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CATALYTIC FUNCTIONS OF METAL IONS AND THEIR COMPLEXES

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CONTENTS

INTRODUCTION

Catalytic processes involving metal ions and their complexes, including organometallic compounds, can be classified into four groups, according to their apparent reaction mechanism.

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(1) *Catalysts for electron transfer reactions.* Since many transition metals can exist in different oxidation states, they can accept an electron from or give an electron to a reactant, thereby producing a radical or an ion. The radical or ion thus formed may initiate or promote a reaction. The metal ion or complex catalyzed autoxidation reaction of such substances as olefins and aldehydes belongs to this catalytic mechanism group of catalysis. Examples are also provided by Fenton's reagent which initiates free radical vinyl polymerization, and metalloenzymes such as xanthine oxidase and the cytochromes. The highly electropositive alkali metals can donate their electron, as does lithium metal in the polymerization of butadiene. Oxygenation or an oxygenase reaction and hydrogenation catalyzed by metal complexes can also be conveniently included in this category.

(2) *Catalysts for acid–base reactions.* Metal ions, with the exception of most of the alkali or alkaline earth metals, being Lewis acids, can coordinate a basic reagent, activating the substrate. Examples include the function of metal ions or metalloenzymes in proteolysis and decarboxylation processes. Ferric chloride and other metal chlorides cause the polymerization of propylene oxide, and zinc or mercury salts promote the hydration or vinylation of acetylene. In the Wacker process palladium chloride forms a complex with ethylene and facilitates the reaction of ethylene with the nucleophilic reagent, OH^-.

(3) *Catalysis by the so-called soft acids.* Metal ions of the first transition series in low valence states (*e.g.*, +1 and 0) stabilized by ligands such as carbon monoxide, triphenylphosphine or trialkylarsine can coordinate to olefins or diolefins *via* π-bonding and to alkyl groups through σ-bonding. Alkyl σ-bonds and olefinic π-bonds often interconvert as the conditions change. This behavior permits the low valent metal ions of the first row transition series to act as catalysts for the reactions of olefins, diolefins and carbon monoxide. The polymerization, oligomerization or isomerization of olefins or diolefins, and the oxoprocess are examples of this group. The complexes of second and third row transition metals act in a similar way.

(4) *Organizational action of metal ions—template effects.* The ability of metal ions to act as a molecular organizer may be defined as follows; such a reaction leads to the formation of a large molecule from small molecules. Consequently the metal ion must compensate for a large negative entropy of activation by the coordinate bond energy. This constitutes a kind of template effect by metal ions. The action of zinc chloride in the synthesis of tetraphenyl porphyrin and that of tetracyanonickelate(II) or of metal carbonyls in the synthesis of benzene and cyclooctatetraene from acetylene may be included in this category. The metal ion function in this class of catalysis is somewhat different in character from those in the preceding three categories. The first three categories are associated with metal ion

participation in the mechanism of bond forming, bond breaking, and the like. In other words, the nature of the metal-to-substrate bonds is important in those cases; the reactions in this fourth group are put together according to their apparent ability to bring the reactants together under proper reaction conditions.

B. CATALYSTS FOR ELECTRON TRANSFER REACTIONS (OXIDATION–REDUCTION REACTIONS)

Reactions in which the metal ion concerned changes its oxidation state are conveniently divided into several classes.

(i) Autoxidation of organic substances

The autoxidation of such substances as aldehydes or olefins is known to occur via a free radical chain mechanism[1]. The chain reactions are generally described as follows:

$$\begin{array}{ll}
\text{Initiation} & \text{I(initiator)} \rightarrow 2R\cdot \\
 & RH \xrightarrow{h\nu \text{ or other}} R\cdot \quad +H\cdot \\
 & ROOH \longrightarrow ROO\cdot \; +H\cdot \\
\text{Propagation} & R\cdot \; + RH \rightarrow R'\cdot \\
 & R\cdot \; + O_2 \rightarrow ROO\cdot \\
 & RO_2\cdot + RH \rightarrow R''\cdot \\
\text{H-abstraction} & RO_2\cdot + RH \rightarrow ROOH + R\cdot \\
\text{Termination} & R\cdot \; + R\cdot \rightarrow RR \quad \text{(etc)}
\end{array} \tag{1}$$

In the above equations RH refers to an olefin, a paraffin or an aldehyde. In this cyclic set of reactions a metal ion with readily convertible valence states participates in either of the following ways[2].

$$\begin{array}{l}
ROOH + M^{+n} \rightarrow ROO\cdot + H^{+} \; + M^{+(n-1)} \\
ROOH + M^{+(n-1)} \rightarrow RO\cdot \; + OH^{-} + M^{+n}
\end{array} \tag{2}$$

Much kinetic[3] and physical[4] data have been published in support of these mechanistic conclusions.

Table 1 relates the redox potential of the metal ion to its catalytic activity in the autoxidation of cyclohexene[5].

In these cases, the metal ion reacts with an intermediate, hydroperoxide ROOH, but in some cases metal ions react directly with the reagent as suggested by the following reactions[6].

$$\begin{array}{l}
Co^{III} + CH_3OH \rightarrow Co^{II} + CH_3O\cdot \; + H^{+} \\
Co^{III} + HCHO \rightarrow Co^{II} + \cdot CHO \; + H^{+} \\
Co^{III} + HCOOH \rightarrow Co^{II} + HCOO\cdot + H^{+}
\end{array} \tag{3}$$

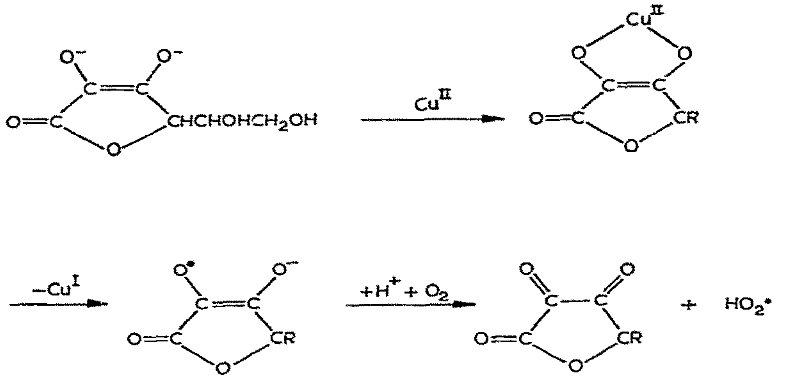
TABLE I

RELATIONSHIP BETWEEN REDOX POTENTIAL AND CATALYTIC ACTIVITY IN THE AUTOXIDATION OF CYCLOHEXENE (CATALYST: METAL HEPTOATE)[5]

Metal ions	*Redox potential (in water)*	*Catalytic activity (maximum oxygen uptake rate)*
Cu^{II}	−0.167 V	0.3
Fe^{III}	−0.771	0.02
Mn^{III}	−1.51	0.4
Co^{III}	−1.843	0.85

(ii) Direct oxidation of a substrate by transition metal ions

If a substance is oxidized by a transition metal ion and the metal ion thus reduced is reoxidized by oxygen, the apparent total reaction is an air oxidation catalyzed by the metal ion. One of the most often cited examples of this type of reaction is the copper salt catalyzed oxidation of ascorbic acid (4); the reaction is related to a biological reaction.



(4)

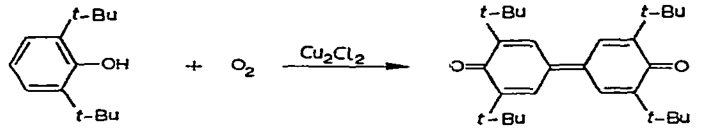
$$HO_2\bullet + Cu^{I} \longrightarrow HO_2^- + Cu^{II}$$

The so-called Wacker process[7] (5) also seems to be of this type. In fact, however, palladium ion is reduced by the action of both the substrate, C_2H_4, and the

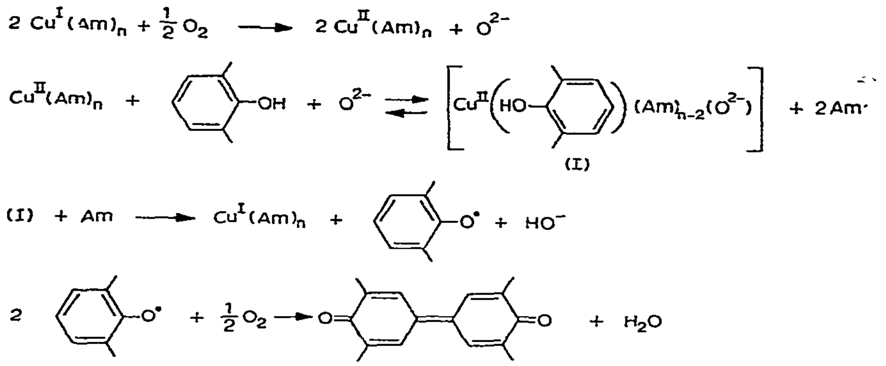
$$C_2H_4 + 1/2O_2 \xrightarrow[\text{in } H_2O]{PdCl_2} CH_3CHO \tag{5}$$

solvent, water, to the zero valent state, and reoxidized by oxygen with the aid of iron(III) chloride or copper(II) chloride.

The oxidative coupling reaction of a phenol (6) is catalyzed by copper(I) chloride[8]. Copper(I) chloride is first oxidized by oxygen in the presence of an amine (Am). It then oxidizes the phenol. The reaction mechanism has been elucidated and is given by the following equations[8a] (7).

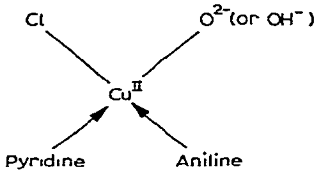


(6)



(7)

The intermediate could not be detected in the case of phenol, but such an intermediate has been detected in the case of aniline which undergoes a similar reaction. The intermediate can be depicted as (II)[8c].



(II)

(iii) Coordination and activation of the oxygen molecule

(1) *Activation of oxygen molecule.* P. George *et al.*[9] suggested the following oxygen activation mechanism, for the transition metal ion catalysis of the autoxidation of tetralin. Other authors[10] have proposed almost the same mechanism for the catalytic action of transition metal phthalocyanines and other complexes in autoxidation reactions.

$$\begin{array}{l} M^{+n} + O_2 \rightarrow (M^{+n} - O_2) \\ (M^{+n} - O_2) + RH \rightarrow M^{+n} + R\cdot + HO_2\cdot \end{array} \quad (8)$$

Complexes of the second and third row group VIII metals, generally involving triphenylphosphine as ligands, have recently been found to add molecular oxygen. The oxygen molecule so coordinated is potentially an oxidizing agent. An example is provided by the following reaction where the coordinated oxygen molecule reacts with NO_2 to form a bis nitrato complex[11a].

$$[Pt(O_2)(PPh_3)_2] + 2NO_2 \rightarrow [Pt(NO_3)_2(PPh_3)_2] \quad (9a)$$

Pd(0) as well as Pt(0) complexes with triphenylphosphine act as catalysts[11b] in reaction (9b). The authors claim the formation of an oxygen complex such as $(PPh_3)MO_2$ as the intermediate.

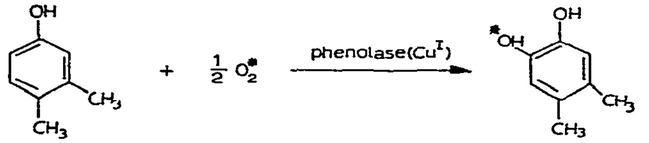
$$\begin{array}{l} PPh_3 \xrightarrow[Pt(PPh_3)_4]{+O_2} Ph_3PO \\ \text{or} \\ C_6H_{10}NC \xrightarrow[+O_2]{Pd(PPh_3)_4} C_6H_{10}NCO \end{array} \qquad (9b)$$

In this connection, photosensitized oxidation reactions are of significance[12]. The photo-oxidation of a substance by molecular oxygen is sensitized by dyes such as chlorophill, eosin or phthalocyanine[13]. Energy is transferred to the oxygen molecule from the excited molecule and the excited oxygen reacts with the substrate.

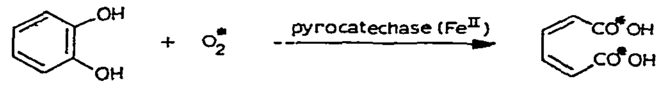
$$\begin{array}{l} S(^1\Gamma)+h\nu \rightarrow S^*(^1\Gamma^*) \rightarrow S'(^3\Gamma) \\ \xrightarrow{+O_2} [S'-O_2] \xrightarrow{+A} S(^1\Gamma)+AO_2 \end{array} \qquad (10)$$

In this equation S means the photosensitizer, the dye, and A the substrate. The $[S'--O_2]$ complex may decompose into $S(^1\Gamma)$ and $H_2(^1\Delta g$ or $O_2(^1\Sigma_9)$, which are the lower quasi stable excited states of the oxygen molecule. These states react with the substrate in different ways[13a].

(2) *Oxidations with oxygenases.* Many oxidation reactions in biological systems have long been known to involve dehydrogenation, whilst true oxidation reactions in which the oxygen adds directly to a substrate have been found in the past decade. The enzymes which catalyze such a reaction, oxygenases, include iron or copper in their lower oxidation state, *i.e.*, Fe^{II} or Cu^{I}. Two examples are shown in the following equations.



(11)



(12)

In these equations O_2^* means $^{18}O_2$ which has been shown to enter the substrates as indicated. There is an indication that no Fe^{II}–Fe^{III} valence change takes place during the reaction in the case of pyrocatechase. A comprehensive monograph[14] and a symposium report[15] should be sought for further details.

