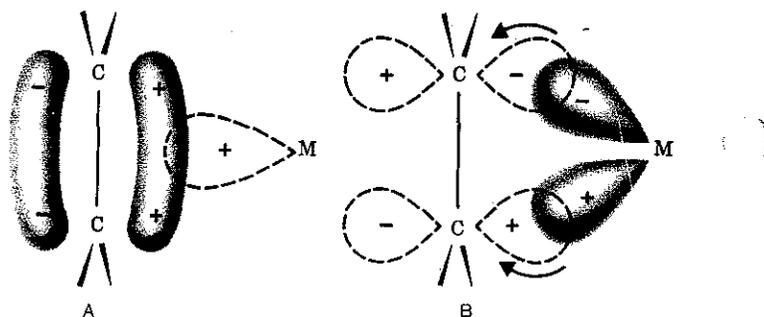


Fig 2

Bonding between an olefin such as ethylene ($\text{CH}_2\text{-CH}_2$) and a transition metal (M) involves two components

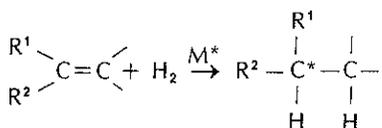
- (a) σ -bonding in which electron density is transferred from the olefin to the metal. This involves the overlap of a filled orbital of the olefin (shaded) with a vacant orbital of the metal
- (b) π -bonding in which electron density is transferred from a filled orbital of the metal (shaded) to a vacant orbital of the olefin.

The resultant transfer of electron density is shown by the arrows. It is equivalent to a movement of electron density from a bonding orbital between the two carbon atoms to antibonding orbitals on the separate carbon atoms.

Advanced Inorganic Chemistry, F.A. Cotton and G. Wilkinson, 97, John Wiley and Sons, New York (1980)

asymmetric catalysts. These are catalysts so discriminatingly selective that they can distinguish between optically active molecules. While this is characteristically common among enzyme catalysts, it has only been achieved with a few homogeneous catalysts. Since asymmetry plays an essential role in biological processes, the ability to synthesize asymmetric molecules has made its greatest impact in the pharmaceutical industry.

A classic example is the synthesis of L-dopa (3,4-dihydroxyphenylalanine), a drug for treatment of Parkinson's disease. The reaction entails an asymmetric hydrogenation:



Here, hydrogenation of a prochiral olefin results in optical activity at C^* . Normal hydrogenation catalysts result in equal (racemic) mixtures of the two optically active forms. If the catalyst (M^*) is asymmetric, however, one optical isomer predominates in the product. Since only two optically active products are formed in the reaction, the term enantiomeric excess (%R-%S) replaces selectivity.

Enantiometric excess values of > 95% have been obtained with rhodium catalysts in synthesizing L-dopa. Asymmetry is introduced by means of tertiary phosphine ligands with an asymmetric center either at the

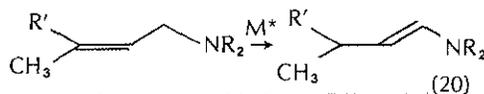
phosphorus or at one of the carbon atoms attached to it.

Since two mirror image products are formed in this hydrogenation, Scheme 1 must be divided into two catalytic cycles which bear a mirror image relationship (Scheme 4). Only the catalyst M^* is common to both cycles. It can be seen that the first catalytic intermediate (I) has a mirror image from (I') though this may not be obvious until one takes into account the two substituents R^1 below the plane of the paper and R^2 above. The subsequent intermediates (II) and (III) also have their mirror image counterparts. Finally, two mirror image products are formed, symbolized by R^*H and H^*R .

Investigating the kinetics of this reaction, Halpern has arrived at unexpected conclusions. Where R^*H is the major product, one would intuitively attribute this selectivity to the preferential formation of (I) rather than (I'). However, Halpern has shown that the concentration ratio of (I)/(I') is in fact only 0.1. The preferential formation of R^*H was accounted for by greater reactivity (580) of (I)/(I') which more than compensated for the low concentration of (I). Halpern's conclusions were unexpected because the specificity of enzymes had traditionally been explained in terms of a lock-and-key concept in which the catalyst surface is the key which exactly fits the substrate lock. If this were true, the preferred formation of R^*H should result from M^* and the olefin combining preferentially to form (I) rather than (I').

To find an explanation of the reverse, I return to the concepts of Fig 1 where P' now represents the intermediate (I) or (I'), and P represents the products R*H or H*R. Since (I') is preferred over (I), the energy level for (I') must be lower than that of (I). The greater reactivity of (I) requires that the ensuing energy barrier S''-P' be less for (I) than for (I').

Based on further experimental results, Halpern now believes that his conclusions apply generally to this class of hydrogenations. He suggests that the lock-and-key concept may still be relevant, but in reverse: to exclude a reaction rather than to promote it. Whether this new explanation applies more generally remains to be seen. Recent results obtained for a different class of asymmetric catalyses has, however, denied its universality. Otsuka reported that in reaction 20, which is also catalyzed by chiral rhodium complexes, the dominant catalytic chiral intermediate leads to the dominant chiral product.



It, therefore, seems likely that the lock-and-key concept may serve a dual function: promoting a selective reaction in some cases and excluding one of two reaction paths in others.

Present and Future Prospects

In the mid '60s, research in organotransition metal catalysis was a rather speculative venture. For some companies it paid off with new commercial processes; for others, the rewards proved less tangible, and management support fluctuated.

A dramatic upswing occurred in the '70s when it became clear that this new approach harbored the potential to solve many environmental problems and as a bonus could reduce energy requirements. This was especially true of the many batch processes run by pharmaceutical and allied industries. A catalytic oxidation with air holds clear advantages over an oxidation requiring a stoichiometric amount of an oxidant such as MnO₂. Here, by-products are formed (manganese sulfate and sulfuric acid), so it is necessary to dispose of them in an environmentally sound manner.