(3) *Oxygen carrying complexes.* The natural product, hemoglobin is the prototype oxygen carrying chelate which reversibly adds an oxygen molecule. Many oxygen carrying chelates have now been found[16]. Those include myoglobin and its analogs, iron(II)-phthalocyanine[17], bis(salicylaldehyde)imine cobalt(II)[18],

bis(histidine) cobalt(II)[19], bis(glycylglycine) cobalt(II)[20], manganese(II)-phthalocyanine[21], hemocyanine (Cu^I), an iridium complex $[IrX(CO)(PPh_3)_2]$[22] where X is a halogen, a rhodium complex $[RhCl(PPh_3)_3]$[23a], and $[Pt(PPh_3)_2]$[23b] which forms the complex $[(PPh_3)_2PtO_2]$. Not all these examples are truly reversible in the sense that hemoglobin is.

It is to be noted that in all of those examples the central metal ion is in a lower oxidation state. Oxygenation, *i.e.*, the coordination of an oxygen molecule to a metal ion, may require back donation of electrons from the metal to the oxygen to such an extent that the metal ion is effectively not oxidized completely. There are two types of bonding of the oxygen molecule to metal ions; one is M–O–O–M, and the other is $M–O_2$. Hemoglobin, myoglobin, the iridium complex (Fig. 1 as determined by X-ray crystallography[22b]), and the rhodium and platinum complexes are considered to be of the latter type, while all others are presumed to involve the former type of bonding. As to the donation of electrons from the metal to the oxygen, the ESR spectrum[24] of a related complex $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$ provides some insight. According to this ESR spectrum, there is electron delocalization through the $Co–O_2–Co$ chain.

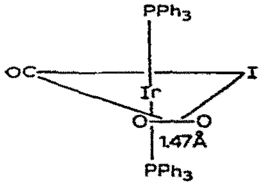


Fig. 1. The structure of $O_2Ir(CO)I(PPh_3)_2$.

(iv) *Coordination and activation of hydrogen*

Many catalysts for hydrogen activation or hydrogenation are known. Most of the reactions are heterogeneous, *i.e.*, the catalyst is a solid, but recently there has been extensive activity in the field of homogeneous hydrogen activation by transition metal complexes[25,26,31,32,34–38].

(1) *Activation of hydrogen.* According to Halpern[25], there are three types of hydrogen activation as exemplified by the following three reactions.

heterolytic splitting: $Ru^{III}Cl_6^{3-} + H_2 \rightarrow Ru^{III}HCl_5^{3-} + H^+ + Cl^-$ (13a)

homolytic splitting: $2Co^{II}(CN)_5^{3-} + H_2 \rightarrow 2Co^{III}(CN)_5H^{3-}$ (13b)

insertion: $Ir^{I}Cl(CO)(PPh_3)_2 + H_2 \rightarrow Ir^{III}H_2Cl(CO)(PPh_3)_2$ (13c)

The heterolytic splitting is in effect a substitution reaction. The other two reactions involve a formal oxidation of the metal ion by hydrogen which abstracts an electron to become a hydride ion. In the last two types of reaction, the reactivity may thus be closely related to the susceptibility of the metal to oxidation. However, this expectation has not yet been thoroughly studied. The reaction (13c), though the author describes it so, is not really an insertion reaction.

There are some interesting related reactions. Those complexes which activate a hydrogen molecule also react with alkyl halides, hydrogen halides or the like in a similar manner. For example:

$$2\mathrm{Co^{II}(CN)_5{}^{3-}} + \mathrm{CH_3I} \rightarrow \mathrm{Co^{III}(CN)_5CH_3{}^{3-}} + \mathrm{Co^{III}(CN)_5I^{3-}} \qquad (14)^{27}$$

$$\mathrm{Ir^{I}I(CO)(PPh_3)_2} + \mathrm{CH_3I} \rightarrow \mathrm{Ir^{III}I_2(CH_3)(CO)(PPh_3)_2} \qquad (15)^{28}$$

$$\mathrm{Ir^{I}Cl(CO)(PPh_3)_2} + \mathrm{HCl} \rightarrow \mathrm{Ir^{III}HCl_2(CO)(PPh_3)_2} \qquad (16)^{29}$$

These reactions also involve the formal oxidation of the central metal ion. There is also a possibility of a reductive cleavage of C–H or C–C bond by a mechanism similar to (14) and (15). Chatt and Davidson[30] observed the following reaction in this connection.

$$\begin{aligned}&\mathrm{Ru^{0}(C_{10}H_8)((CH_3)_2PCH_2CH_2P(CH_3)_2)} \rightleftharpoons \\ &\qquad \rightleftharpoons \mathrm{Ru^{II}H(2\text{-}C_{10}H_7)((CH_3)_2PCH_2CH_2P(CH_3))_2} \qquad (17)\end{aligned}$$

(2) *Catalytic hydrogenation.* Bath and Vaska[31] reported the following reaction where the iridium complex acts as a catalyst. Individual experiments[26] with

$$[\mathrm{IrH(CO)(PPh_3)_3}] + \mathrm{C_2H_4} + \mathrm{H_2} \rightarrow [\mathrm{IrH(CO)(PPh_3)_3}] + \mathrm{C_2H_6} \qquad (18)$$

H_2 and C_2H_4 indicate that they react reversibly with the dissolved iridium complex in toluene under normal conditions.

$$[\mathrm{IrH(CO)(PPh_3)_3}] + \mathrm{H_2} \rightarrow [\mathrm{IrH_3(CO)(PPh_3)_3}] \qquad (19a)$$

$$[\mathrm{IrH(CO)(PPh_3)_3}] + \mathrm{C_2H_4} \rightarrow [\mathrm{Ir(C_2H_4)H(CO)(PPh_3)_3}] \qquad (19b)$$

The isostructural rhodium complex $[\mathrm{RhH(CO)(PPh_3)_3}]$[31] does not add hydrogen, but acts as a catalyst for the hydrogenation of ethylene and for hydrogen–deuterium exchange. An octahedral hydride complex of osmium $[\mathrm{OsHCl(CO)(PPh_3)_3}]$[32] catalyzes the hydrogenation of acetylene to ethylene and ethane. Vaska[26] suggests the following mechanism.

$$\left.\begin{aligned}&\mathrm{L_4Ir^{I}H} + \mathrm{C_2H_4} \rightleftharpoons \mathrm{L_4Ir^{I}H(C_2H_4)} \rightleftharpoons \mathrm{L_4Ir^{I}(C_2H_5)}\\ &\mathrm{L_4Ir^{I}(C_2H_5)} + \mathrm{H_2} \rightleftharpoons \mathrm{L_4Ir^{III}H_2(C_2H_5)} \rightleftharpoons \mathrm{L_4Ir^{I}H} + \mathrm{C_2H_6}\end{aligned}\right. \qquad (20)$$

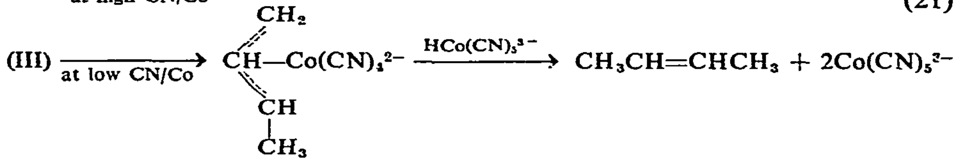
Wilkinson and his coworkers[33] claims that the rhodium complex $\mathrm{RhCl(PPh_3)_3}$ is a more active hydrogenation catalyst than all the complexes mentioned above. This complex adds to hydrogen at one atmospheric pressure in an organic solvent to form the dihydride complex $[\mathrm{RhCl(PPh_3)_2H_2}]$. The NMR spectrum of this complex shows hydride peaks at $\tau = 18.8, 21.5$ and 28.8. These peaks disappear when the solution is flushed with nitrogen or an olefin, but reappear when saturated with hydrogen. Inspection of the NMR spectrum leads the authors to conclude that the dihydrido complex has a *cis* configuration and that the hydrogenation of an olefin by this complex takes place through the simultaneous attack of both hydrides on the olefin, not through metal-alkyl bond formation as suggested in the case of the iridium complex. The ruthenium analogue of this complex, $[RuCl(H)(PPh_3)_3]$, was recently reported to be a highly selective catalyst for the hydrogenation of terminal olefins[34]. The NMR spectrum of the reaction system with ethylene as substrate showed the reversible formation of $Ru–C_2H_5$, in contrast to the behaviour of the rhodium complex.

The hydrogenation of butadiene catalyzed by pentacyanocobaltate is of interest. The nature of the products depends upon the CN/Co ratio. In the case of high values of CN/Co, butene-1 is obtained, whereas butene-2 is the main product in the case of small values of CN/Co[35]. Kwiatek *et al.*[35] explains this phenomenon on the basis of the following mechanism.

$$2Co(CN)_5^{3-} + H_2 \longrightarrow 2HCo(CN)_5^{3-}$$

$$HCo(CN)_5^{3-} + CH_2{=}CHCH{=}CH_2 \longrightarrow CH_3CH{=}CHCH_2Co(CN)_5^{3-} \text{(III)}$$

$$\text{(III)} \xrightarrow[\text{at high CN/Co}]{HCo(CN)_5^{3-}} CH_3CH_2CH_2{=}CH + 2Co(CN)_5^{3-} \qquad (21)$$



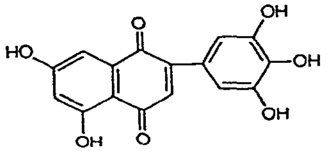
$$\text{(III)} \xrightarrow[\text{at low CN/Co}]{} \overset{CH_2}{\underset{\underset{CH_3}{CH}}{CH}}{-}Co(CN)_4^{2-} \xrightarrow{HCo(CN)_5^{3-}} CH_3CH{=}CHCH_3 + 2Co(CN)_5^{3-}$$

Another type of homogeneous catalyst for the hydrogenation of olefins and acetylenes is $MX_n–M'R_m$[36] where M is a metal of the first row transition series, M' is an alkaline earth metal or aluminum, X a halide, of acetylacetonate and R an alkyl group. The effective metal ion of this system is a lower oxidation state and is a soft acid like Ru^{II}, Rh^{I} or Ir^{I}. Among the other homogeneous catalysts for hydrogen activation or hydrogenation are Cu^{II}, Cu^{I}, Ag^{II}, Hg^{II} (ref. 37) and $PdCl_4^{2-}$ (ref. 38).

(v) Miscellaneous reactions

Several other interesting observations may be made, though some of them have not yet been thoroughly studied.

(1) *Activation of a water molecule.* Shibata *et al.*[39] extensively studied the catalytic effects of many metal complexes upon the air-oxidation of myricetin(IV).



(IV)

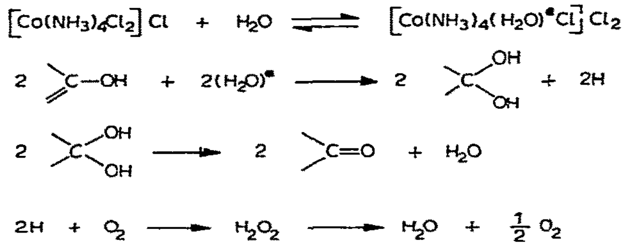
Their results are summarized in Table 2. As the table shows, some of the active complexes contain metals which cannot change their oxidation states; they are

TABLE 2

THE CATALYTIC ACTIVITY OF VARIOUS METAL COMPLEXES UPON THE OXIDATION OF MYRICETIN

(A > B > C > D ≈ O)	
(A)	$[Co(NH_3)Cl_2(H_2O)]Cl$, *trans*-$[Co(NH_3)_4Cl_2]Cl$, $[Co(NH_3)_3(NO_3)_3]$, $[(NH_3)_5Co(NH)Co(NH_3)_5]Cl_4$, $[(NH_3)_4Co\begin{smallmatrix}NH_2\\OH\end{smallmatrix}Co(NH_3)_4]Cl_4$, $[Ni(NH_3)_3(H_2O)_3]Cl_2$ $[Cu(NH_3)_2(C_2H_3O_2)_2]$, $[Zn(NH_3)_4]SO_4$, $[Zn(NH_3)_4]I_2$, $[Cd(NH_3)_4]Cl_2$
(B)	$[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_4(H_2O)Cl]Cl_2$, $[Cu(NH_3)_4]SO_4$, $[Cu(py)_6](NO_3)_2$
(C)	$[Co(NH_3)_4(H_2O)_2]Cl_3$, $[Co(NH_3)_4CO_3]Cl$, $[Co(NH_3)_4C_2O_4]Cl$, $[Co(NH_3)_5(NO_2)]Cl_2$
(D)	$[Co(NH_3)_6]Cl_3$, $[Co(en)_3]Cl_3$, $[Cr(NH_3)_4Cl(H_2O)]SO_4$, $[Cr(NH_3)_5Cl]Cl_2$ $Ag_2S_2O_4 \cdot NH_3$, $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$

complexes of zinc and cadmium. Their catalytic activity, therefore, cannot be ascribed to a valence change of the metal. The catalytically active complexes, however, are found to be susceptible to aquation. An aquo-activation mechanism (22) was proposed:

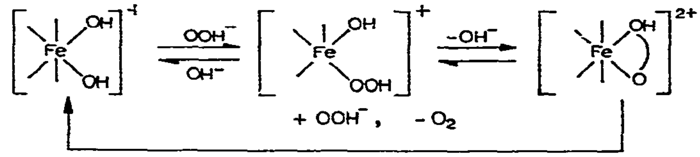


(21)

In the above equations, $(H_2O)^*$ means the activated water molecule. It is an interesting observation[39] that an asymmetric reaction took place in the air oxidation of *o*-hydroxytyrosine with catalysts like $[Co(en)_2(NH_3)Cl]Cl_2$. The rate of the reaction was greater for the reaction of the *l*-substrate with the *l*-catalyst than for that of the *l*-substrate with *d*-catalyst. This shows that the substrate has to coordinate to the metal in order to be activated.

(2) *Activation and decomposition of hydrogen peroxide.* There are two enzymes which catalyze the decomposition of hydrogen peroxide or which catalyze an oxidation reaction with hydrogen peroxide. The first is catalase and the second is peroxidase, both of which have iron-heme groups as the prosthetic group. The mechanism of the decomposition of hydrogen peroxide with catalase or with ferric complexes which are models for catalase, have been intensively studied. Complexes like $[Fe^{III}\text{–}H_2O_2]$ and $[Fe^{III}\text{–}OOH]$ have been shown to form in the reaction of ferric complexes with hydrogen peroxide[40]. The mechanism proposed by Wang[41] for the Fe^{III}-triethylenetetramine complex is given in (23).

This particular complex is highly active being 10^4 times as effective as hemoglobin, and far more active than other iron complexes with polyamines and/or aminocarboxylic acids; it is less active however than the enzyme, catalase. In the



(23)

above mechanism (23), the possibilities of a change in the valency of iron and the formation of radical species have not been taken into consideration; these are known to take place, *e.g.*, in the system Fe^{II}–H_2O_2. The fundamental formulation for such a reaction is called the "Haber-Weiss" mechanism[2] (24).

$$
\begin{array}{lll}
Fe^{II} & +H_2O_2 & \rightarrow Fe^{III} + OH^- + \cdot OH \\
\cdot OH & +H_2O_2 & \rightarrow H_2O + HOO\cdot \\
HOO\cdot & +H_2O_2 & \rightarrow O_2 + H_2O + \cdot OH \\
Fe^{II} & +\cdot OH & \rightarrow Fe^{III} + OH^- \\
Fe^{III} & +HOO^- & \rightarrow Fe^{II} + HOO\cdot
\end{array}
\qquad (24)
$$

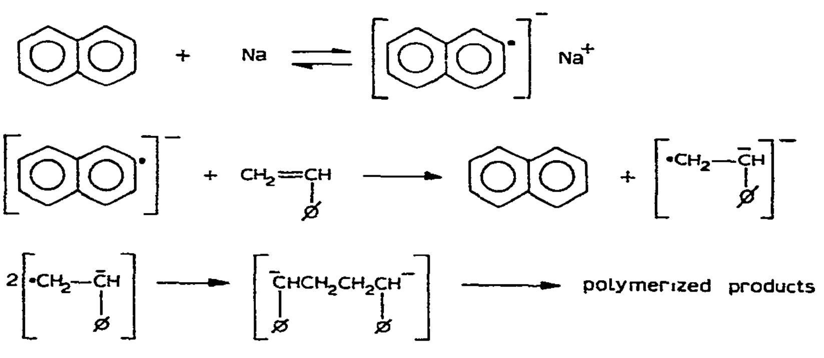
A similar mechanism has been proposed by Chance[42] on the basis of kinetic and spectrophotometric studies for the action of peroxidase, namely:

$$
\begin{array}{l}
[Fe^{III}-H_2O] + H_2O_2 \rightarrow [Fe^{III}-H_2O_2] + H_2O \\
[Fe^{III}-H_2O_2] + AH_2 \rightarrow [Fe^{III}-OH\cdot] + AH\cdot + H_2O \\
[Fe^{III}-OH\cdot] + AH\cdot + AH_2 \rightarrow [Fe^{III}-H_2O] + A + AH_2
\end{array}
\qquad (25)
$$

In this reaction AH_2 means the substrate. Metal ions or complexes with interconvertible valencies like manganese, cobalt and copper have also been known to catalyze the decomposition of hydrogen peroxide.

(4) *The electron transfer mechanism of vinyl polymerisation.* Oxidation or hydrogenation is not the only reaction which will take place *via* an electron transfer mechanism. A mixture of hydrogen peroxide or a hydroperoxide with a metal ion of variable valence has for a long time been known to catalyze the polymerization of vinyl monomers. This reaction can be understood on the basis that the mixture produces free radicals as indicated above (24).

Sodium metal transfers its valence electron to an aromatic hydrocarbon[43,44].



(26)

forming a radical anion. The radical thus formed can initiate the polymerization of an α-olefin.

The catalytic polymerization of α-olefins and dienes, by metallic lithium or by an alkyl lithium probably proceeds by a similar mechanism.

C. CATALYSTS FOR ACID–BASE REACTIONS

(i) Acidity scale

There are several types of catalyzed acid–base or nucleophilic–electrophilic reaction. A model of a typical reaction is:

$$\begin{aligned}&\text{reaction: S(substrate)+B(nucleophilic reagent)} \rightarrow \text{SB}\\ &\text{action of catalyst (M): } S+M \rightarrow (M^{-\delta} \leftarrow S^{+\delta}) \qquad (27)\\ &\xrightarrow{+B} (M\ldots S \leftarrow B^{+\delta}) \rightarrow M+SB\end{aligned}$$

In the above equations B may be the same as S, as in a polymerization process. There is also another case in which both S and B coordinate to the catalyst M. The factors influencing this type of reaction include (i) the acidity of the active site of M, (ii) the degree of charge transfer in the complex (M ← S), and (iii) the rate of coordination of S or substitution by S. The second factor is related to the covalency of the M–S bond[45]. Several review articles[46] discuss the third factor.

The so-called "acidity" will be discussed here in some detail. Several definitions of an acid exist; Brønsted, Lewis and so forth. The definition by Mulliken[47] should theoretically be the most versatile. However, this theory does not seem to be applicable successfully to metal ions and complexes. Stability constant data has been accumulated for a variety of metal complexes. Attempts have been made to establish some empirical correlation between the acidity of a metal ion in a complex and its stability constant. Chatt, Ahrland and Davis[48] surveyed the stability constants of many complexes and proposed classifying metal ions into two groups, A and B. A metal ion in group A is one whose complexes with halide ion decrease in stability with the series $F^- \gg Cl^- > Br^- > I^-$; in the case of oxygen family and nitrogen family elements the orders of stability are $O \gg S \sim Se \sim Te$ and $N \gg P > As > Sb$, respectively. For a metal ion of group B their orders are reversed; $F^- < Cl^- < Br^- < I^-$, $O \ll S > Se \sim Te$, and $N \ll P > As > Sb$.

Pearson[49] extended this idea, and included non-metals and metal ions of unusual oxidation states. His definition of "soft" and "hard" corresponds roughly to B- and A-group metal ions, respectively. Later on, Pearson *et al.*[50] proposed empirical parameters for ligand bases, n_{Pt} which were obtained from the relative rate constants of the substitution reaction of *trans*-$Pt(py)_2Cl_2$. They, however, have not yet proposed any theoretical or empirical parameter expressing softness or acidity in general. Misono *et al.*[51] have recently proposed a dual parameter

(X, Y) for metal ions and (α, β) for ligands, which can quantitatively describe softness and many other related phenomena. The classification of metal ions into hard-borderline-soft as proposed by Pearson[49] is tabulated in Table 3, together with the Y values. This table shows that Y is a good parameter for expressing softness. β-Values for halogen series fall in the order $I^- > Br^- > Cl^- > F^-$; β, therefore, seems to be a reasonable parameter for expressing the softness of a ligand. Several applications including those to catalytic reactions are discussed in the paper.

TABLE 3

THE PEARSON'S CLASSIFICATION[49] OF METAL IONS INTO SOFT, HARD AND BORDER LINE ELEMENTS AND THEIR Y VALUE[51]

		Metal ions
Hard acid (class A)	<2.8	Li^+(0.36), Na^+(0.93), K^+ (0.92), Mg^{2+} (0.87), Ca^{2+}(1.62), Mn^{2+}(3.03), Al^{3+}(0.70), In^{3+}(2.24), Fe^{3+}(2.37), Co^{3+}(2.56), Sr^{2+}(2.08), Cr^{3+}(2.70).
Borderline	2.8 ~3.2	Fe^{2+}(3.09), Co^{2+}(2.96), Ni^{2+}(2.82), Zn^{2+}(2.34), Pb^{2+}(3.58), Sn^{2+}(3.17), Cu^{2+}(2.89).
Soft acid (class B)	>3.2	Cu^+(3.45), Ag^+(3.99), Au^+(5.95), Tl^+(3.78), Hg^{2+}(4.25), Pt^{2+}(4.82), Cd^{2+}(3.04), Pd^{2+}(4.27), Tl^{3+}(3.23), Au^{3+}(3.90), Cs^+(2.73).

(ii) Hydrolysis reactions

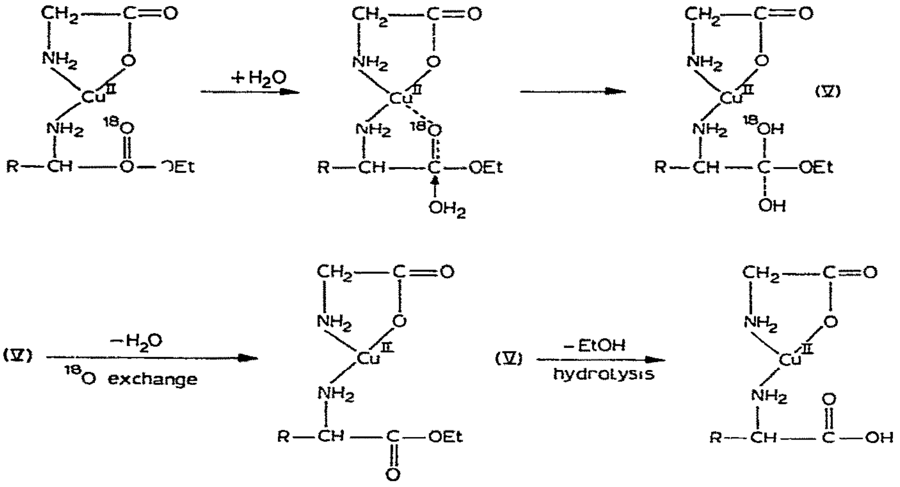
A water molecule or a hydroxide ion is one of the most commonly encountered nucleophilic reagents. These reagents generally attack substances like carbonium and phosphonium ions which have positive sites. Some reactions of this type which have attracted much attention are the hydrolysis of amino acid derivatives and phosphate esters.

(1) *The hydrolysis of esters and amides of amino acids.* This reaction is of great importance in biological system; there are a great number of enzymes which catalyze the hydrolysis of a peptide linkage. Pepsin, chymotrypsin, carboxypeptidase and glycylglycinepeptidase are a few examples. Pepsin and chymotrypsin are pure proteins composed of amino acids alone, and active without any cofactor like a metal ion. Metal ions are required, however, for the activation of the latter two enzymes; Zn^{II} for carboxypeptidase and Co^{II} for glycylglycinepeptidase. There are three possible ways in which a metal ion participates in the activation of an enzyme; it may act as an acid promoting the nucleophilic hydrolysis, as a bridge connecting the substrate with the enzyme or as a factor to induce a change of the conformation of the enzyme protein so as to become active.

Carboxypeptidase loses its activity when it loses Zn^{II} ion but its activity is restored when Zn^{II} is added[52]. Ions other than Zn^{II} such as Mn^{II}, Fe^{II}, Ni^{II} and

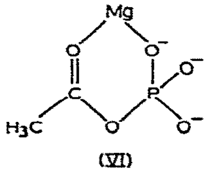
Co^{II}, when added to the apo-enzyme, activate it though the degree of activation differs. A substrate-enzyme adduct can be formed even in the absence of Zn^{II} ion; this adduct, however, cannot by hydrolyzed nor bind Zn^{II} ion. This behaviour suggests that Zn^{II} acts as an acid activator promoting the hydrolysis.

A model reaction[53] for a metalloenzyme catalyzed hydrolysis is the hydrolysis of ethylphenylalaninate by Cu^{II} complexes. On the basis of ^{18}O exchange studies a mechanism has been proposed as shown in (28)[53].



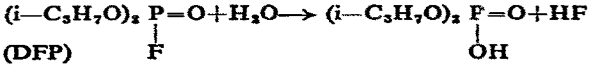
(28)

(2) *Hydrolysis of phosphate esters and their derivatives.* Phosphate esters like ATP are of importance in biological system. Many enzymes which catalyze the hydrolysis and transphosphorylation of phosphate esters require metal ions like Mg^{II} and Ca^{II}. One of the simplest compounds, acetylphosphate is hydrolyzed with a catalyst such as $CaCl_2$ or Mg^{II}. An intermediate, VI, is proposed[54]. The hydrolysis of some phosphate analogues such as di(isopropyl)fluorophosphate-



(VI)

(DFP) and isopropylmethylphosphonofluoridate(SARIN) has attracted much attention and yielded interesting results. Cu^{II}-chelates catalyze the hydrolysis of DFP[55], but cupric sulfate is less active than the chelating agents. Table 4 gives some data concerning the catalytic activities of several copper-chelates in this reaction. All of the complexes listed in the table have a chelating agent/copper



$$\underset{\text{(DFP)}}{(i\text{—}C_3H_7O)_2}\underset{\textstyle F}{\overset{}{P}}{=}O + H_2O \longrightarrow (i\text{—}C_3H_7O)_2\underset{\textstyle OH}{P}{=}O + HF \qquad (29)$$

TABLE 4

CATALYTIC ACTIVITIES OF COPPER CHELATES IN THE HYDROLYSIS OF DFP[55]

Chelating agent	$t_{\frac{1}{2}}$ *(min)*	*Chelating agent*	$t_{\frac{1}{2}}$ *(min)*
No catalyst	2500	Threonine	18
β-Alanine	29	Ethylenediamine	16
Glycine	27	Imidazole	14
Aspartic acid	26	*o*-Phenanthroline	14
Glutamic acid	25	4,4′-Dimethyl-2,2′-dipyridyl	9
Arginine	23	*l*-Histidine	8
Lysine	23	α,α′-Dipyridyl	4.5

ratio of unity. Complexes for which the ratio is two are far less active than these complexes. The [Cu^{II}–EDTA] complex, though having a ratio of unity, is inactive because EDTA occupies all of the four coordination sites. These data suggest that at least two coordination sites should be available for the substrate in order for the complex to be catalytically active. Three structures have been proposed for the intermediate complex (Fig. 2). The order of catalytic activity for the hydrolysis of

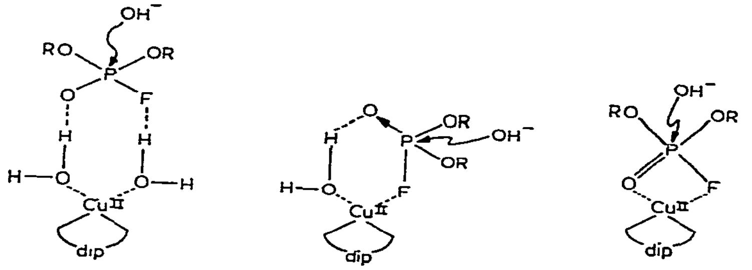


Fig. 2. Substrate-catalyst complexes proposed in the hydrolysis of DFP.