Catalytic reactions can also bestow the benefits of greater selectivity and sometimes even reduce the number of steps in a multistep synthesis. These considerations ensure that catalysis by organo-transition metal complexes will continue to thrive in the '80s. It will probably do so in closer alliance with heterogeneous and enzyme catalysis,

however. These subjects have, in the past, been pursued independently with the result that each has developed its own concepts and nomenclature. The need for a cross-fertilization provided the impetus for an interdisciplinary conference in 1972 sponsored by the NATO Science Committee.

A number of practical developments are now helping to unify the three catalytic modes. Transition metal complexes have been "heterogenized" by supporting ligands on polymers. These catalysts embody the advantages of both homogeneous and heterogeneous catalysts. Thus, all the metal atoms are potentially available for catalysis while removal of the catalyst is facilitated. Ligand variation can also modify catalytic properties. Numerous patents describe applications of these catalysts, but their commercial exploitation has yet to be consummated.

Enzymes have also been "heterogenized," but here the word "immobilized" is preferred. Immobilization is achieved in a variety of ways, but the end result is to convert them to heterogeneous catalysts absorbed on some type of support to make separation from reaction mixtures easier. Whole microbial cells containing multiple enzyme systems may also be immobilized. These modified enzymes are already being exploited in the food and pharmaceutical industries. Although enzyme processes are presently confined to reactions in aqueous media, attempts to add immobilized enzymes to organic solvents or two-phase liquid systems could lead to their wider applications in organic synthesis.

A most challenging goal in catalysis is finding catalysts capable of activating the most stable chemical bonds like the one in molecular nitrogen or the C-H and C-C bonds in alkanes. If the bond in nitrogen could be economically cleaved to produce nitrogen compounds suitable for fertilizers (nitrogen fixation) or C-H and/or C-C bonds could be broken to form valuable derivatives selectively, the economic returns could be enormous.

At the moment, these difficult reactions are only possible at high temperatures on heterogeneous catalysts. A great deal of research is currently being directed to finding homogeneous transition metal catalysts capable of catalyzing such reactions under milder conditions. Since these reactions presently work well on supported metal catalysts, metal-metal bonds might be required or at least offer a significant advantage. For this reason, catalytic chemists are investigating metal clusters as potential catalysts. These are complexes in which two or more metal atoms are bonded directly together.

Accordingly, metal cluster research is another area where the traditional differences between homogeneous and heterogeneous catalysis are fusing. Of course, Nature long ago solved the nitrogen fixation problem with enzymes, but we do not yet fully understand how. When we do, the knowledge is sure to have important ramifications for the other branches of catalysis and the whole subject will move another step closer to integration.

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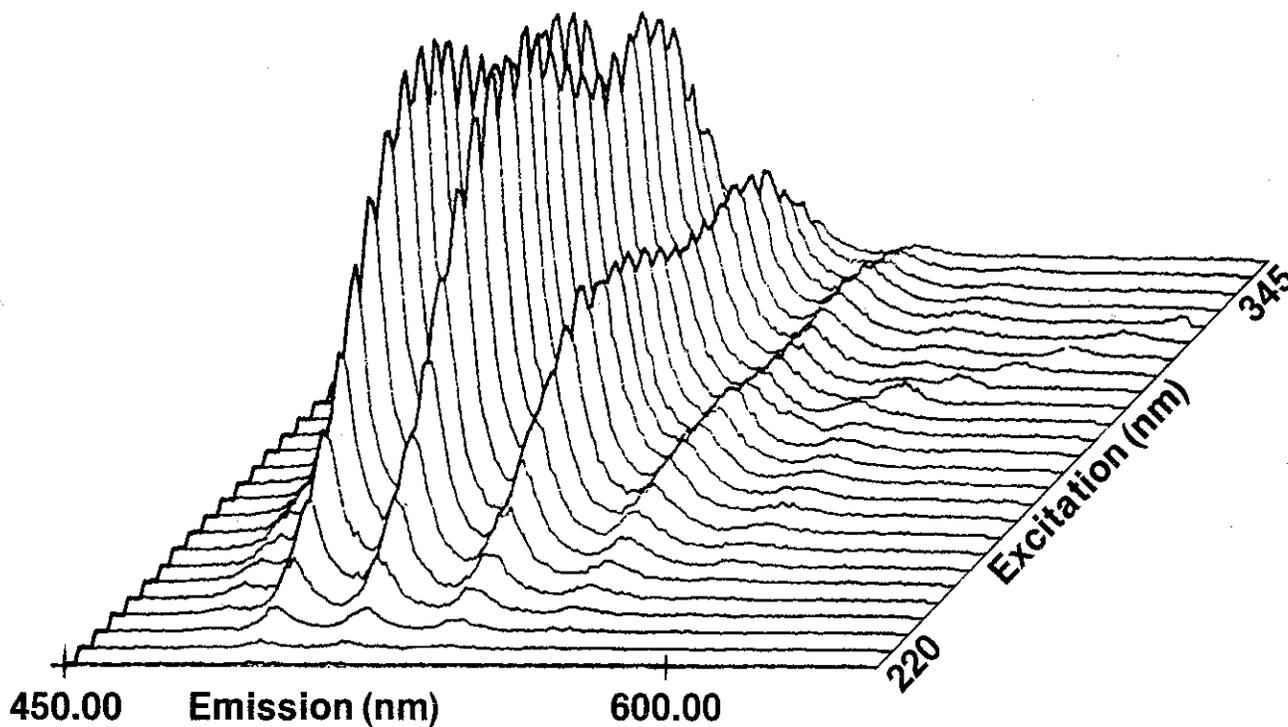
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