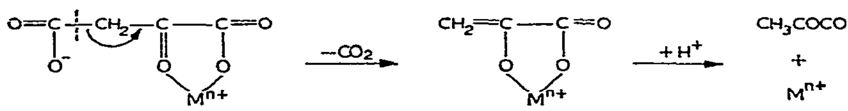
SARIN is Cu(*N,N,N′,N′*-tetramethylethylenediamine) > Cu(*N,N′*-dimethylethylenediamine) > Cu(ethylenediamine)[56]. This is just the reverse of the order of their stabilities. All the data mentioned above indicate that the acidity of the central metal ion is a controlling factor in their catalytic activity.

(iii) Miscellaneous reactions

(1) ***Decarboxylation.*** Decarboxylation is exemplified by the following reaction. Decarboxylase, the enzyme which catalyzes reactions of this type usually

$$RCOOH \rightarrow RH + CO_2\uparrow \qquad (30)$$

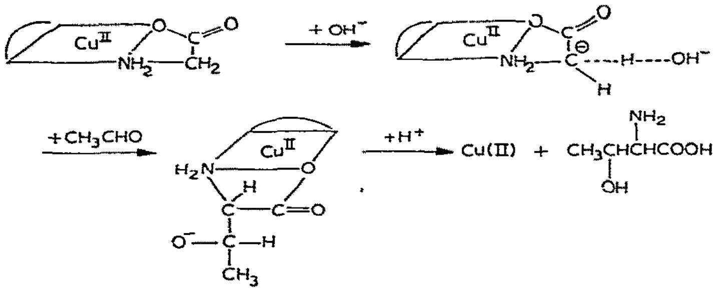
requires metal ions such as Mg^{II} and Mn^{II} for its activation. The decarboxylation of oxaloacetic acid first studied by Krebs[57] has attracted much attention. The



(31)

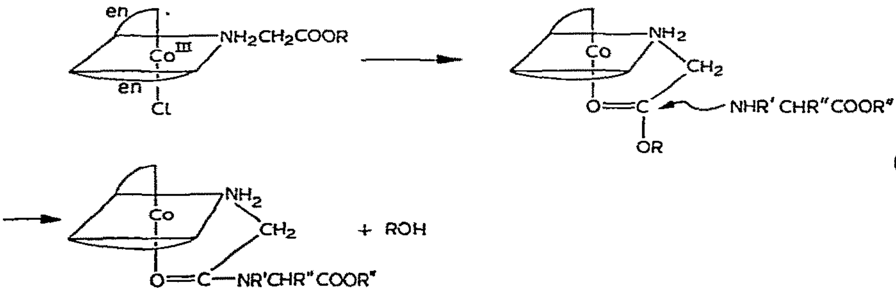
order of activity of the divalent metals of the first transition series[58] in this reaction is $Mn^{II} < Fe^{II} < Co^{II} < Ni^{II} < Cu^{II} > Zn^{II}$, being identical with that of the Irving–Williams order. This suggests that the acidity of the metal ion is the controlling factor in its activity.

(2) *Synthesis of* threo-*threonine.* A glycine-copper complex was allowed to react with acetaldehyde to give specifically *threo*-threonine[59]. In this case the copper ion is not a catalyst in the proper sense of the word. The reaction is shown in (32). Copper ion labilizes the hydrogen attached to the α-carbon atom, making the carbon a carbanion which is attacked by the carbon atom of the carbonyl group of acetaldehyde.



(32)

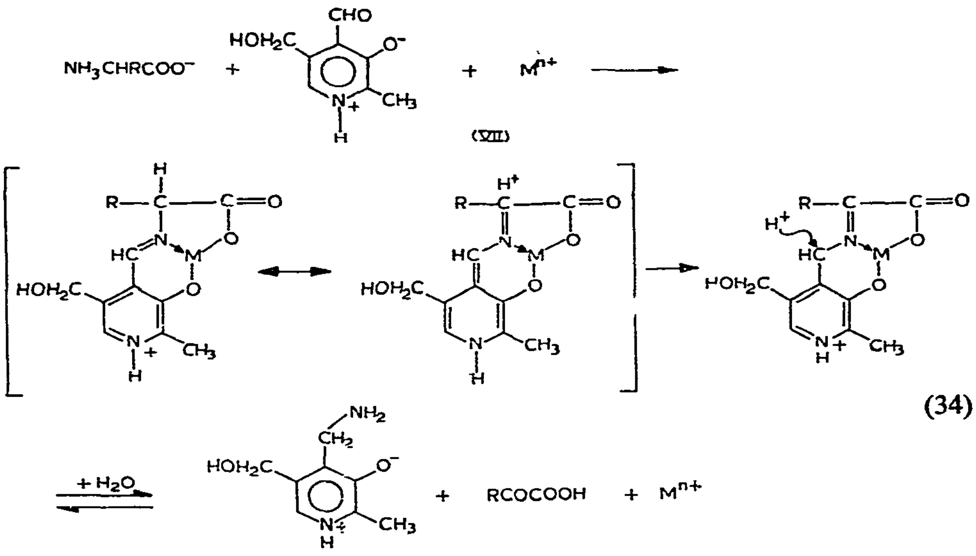
(3) *Formation of a peptide.* In the hydrolysis of amino acid esters described above, the nucleophilic reagent, water, attacks the carbonyl carbon atom. Other nucleophilic reagents can do the same. If the nitrogen atom of an amino acid does so, the reaction may lead to formation of a peptide linkage. Buckingham and his coworkers[60] recently observed the reaction depicted in (33).



(33)

The attacking reagent may be an amino acid or polypeptide; the authors have prepared polypeptides of glycine up to four units large. The amino acid ester being attacked need not be glycine ester; alanine, phenylalanine, histidine and proline have been tried. The reaction is very fast, being complete within 1 min at 20 °C in anhydrous sulfolane, dimethylsulfoxide or acetone.

(4) *Transamination.* Transamination is an important reaction in biological metabolism. An enzyme called transaminase exists. It requires a coenzyme, pyridoxal (structure VII) phosphate (vitamin B_6). Pyridoxal condenses readily with an amino acid to form a Schiff base even in the absence of the enzyme. This condensation has been found to be enhanced by metal ions[61] such as Fe^{III}, Cu^{II} and Al^{III}. Metzler and Snell[61] proposed the mechanism (34).



(34)

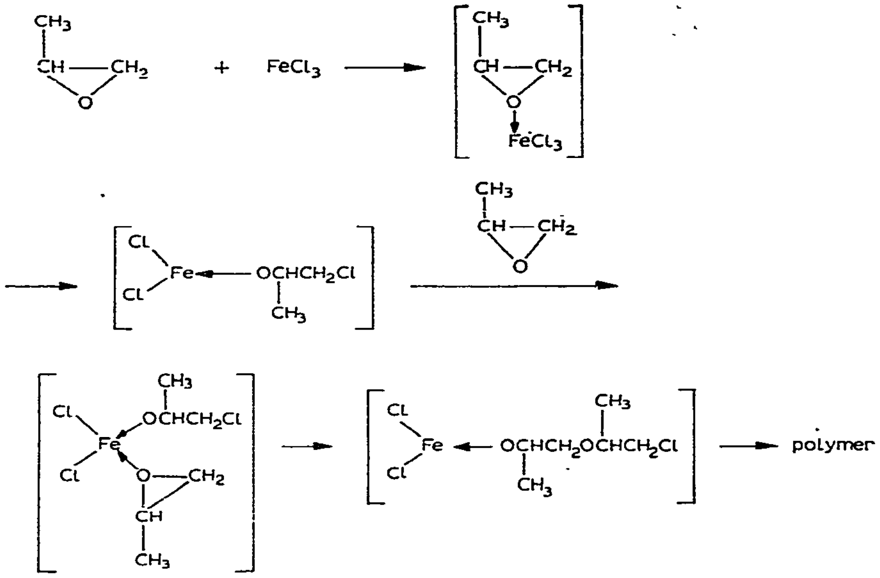
As suggested by the mechanism this system also involves catalytic racemization and decarboxylation of an amino acid.

(5) *Polymerization of propylene oxide.* Lewis acids like $AlCl_3$, $SnCl_4$, and $FeCl_3$ are used as catalysts for the cationic polymerization[62] of α-olefins and vinyl compounds. A protonic acid like HCl and H_2O is usually required as a cocatalyst; thus a proton initiates the polymerization. For example,

$$\begin{aligned} &HX + AlX_3 \rightleftharpoons H^+AlX_4^- \\ &H^+ + CH_2{=}CHR \rightarrow CH_3CHR^+ \xrightarrow{+CH_2=CHR} \\ &CH_3CHRCH_2CHR^+ \rightarrow \text{polymerize} \end{aligned} \tag{35}$$

Solid acids such as Cr_2O_3, Al_2O_3 and MoO_3 polymerize olefins and acetaldehyde.

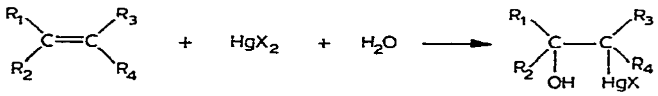
Lewis acids have been found[63] to polymerize propyleneoxide stereospecifically in a homogeneous phase. Some of the active catalysts are $FeCl_3$, $ZnCl_2$[63], $Zn(Et)_2H_2O$ and $Zn(Et)_2ROH$[64]. The active species of the last two organometallic compounds has been found[64] to be $Zn(OR)_2$ which adds OR^- to propyleneoxide initiating an anionic polymerization. $FeCl_3$, a Lewis acid, opens the epoxide ring through its inductive effect[65] (36).



(36)

(iv) Nucleophilic addition reactions to carbon–carbon multiple bonds

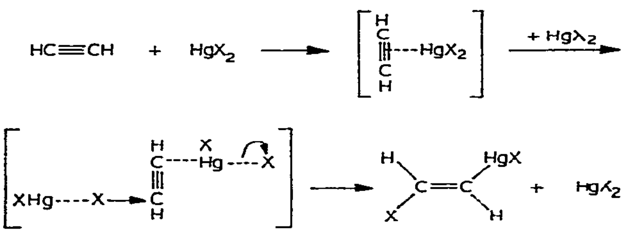
(1) *Reaction of mercuric salts with olefins and acetylenes*[66]. Such addition reactions (37, 38) have been known for a long time. A mechanism which included



(37)

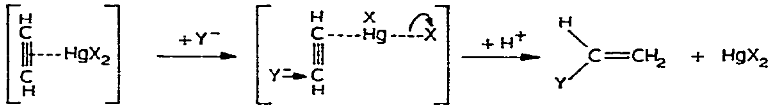
(38)

a π-complex was proposed for the latter reaction; thus:



(39)

(2) *Catalysis of the hydration and vinylation of acetylene.* In the mechanism (39) HgX_2 acts both as an acid to acetylene, *i.e.* as an acceptor, and as a nucleophilic agent in the form X...HgX. When another nucleophilic agent is included in the reaction, the reagent attacks acetylene in place of X...HgX, for example,



(40)

Examples of this type of reaction are the hydration and vinylation of acetylene (41, 42). In the addition of acetic acid, a zinc salt is used as catalyst instead of the

$$HC \equiv CH + H_2O \xrightarrow{HgSO_4} [CH_2 = CHOH] \rightarrow CH_3CHO \qquad (41)$$

$$HC \equiv CH + HCl \xrightarrow{HgCl_2} CH_2 = CHCl \qquad (42)$$

mercuric salt. Flid *et al.*[67] found a linear relationship between the rate constant *k*

$$HC{\equiv}CH{+}HOAc \xrightarrow{Zn(OAc)_2} CH_2{=}CHOAc \qquad (43)$$

and the redox potential *E* of the solution of the mercuric salt in the hydration of acetylene. This is

$$\log k = a - bE \qquad (44)$$

another expression of the Brønsted law which is known to hold generally for acid-base reactions, because *E* is related to the acidity of the solution.

D. CATALYTIC ACTIVITY OF SOFT ACID COMPLEXES

(i) General remarks

Soft acids, such as the first row transition metals in low oxidation states (+1, 0, −1 etc.), and the second and third row transition metal ions can form complexes with olefins, alkyls, carbon monoxide, and hydride ion through π-back bonding as well as σ-bonding. π-bonded complexes of this group can often be reversibly interconverted into σ-bonded complexes. The reaction scheme (45–47) is a general presentation of those reactions which may occur.

$$[(\pi\text{–R})M \xrightarrow{+A} [((\pi\text{–R})A)M] \xrightarrow{-M} (\pi\text{–R})A \qquad (45)$$

$\upharpoonleft\downharpoonright$ or $\upharpoonleft\downharpoonright$ $+X$ (45a)

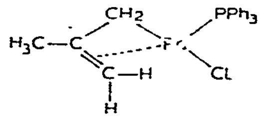
$$[(\sigma\text{–R}')M] \xrightarrow{+B} [((\sigma\text{–R}')B)M] \xrightarrow{-M} (\sigma\text{–R}')B \qquad (46)$$

$$[(\pi\text{–R})M] \xrightarrow{+X} [(\sigma\text{–R}')M] \xrightarrow{-X} [(\pi\text{–R}')M] \qquad (47)$$

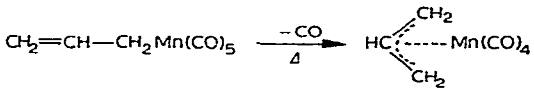
Reaction (48) is an example of the route (45a), where X is $(CH_3)_2SO$[68] or PPh_3[69].

$$[(\pi\text{-allyl})PdCl]_2 + X \rightleftharpoons 2[(\sigma\text{-allyl})PdClX] \qquad (48)$$

An intermediate with the structure (VIII) was proposed[69], on the basis of NMR data. A similar example is the reaction (49)[70].

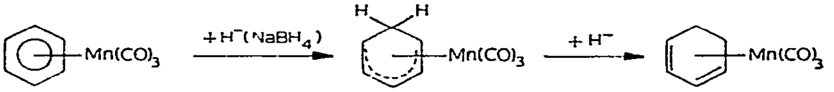


(VIII)



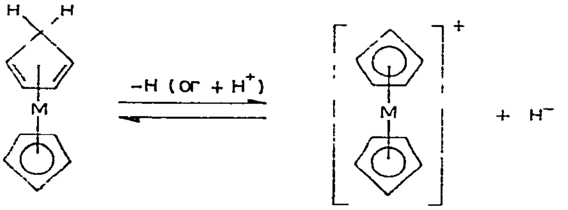
(49)

One of the most important species which acts as A, B, or X in the reaction scheme (45–47) is a hydrogen atom, proton or hydride. Hydrogen is so small, so light and therefore so movable that it can participate fairly readily in a variety of reactions. An example of reaction type (45) where A is hydrogen is[71]:



(50)

The central compound in this reaction has an inert gas electronic configuration and is therefore stable. Cyclopentadienyl complexes of cobalt and rhodium undergo a similar reaction[72];



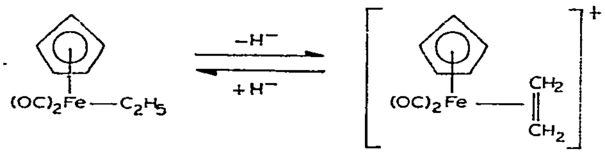
(51)

Two further examples are shown by the following reactions[73,74].

$$[(\pi\text{-}C_7H_8)Mo(CO)_3] \underset{+\,H^-(NaBH_4)}{\overset{-\,H^-(Ph_3)}{\rightleftharpoons}} [(\pi\text{-}C_7H_7)Mo(CO)_3]^+ \qquad (52)$$

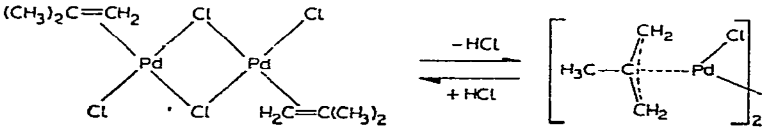
$$[(\pi\text{-}C_6H_8)Fe(CO)_3] \underset{+\,H^-}{\overset{-\,H^-}{\rightleftharpoons}} [(\pi\text{-}C_6H_7)Fe(CO)_3]^+ \qquad (53)$$

A reaction of the type (45a–46) is exemplified by[75]:



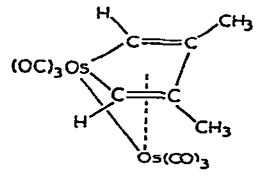
(54)

$[Mn(CO)_5C_2H_5]$ also undergoes the same reaction. Reaction (55) involves a proton rather than hydride transfer[76].



(55)

The reaction of $OS_3(CO)_{12}$ with $CH_2{=}C(CH_3)C(CH_3){=}CH_2$ involves a dehydrogenation process to yield a σ-complex (IX) instead of a diene π-complex[77]. Compounds of this type are readily prepared by the reaction of an acetylene with a metalcarbonyl[78].



(IX)

(ii) Double bond migration and isomerization

The isomerization of double bonds in olefins is catalyzed by a variety of catalysts. Solid acids like SiO_2–Al_2O_3 and strong protonic acids such as sulfuric acid isomerize olefins through addition and abstraction of a proton. Isomerization presumably involving a π-complex intermediate occurs when the catalysts are metal carbonyls, hydrocarbonyls of the first transition series metals, and complexes of second and third row transition series metals.

Fig. 3 shows an example of the reaction course of isomerization of hexene-1 catalyzed by ruthenium chloride[80]. The composition of the products is governed thermodynamically. In the intermediate stage, however, the composition of the products mixture does not agree with that of the equilibrium situation. Three possible mechanisms have been discussed.

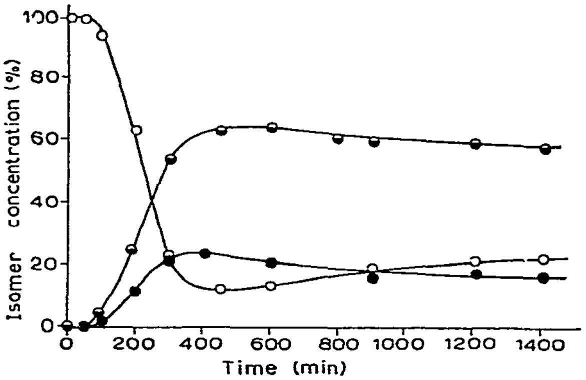
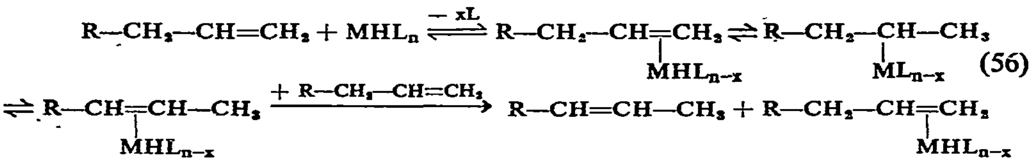


Fig. 3. Isomerization of hexene-1 catalyzed by $RuCl_3$ in ethanol at 65 °C; –o– hexene-1+*trans*-hexene-3, –◑– *cis*-hexene-2+*trans*-hexene-2, and –● · *cis*-hexene-2; the calculated equilibrium values are: –o– 24%, –◑– 56.5% and –●– 19.5%.

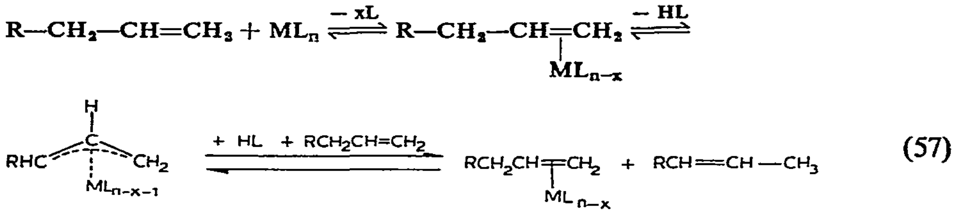
Mechanism I (Hydride addition and elimination mechanism)[81]



$$\mathrm{R{-}CH_2{-}CH{=}CH_2 + MHL_n \overset{-xL}{\rightleftharpoons} R{-}CH_2{-}CH{=}\underset{\displaystyle MHL_{n-x}}{CH_2} \rightleftharpoons R{-}CH_2{-}\underset{\displaystyle ML_{n-x}}{CH}{-}CH_3} \quad (56)$$

$$\mathrm{\rightleftharpoons \underset{\displaystyle MHL_{n-x}}{R{-}CH}{=}CH{-}CH_3 \xrightarrow{+\,R{-}CH_2{-}CH{=}CH_2} R{-}CH{=}CH{-}CH_3 + R{-}CH_2{-}CH{=}\underset{\displaystyle MHL_{n-x}}{CH_2}}$$

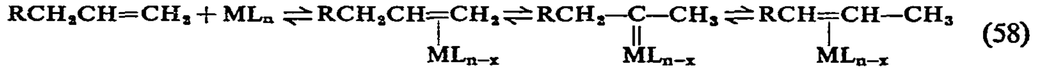
Mechanism II (π-Allyl mechanism)[82]



$$\mathrm{R{-}CH_2{-}CH{=}CH_2 + ML_n \overset{-xL}{\rightleftharpoons} R{-}CH_2{-}CH{=}\underset{\displaystyle ML_{n-x}}{CH_2} \overset{-HL}{\rightleftharpoons}}$$

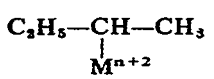
$$\mathrm{\xrightleftharpoons{+\,HL\ +\,RCH_2CH{=}CH_2} RCH_2CH{=}\underset{\displaystyle ML_{n-x}}{CH_2} + RCH{=}CH{-}CH_3} \quad (57)$$

Mechanism III (Carbene mechanism)[83]



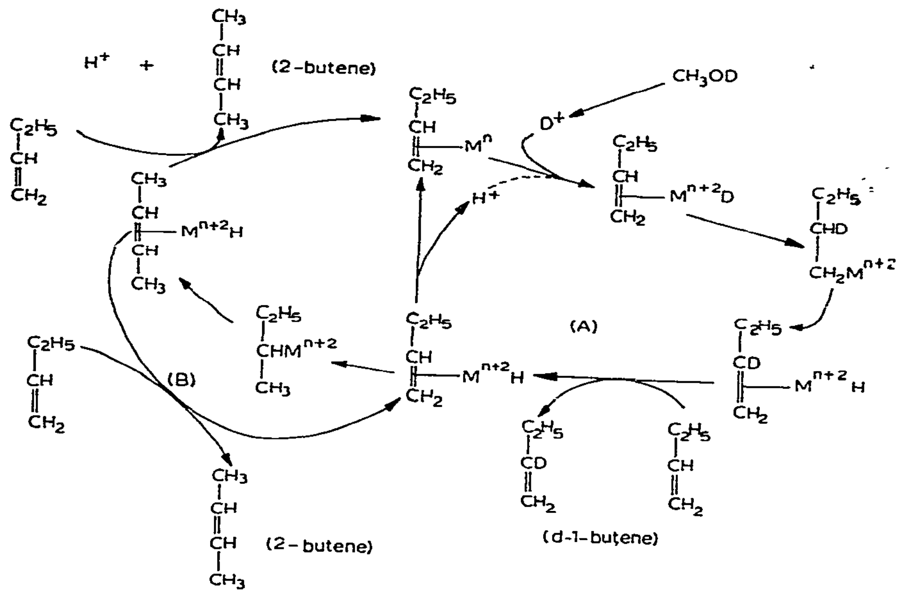
$$\mathrm{RCH_2CH{=}CH_2 + ML_n \rightleftharpoons RCH_2CH{=}\underset{\displaystyle ML_{n-x}}{CH_2} \rightleftharpoons RCH_2{-}\underset{\displaystyle \overset{\|}{ML_{n-x}}}{C}{-}CH_3 \rightleftharpoons RCH{=}\underset{\displaystyle ML_{n-x}}{CH}{-}CH_3} \quad (58)$$

Mechanism I predicts that the product will be deuterated if a deuterated material is used as the hydrogen source. Mechanism II predicts 1 → 3 hydrogen transfer, whereas mechanism III predicts 1 → 2 hydrogen transfer and that a compound like $RCH_2-CR'=CH_2$ will not isomerize. The isomerization of $CH_2=CH-CH_2OH$ catalyzed by $DCo(CO)_4$ produces CH_2DCH_2CHO[84]; this supports mechanism I. In the isomerization of allylbenzene with $HCo(CO)_4$ and $DCo(CO)_4$, the product propenylbenzene is not deuterated and no isotopic effect ($D/H = 1$) is observed[85]; this result indicates no participation of the H–Co bond in the reaction. The reports of Cramer and coworkers[81c] are concerned with the isomerization of butene catalyzed by Rh^{I}, Pt^{II}, Pd^{II}, Ni^{0} and Fe^{0}-complexes. Their results are: (i) a cocatalyst which can supply hydrogen like protonic acid is required, (ii) deuterated olefins are obtained in a deuterated solvent, and (iii) the isomerization of 1-butene in CH_3OD produces d-1-butene but not d-2-butene. These results can be interpreted by mechanism I as rewritten in equation (59) (Scheme 7). The cycle (A) represents H–D exchange reaction and the cycle (B) the isomerization. The participation of a σ-bonded intermediate like



$$\mathrm{C_2H_5{-}\underset{\displaystyle M^{n+2}}{CH}{-}CH_3}$$

also explains the observed *cis-trans*-isomerization. The authors did not offer any unequivocal evidence for the existence of the hydride species. They rely on the fact that rhodium, iridium or osmium compounds form hydride complexes in a protonic solvent like alcohol[25,26]. A related catalyst $RhD(CO)(PPh_3)_3$, whose formula is definitely established, catalyzes both the isomerization and H–D exchange reaction of olefins as well as their hydrogenation[34]. The ruthenium analogue,



(59

Scheme 7

$RuClD(PPh_3)_3$, however, does not catalyze the isomerization of olefins though it is active for H–D exchange and hydrogenation[34].

With palladium compounds, a π-allyl compound is known to inhibit the isomerization of olefins, providing a negative proof for mechanism II[86,81a]. π-Allyl complexes of palladium are usually so stable that the π-allyl ligand cannot be replaced by olefins; thus the above result is not enough to eliminate a π-allyl-isomerization mechanism via a labile π-allyl complex. Mechanism III has been proposed to explain 1 → 2 transfer in deuterated olefins[83], but no definite evidence for the carbene complex has yet been provided.

The isomerization of cyclooctadiene(COD) merits mention. $Fe(CO)_5$ catalyzes 1,5-COD → 1,3-COD[81b], whereas the reaction of 1,3-COD with rhodium trichloride produces 1,5-COD[82a]. The conjugated diene 1,3-COD is thermodynamically more stable than 1,5-isomer; the catalysis by $Fe(CO)_5$ is, therefore, normal. Rhodium compounds form stable chelated π-complexes with 1,5-COD; therefore, the reaction takes place. An iridium complex $IrHCl_2(PPhEt_2)_3$ and a rhodium complex $RhCl_3(PPhEt_2)_3$ which do not form stable complexes with COD, catalyze the normal isomerization, 1,5-COD → 1,3-COD[81b].

(iii) Oligomerization and coupling of olefins, diolefins and acetylenes

The oligomerization or coupling reaction of olefins and others requires hydrogen transfer unless the reaction forms ring compounds. For example, the reactions of mono-olefins are as follows.

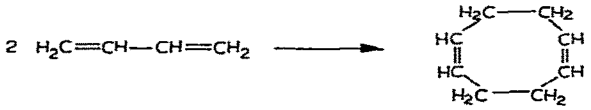
$$2RHC{=}CHR' \rightarrow (RHC{=}CR' \cdots H \cdots RHC{=}CHR') \rightarrow RHC{=}CR'{-}CHR{-}CH_2R' \text{ or } RHC{=}CR'{-}CHR'{-}CH_2R \quad (60)$$

$$RHC{=}CHR + R'HC{=}CHR' \rightarrow RHC{=}CR{-}CHR'{-}CH_2R' \text{ or } RH_2C{-}CHR{-}R'C{=}CHR' \quad (61)$$

In the case of diolefins, the following reactions may occur.

$$2RHC{=}CH{-}CH{=}CHR' \rightarrow RHC{=}CH{-}CH{=}CR'{-}CHR{-}CH{=}CH{-}CH_2R' \text{ or } RHC{=}CH{-}CH{=}CR'{-}CH(CHR_2){-}CH{=}CHR' \quad (62)$$

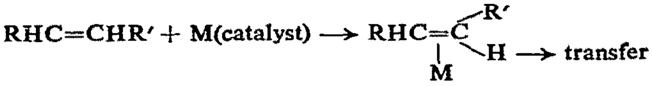
Reaction (63) is an example of ring formation.



(63)

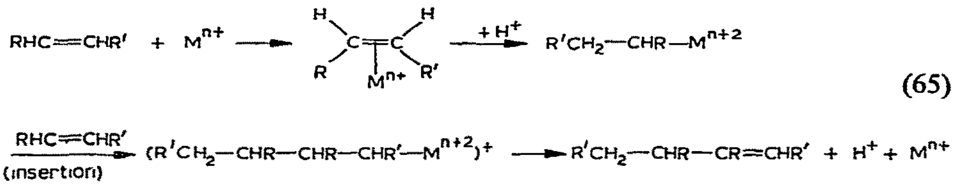
This reaction is similar to Diels–Alder coupling.

In the reaction where a hydrogen transfer process is involved, a catalyst is required which can activate hydrogen in the hydrocarbon. There are two possible rates for hydrogen transfer. One is a direct process (64).



$$RHC{=}CHR' + M(\text{catalyst}) \rightarrow RHC{=}C(R')(H) \ (M) \rightarrow \text{transfer} \quad (64)$$

In another the hydrogen atom comes from outside; for example:

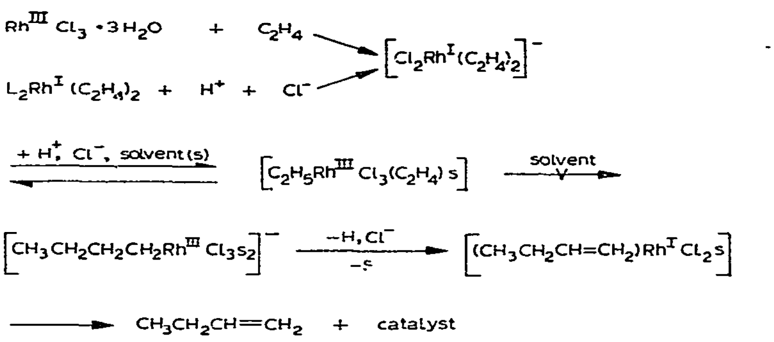


(65)

In reaction (64), the hydrogen transferred is considered to be a hydride.

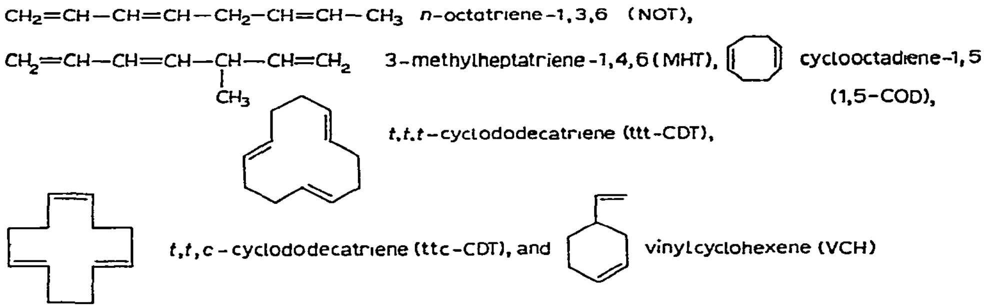
(1) *Olefins.* Chlorides of rhodium, ruthenium and palladium can catalyze the linear dimerization of olefins and vinyl compounds[87]. The reaction of ethylene catalyzed by $RhCl_3$ produces exclusively 1-butene (yield > 99%)[88]. Mechanism (65) has been proposed by Cramer[88] for this reaction. In the case of ethylene, reaction (65) can be rewritten as (66).

The NMR spectrum of $[(\pi\text{-}C_5H_5)Rh(C_2H_4)_2]$-HCl shows bands at $\tau = 8.43$ (CH_3) and 7.02 (CH_2) in addition to the bands due to C_2H_4 and π-C_5H_5, indicating the formation of C_2H_5–Rh. Ethylene is found to be deuterated by $[(acac)Rh(C_2H_4)_2]$–C_2H_4–DCl–CH_3OD. This result can be explained in terms of the reversibility of the C_2H_5–Rh formation step. The insertion step in which the coordinated C_2H_4 group inserts into the C_2H_5–Rh bond is considered to be rate-determining.

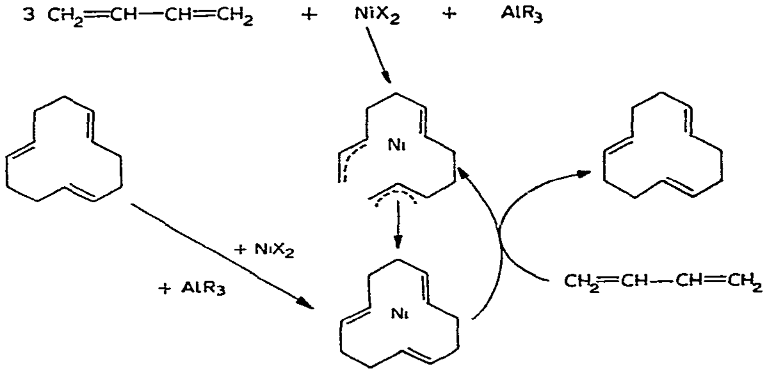


(66)

(2) *Butadiene.* The oligomerization of butadiene[89] is of great interest. Some of the oligomerizations and polymerizations of butadiene are summarized in Table 5 (the references are omitted). Some of the possible oligomers of butadiene are:



Points of interest concerning the data in Table 5 include (i) the relation of the reaction mode (selectivity) with the nature of the metal, (ii) the structure of the active catalytic species and (iii) the effect of the ligand. It is to be noted that only cobalt and iron complexes catalyze linear dimerization. Complexes of other metals catalyze the ring forming oligomerization. Linear oligomerization requires a hydrogen transfer. The catalysts for linear oligomerization, therefore, should be



(67)

Scheme 8

TABLE 5

CATALYZED REACTIONS OF BUTADIENE

Catalyst	*Reaction product*				
	Oligomerization		*Polymerization** *(%)*		
	main product	*by-product*	*cis-1,4*	*trans-1,4*	*1,2-*
$TiCl_4$–$AlEt_3$ (1:1.5)				80	
$TiCl_4$–$AlEt_2Cl$ (1:4.5)	ttc-CDT	PB**			
$Ti(OR)_4$–$AlEt_3$ (1:20)	ttc-CDT	PB			
$TiBr_4$–$AlEt_3$ (1:1.5)			65	30	5
TiI_4–$AlEt_3$ (1:1.5)			86	10	4
VCl_4 or VCl_3–$AlEt_3$				98	
$V(acac)_3$–$AlEt_3$					synd.
$CrCl_3$–$AlEt_3$ (1:<6)					synd.
$CrCl_3$–$AlEt_3$ (1:>15)					isot.
CrO_2Cl_2–AlR_3 or AlH_3 or $AlHR_2$	ttt-CDT (6)	ttc-CDT (4)			
CrO_3–AlR_3	CDT	COD			
$MnCl_2$–$AlEt_3$					90
$Mn_2(CO)_{10}$–$AlEt_3$	COD				
$Mn(acac)_2$–$AlEt_3$	COD	VCH			
$Fe(acac)_3$–dip(or phen)–$AlEt_3$	COD	MHT, VCH			
$Fe(acac)_3$–PPh_3–$AlEt_3$ (1:8:30)	MHT, VCH	COD			
$CoCl_2$–$AlEt_3$			87		
$CoCl_2AlCl_3$–thiophen			94		
$Co_2(CO)_8$–$AlEt_3$ (1:30)	MHT	VCH, COD			
$Co(acac)_3$–$AlEt_3$ (1:3)	MHT	NOT			
$NiCl_2$–$AlEt_3$			97		
$Ni(CO)_2X_2(XPPh_3,P(OR)_3,SbPh_3)$	COD	VCH			
$Ni(CO)_4$–$AlEt_3$ (1:10)	ttt-CDT	VCH, COD			
$Ni(acac)_2$-$AlEt_2(OEt)$	ttt-CDT	VCH, COD			
$RhCl_3$ in emulsion				99.5	0.5
$PdCl_2$ in emulsion				2–17	98–83
$IrCl_3$ in alcohol				99–100	
$RuCl_3$-$P(n\text{-}Bu)_3$ (1:10)			15	15	70
$RuCl_3$ in alcohol	[(trimer)$RuCl_2$]***				
BuLi			40	40	10

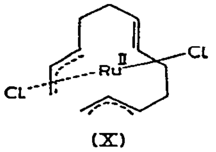
* *cis*-1,4, *trans*-1,4, and 1,2- mean the microstructure of polybutadiene; synd.: syndiotactic, isot.: isotactic.

** PB polybutadiene.

*** See the text (structure (X)).

capable of coordinating a hydride which must be transferable between metal and butadiene. The hydrogen-to-metal bonds in complexes of cobalt and iron in low oxidation states are considered to be too weak to be stabilized. Nickel species cannot form such a transferable hydrogen-to-metal bond.

The mechanism of cyclooligomerization elucidated by Wilke *et al.*[89] is shown in (67) The complex Ni(CDT) has been obtained as red crystals. This compound is short by two electrons of the inert gas configuration and so can be coordinated by a nucleophilic reagent like triphenylphosphine. Instead of triphenylphosphine, butadiene may coordinate, expelling CDT from the coordination sphere, and form the intermediate π-allyl complex. The reaction of ruthenium chloride with butadiene in alcohol produces a π-allyl complex of the butadiene trimer(X) which corresponds to the intermediate nickel complex in the reaction scheme (67). This ruthenium complex has an inert gas configuration.



(X)

As is shown in Table 5, whether dimerization(COD) or trimerization(CDT) occurs or whether ttt-CDT or ttc-CDT is obtained depends largely upon the catalyst. The number of coordination sites available for butadiene, the structure of the coordinated butadiene, the electronic structure of the metal in the catalyst complex represent factors which require evaluation on the basis of more data.

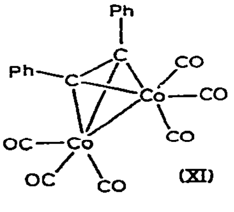
The coupling reaction between different olefins or an olefin and a diolefin is of great interest. Two products are possible in the reaction between ethylene and butadiene.

$$H_2C{=}CH_2 + H_2C{=}CH{-}HC{=}CH_2 \rightarrow H_2C{=}CH{-}CH_2{-}HC{=}CH{-}CH_3 \quad (68a)$$

$$H_2C{=}CH_2 + H_2C{=}CH{-}HC{=}CH_2 \rightarrow H_3C{-}CH_2{-}HC{=}CH{-}HC{=}CH_2 \quad (68b)$$

$RhCl_3 \cdot 3H_2O$[91] and $NiCl_2$–PR_3–AlR_2Cl[92] catalyze the former reaction, but the latter reaction is catalyzed by $Co(acac)_3$–$AlEt_3$[93]. The last catalyst may activate the hydrogen of butadiene as suggested by the fact that it dimerizes butadiene linearly. The first two catalysts activate the hydrogen of the olefin, as suggested by reaction (66).

(3) *Acetylene.* One of the characteristics of acetylene is that it has two π-orbitals perpendicular to one another. If both of the two orbitals participate in bonding at the same time, acetylene can coordinate to two metal atoms. An example of a compound of this type is the adduct of phenylacetylene with dicobalt-octacarbonyl (XI)[94]. When only one of the two π-orbitals participates in bonding, it will give rise to a conjugated polyene with terminal unpaired electrons.

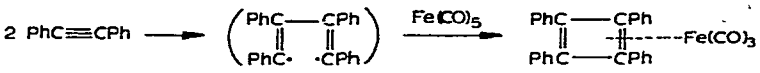


(XI)

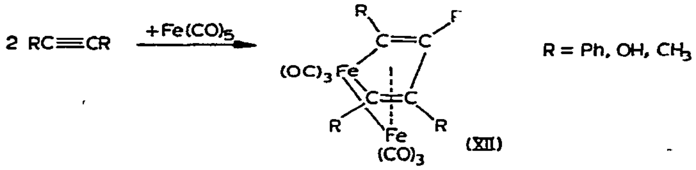
(69)

$$2HC{\equiv}CH \longrightarrow \cdot HC{=}CH{-}HC{=}CH\cdot \xrightarrow{+C_2H_2} \cdot HC{=}CH{-}HC{=}CH{-}HC{=}CH\cdot \dashrightarrow$$

The unpaired electrons on each end of the chain can be stabilized by forming a ring compound by combination with one another, or by forming σ-bonds or a π-allylic bond with a metal or other group. A few examples are cited below[95–99].

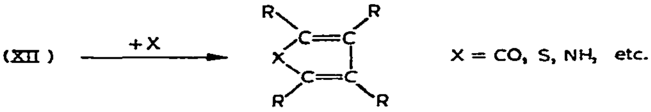


(70)



(XII)

(71)



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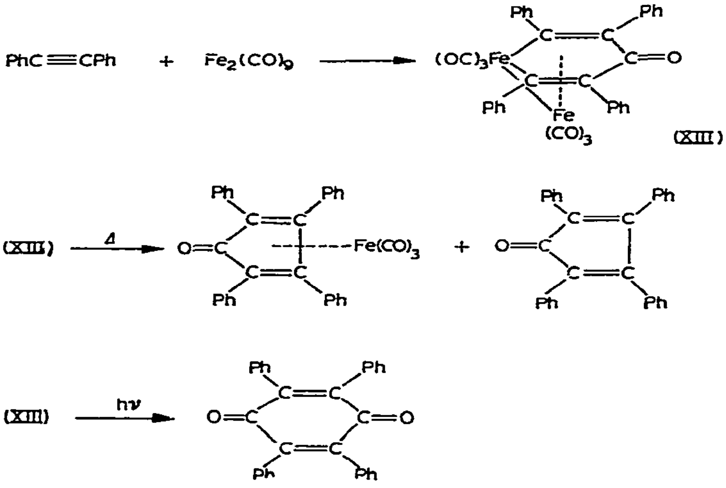
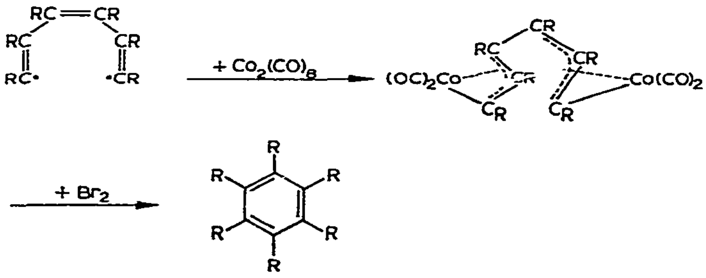


(XIII)

(73)



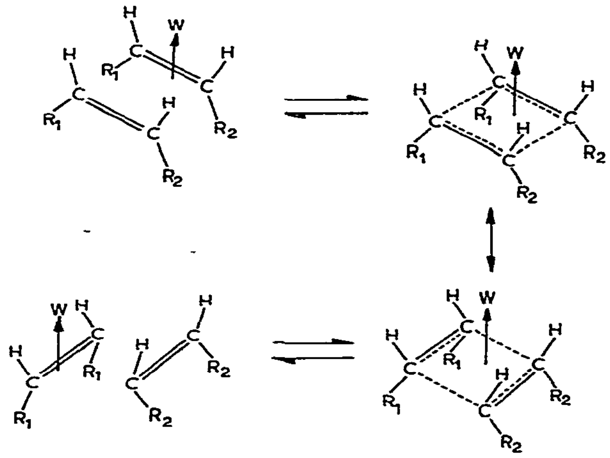
(74)

In the course of the Reppe reactions which synthesize benzene, benzoquinone, cyclooctatetraene or their derivatives from acetylene with metal complex catalysts, complexes of the types described above may be intermediates.

(4) *Double bond cleavage reactions.* Calderon and his coworkers[100] recently discovered a new type of reaction formulated as follows.

$$2\ R_1\text{—}HC{=}CH\text{—}R_2 \xrightleftharpoons{WCl_6\text{–}AlEtCl_2} R_1\text{—}HC{=}CH\text{—}R_1 + R_2\text{—}HC{=}CH\text{—}R_2 \quad (75)$$

For example, 2-pentene is converted to 2-butene and 3-hexene in the ratio of 1:2:1 = 2-butene:2-pentene:3-hexene at equilibrium. The reaction proceeds very fast even at room temperature to reach thermodynamic equilibrium. The reaction between $CH_3CH{=}CHCH_3$ and $CD_3CD{=}CDCD_3$ produces only $CH_3CH{=}CDCD_3$. These data indicate that the reaction is not transalkylation but transalkylidenation, depicted in (76).



(76)

(iv) Polymerization

A catalyst in a polymerization process may act as: (i) initiator (a) only for initiation or (b) providing a controlling fragment at the growing chain end, (ii) an activator of the growing chain end, and (iii) an activator of the approaching monomer. These possibilities are depicted in Fig. 4.

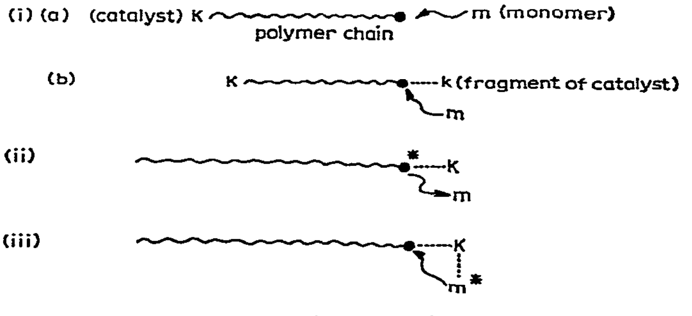


Fig. 4. The roles of catalysts in polymerization.

A monomer to be polymerized forms an unsaturated terminal with the action of a catalyst. Such an unsaturated bond can be formed by the cleavage of a single bond like C–O, C–N, and C–C, or by the localization of π-electrons in such bonds as C=O, C=N, and C=C. A classification of the type of polymerization into "radical", "cationic" or "anionic" according to the character of the growing chain end is not essential. One of the crucial points is whether the catalyst can maintain the reactivity of the growing chain end, that is, the unsaturation, or not. The growing chain end may be deactivated externally or internally. An example of the former is chain transfer to the solvent. Internal deactivation is exemplified by the recombination of one growing chain end with another, or a reaction between the entering monomer and the chain end through the catalyst. If the deactivation process is faster than the polymerization, propagation process the reaction would be oligomerization at best; it would be polymerization if the reverse is the case. Recombination of the growing chain ends is difficult if they carry charges of the same sign. It takes place very readily when the chain ends are radical and on the same atom of the catalyst (Fig. 5). An example of this type of recombination is the ring forming oligomerization of butadiene as mentioned above.

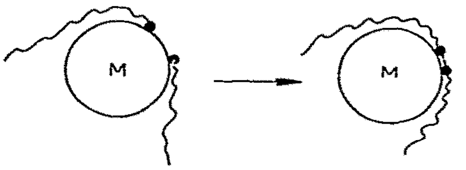


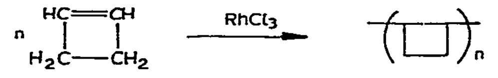
Fig. 5. The recombination of radicals on the same catalyst metal atom.

Eqn. (77) shows an example of the reaction of the growing chain end with the monomer through the catalyst.

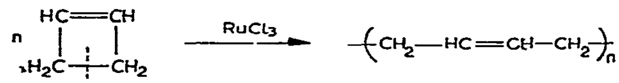
$$\begin{array}{l} =CH-HC=CH_2 + MR(M=\text{metal}, R=H \text{ or alkyl group}) \\ CH_2R-HC=CH-CH_2-M \xrightarrow{+H_2C=CH-HC=CH_2} RCH_2HC=CHCH_2CH_2HC=CHCH_2-M \\ \qquad + H_2C=CH-HC=CH_2 \quad \swarrow \qquad \text{or} \qquad \downarrow \qquad\qquad (77) \\ \qquad\qquad \text{polymerize} \qquad RCH_2HC=CHCH_2HC=CHHC=CH_2 + MH \end{array}$$

The catalysts listed in Table 5 will be reviewed briefly for this particular reaction. Lithium alkyl cannot abstract a hydrogen from butadiene but rather continues the insertion of butadiene. Cobalt and iron complexes are capable of transferring hydrogen as previously discussed, thus oligomerizing butadiene in their low oxidation states (0 and −1), but they polymerize it in +1 or higher oxidation states. Zero oxidation state nickel species trimerize butadiene but higher oxidation state nickel complexes such as $[Ni(\pi\text{-allyl})Br]_2$[101] catalyze the polymerization process. Rh^{I}, Ru^{II}, Pd^{II} and Pt^{II} oligomerize butadiene in non-aqueous solvents, but polymerize it under suitable conditions[102].

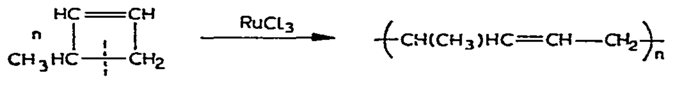
The strain in a ring is an important factor in a ring-opening polymerization. Cyclobutene polymerizes through double bond opening (78a) with a catalyst such as $RhCl_3$, $[Ni(\pi\text{-allyl})Br]_2$, VCl_4-$AlEt_3$ or CrO_2Cl_2–$AlEt_2Cl$, while it polymerizes through ring opening (78b) with $RuCl_3$, $TiCl_3$–$AlEt_3$, or $MoCl_5$–$AlEt_3$[103]. The



(78a)



(78b)



(78c)

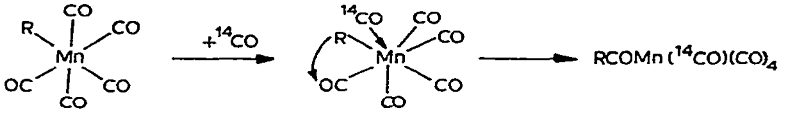
mode of polymerization depends up on the catalyst, but the polymerization of norbornene is always ring-opening with catalysts such as $RuCl_3$, $OsCl_3$ or $IrCl_3$[104]. This is due to the considerable ring strain.

(v) Insertion reactions[105]

Pentacarbonylmethyl manganese $CH_3Mn(CO)_5$ forms pentacarbonylacetyl manganese $CH_3COMn(CO)_5$ when subjected to a high pressure of carbon monoxide at room temperature, but the latter is reconverted to the former upon heating[106].

$$CH_3Mn(CO_5) \underset{-\,CO,}{\overset{+\,CO,\ 35\ \text{atm.},\ 20°C}{\rightleftharpoons}} CH_3COMn(CO)_5 \qquad (79)$$

Since in an atmosphere of ^{14}CO the reaction does not yield $CH_3{}^{14}CO$, this reaction must be intramolecular and is therefore an insertion reaction.



(80)

The same type of reaction takes place with a base such as an amine[108] or phosphine[109] in place of carbon monoxide.

$$RMn(CO)_5 + B(\text{amine or phosphine}) \rightleftharpoons RCOMn(CO)_4B \qquad (81)$$

The insertion reaction may be generally described as follows[105]. Y is an unsatur-

$$M{-}Z + {:}Y \rightarrow M{-}Y{-}Z \qquad (82)$$

ated compound, exemplified by carbon monoxide, olefin, acetylene or carbonyl compound. Reactions (83) and (84) are examples of this type of behaviour.

$$M{-}Z + R_2C{=}CR_2 \rightarrow M{-}CR_2CR_2Z \tag{83}$$

$$M{-}Z + R_2C{=}O \rightarrow M{-}CR_2OZ \tag{84}$$

Reaction (83) may be regarded as an addition of M–Z upon the olefin. Reaction (84) may also be an addition. There is some doubt about the definition of insertion except in the well established case of acylation.

The compound $RCOCo(CO)_4$ can be prepared by several methods[110]. The reactivity of this compound is greater than that of the manganese compound and depends more strongly upon the pressure of carbon monoxide. The mechanism of the oxo-process with a cobalt carbonyl catalyst can reasonably be explained in terms of these reactions; thus:

$$\begin{aligned} &RHC{=}CH_2 + HCo(CO)_4 \rightleftharpoons RH_2C{-}CH_2{-}Co(CO)_4 \\ &\underset{-\,CO}{\overset{+\,CO}{\rightleftharpoons}} RH_2CCH_2COCo(CO)_4 \overset{+\,H_2}{\rightleftharpoons} RH_2CCH_2CHO + HCo(CO)_4 \end{aligned} \tag{85}$$

A Reppe reaction can be similarly written; for example in the case of acetylene with nickel catalyst:

$$\begin{aligned} &Ni(CO)_4 + HX \rightleftharpoons HNi(CO)_2X + 2CO \overset{+\,HC\equiv CH}{\rightleftharpoons} H_2C{=}CH{-}Ni(CO)_2X \\ &\overset{+\,CO}{\rightleftharpoons} H_2CCHCO{-}Ni(CO)_2X \xrightarrow{+\,ROH} H_2C{=}CHCOOR + HNi(CO)_2X \end{aligned} \tag{86}$$

E. ORGANIZATIONAL ACTION OR TEMPLATE EFFECT

Catalytic action can be described in terms of absolute rate theory as an effect to decrease the activation free energy of a reaction. Since $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S$, decreasing $\Delta H^{\neq}$ and/or increasing $\Delta S^{\neq}$ decrease the activation free energy $\Delta G^{\neq}$. In many synthetic reactions, $\Delta S^{\neq}$ may have a large negative value; in order to effect such a reaction, the large negative value of $\Delta S^{\neq}$ must be overcome by $\Delta H^{\neq}$. $\Delta H^{\neq}$ can be decreased by the bonding energy of a catalyst with the intermediate, the activated complex or even the starting reactants. This can be defined as organizational action, and occurs for example in the synthesis of phthalocyanine from four moles of phthalonitrile.

Busch *et al.*[110] have proposed the term "template effect" to describe the action of a metal ion which, for example, produces a macrocyclic ligand complex in the reaction:

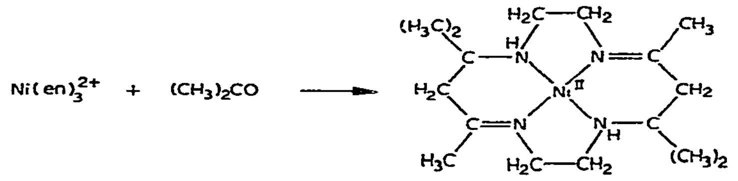
$$A + B + M(\text{metal ion}) \rightarrow [(\text{macrocycle})M] \tag{87}$$

The reaction does not take place in the absence of the metal ion. This is specifically termed a kinetic template effect, and may be considered the same in essence as the organizational action defined above, though it is not catalytic. There is another type of template effect, a thermodynamic one. It is the effect of a metal ion upon the following equilibrium reaction.

$$A + B \rightleftharpoons AB \tag{88}$$

The addition of a metal ion displaces the equilibrium toward the right hand side, by forming a complex [(AB)M].

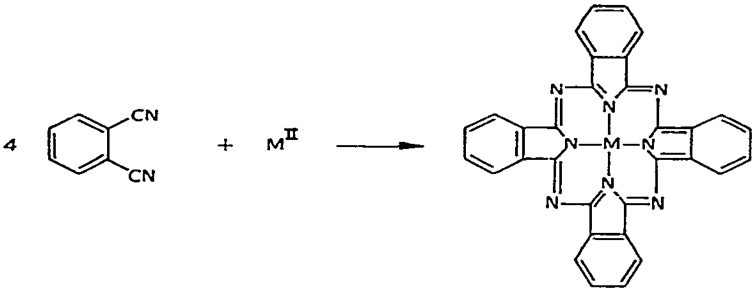
Curtis[112] synthesized a macrocyclic ligand complex by the condensation of tris(ethylenediamino)nickel with acetone:



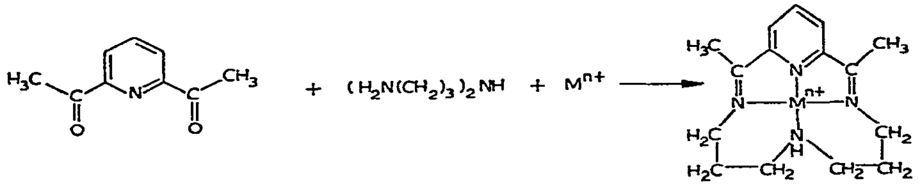
(89)

This same macrocylic ligand has been found to form in the condensation of acetone with a protonic acid salt of ethylenediamine even in the absence of a metal ion[113]. This reaction, therefore, is considered a thermodynamic template effect.

Phthalonitrile forms a phthalocyanine metal complex when heated with a metal salt, though it does not do so in the absence of it (90).



(90)



(91)

Reaction (91) illustrates[114] another example of template effect.

The condensation of 2,6-diacetylpyridine with bis(aminopropyl)imine produces a resinous material, however, in the absence of a metal ion such as Ni^{II}, Co^{II}, Fe^{II} or Cu^{II}.

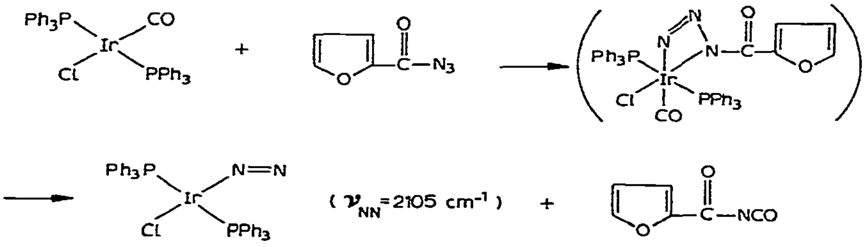
The reactions cited here are non-catalytic. The ring-forming dimerization or trimerization of butadiene or acetylene mentioned earlier are examples of catalytic template or organizational action.

F. NITROGEN FIXATION

Catalysts which produce ammonia from nitrogen and hydrogen under mild condition are eagerly searched for. Some bacteria fix nitrogen at normal temperature and under normal pressure; they are considered to contain a nitrogenase in which metal complexes of iron and molybdenum participate.

Several complexes containing a coordinated nitrogen molecule have been prepared recently. Such complexes are not promising however as far as the production of ammonia is concerned.

Collman *et al.*[115] observed the following reaction. The nitrogen of the iridium



(92)

complex comes from the azide but not from molecular nitrogen. A ruthenium complex was prepared by Allen and Senoff[116]. The same complex

$$NH_2NH_2H_2O + RuCl_3 \xrightarrow[\text{at 25C°}]{\text{in } H_2O} [Ru(NH_3)_5N_2]X_2 \quad X{=}Br^-, I^-, BF_4^-, PF_6^- \qquad (93)$$

was recently claimed to form spontaneousely from $[Ru^{II}(NH_3)_5(H_2O)]$ in a nitrogen atmosphere [117]. In this complex $\nu_{NN} = 2170\text{–}2115\ cm^{-1}$. The cobalt complex $[N_2CoH(PPh_3)_3]$ ($\nu_{NN} = 2088\ cm^{-1}$) has been prepared by three groups[118-120]. The Japanese groups[118,119] prepared it by the reduction of a mixture of triacetylacetonatocobalt and triphenylphosphine by diethylethoxyaluminum or tributylaluminum under nitrogen. This is the first reaction in which atmospheric nitrogen gas has been fixed as a ligand in a metal complex. Their formula was $[N_2Co(PPh_3)_3]$ but later it was shown by Sacco and Rossi[120] to be $[N_2CoH(PPh_3)_3]$. This latter formulation has an inert gas configuration around cobalt. The complex forms yellow crystals and decomposes to give the calculated amount of nitrogen at temperature higher than 80 °C. The coordinated nitrogen molecule is displaced by hydrogen in a hydrogen atmosphere; *i.e.*, the nitrogen is not hydrogenated.

Vol'pin and Shur[121] reported the formation of ammonia in the system MX_n–$M'R_m$ where M is a transition metal such as Cr, Mo, W, Fe and Ti, and $M'R_m$ is an organometallic compound such as RMgBr, RLi, AlR_3 and so forth. The yield of ammonia is not over 100% per mole of transition metal, being at most 70%; therefore the reaction is not catalytic. A similar process involving Ti^{II} was reported recently[122].

There are two important steps in the fixation of nitrogen to form ammonia; the coordination of nitrogen and the hydrogenative splitting of the N–N bond.

$$\text{(i) } \mathrm{M(catalyst)} + \mathrm{N_2} \rightleftharpoons \mathrm{M{-}N_2}$$

$$\text{(ii) } \mathrm{M{-}N_2} \xrightarrow{+\mathrm{H_2}} \left(\mathrm{M{-\!-}}\overset{\mathrm{H}}{\mathrm{N}}{=}\overset{\mathrm{H}}{\mathrm{N}}\right) \longrightarrow \mathrm{M} + 2(\mathrm{NH}) \qquad (94)$$

The first step has been observed. The second step has not yet been effected by complexes which coordinate nitrogen, but is observed with nitride forming metals including the binary complex systems cited above. A binary complex system, M_1(nitrogen fixation)-M_2(hydrogenation), would be required for the complete ammonia forming catalyst[123].

G. CONCLUDING REMARKS

No attempt has been made to write an exhaustive review of this subject. The material has been chosen according to the author's interest. The references have been surveyed up to the middle of 1967. In the course of preparation of this manuscript, an excellent review by J. P. Collman[124] on "Reactions of Coordinated Ligands" was published. Much may be learned about catalytic reactions from Collman's review, since catalytic reactions and the reactions of coordinated ligands, are closely related to one other.

Though the text is not exhaustive, some comments on the general features of metal complex catalysts may be made.

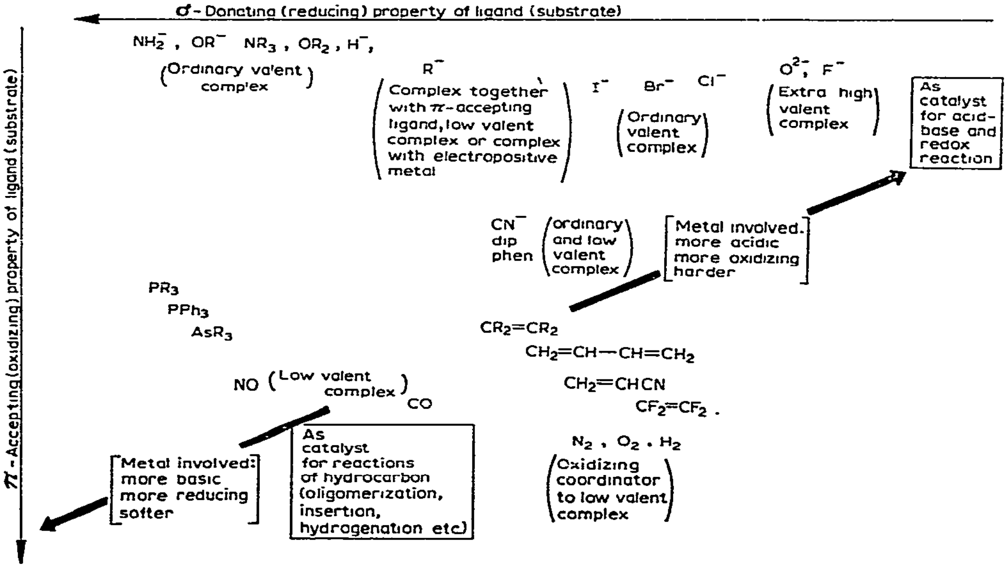


Fig. 6. A qualitative correlation of the catalytic functions and the bonding nature of complex catalysts.

(1) Catalytic functions of metal complexes and the nature of their metal-to-ligand bonds:

A general principle of chemical reactivity was proposed by Pearson[49]: "A hard acid prefers a hard base and a soft acid prefers a soft base". This principle can be extended to catalytic reactions with metal complex catalysts, as depicted in Fig. 6. The next step is to make this scheme quantitative, as suggested, for example, in section C (i).

(2) Catalytic functions of metal complexes with their properties:

A catalyst K_i has several catalytic functions, which may be expressed by the rate constant $r_u(K_i)$ for a reaction u. The activities of catalysts for a certain reaction u can thus be compared by use of $r_u(K_i)$, $r_u(K_j)$... Another function of a catalyst is a selectivity over, for example, two reactions u and v, which can be expressed by the ratio $r_u(K_i)/r_v(K_i)$. The function $r_u(K_i)$ and catalyst parameters K_i may be continuous or discontinuous (discrete); the continuous properties such as the acidity of the central metal ion and the *trans*-effect of the ligands change gradually from one species to another, while the discrete properties like the number of available coordination sites and the effective atomic number have discrete values. The symmetry of the orbitals of the central metal ion is one of the discrete properties. If r_u is a continuous function which depends largely on a continuous catalyst parameter then r_u changes gradually from one catalyst to another. On the other hand, if r_u is a discontinous function like a delta function, in a case where, for example, just two coor-

TABLE 6

MPORTANT PROPERTIES OF METAL COMPLEXES AND THEIR CORRELATION WITH CATALYTIC FUNCTIONS

<table>
<tr><th><i>Continuous property</i></th><th><i>Discrete property</i></th></tr>
<tr><td>Bond nature and stability:</td><td>Symmetry of the orbitals</td></tr>
<tr><td>covalency of metal-to-ligand bond (substrate is a ligand)</td><td>Effective atomic number (number of electrons)</td></tr>
<tr><td>acidity of the metal in the complex (including softness)</td><td>Unsaturated nature of the electron configuration (inert gas rule)</td></tr>
<tr><td>electronegativity, energy level</td><td>Number of coordination sites</td></tr>
<tr><td>ionic radius</td><td>Number of transferable electrons</td></tr>
<tr><td>Liability to substitution:</td><td></td></tr>
<tr><td><i>trans</i> effect</td><td></td></tr>
<tr><td>π-bonding effect</td><td></td></tr>
<tr><td>ligand field effect</td><td></td></tr>
<tr><td>Liability to electron transfer:</td><td></td></tr>
<tr><td>redox potential</td><td></td></tr>
<tr><td>electron transfer rate</td><td></td></tr>
<tr><td colspan="2">Steric hindrance</td></tr>
<tr><td>contribute mainly to
CATALYTIC ACTIVITY</td><td>contribute mainly to
CATALYTIC SELECTIVITY</td></tr>
<tr><td colspan="2">CATALYTIC FUNCTION</td></tr>
</table>

dination sites should be available for the reaction, the r_u function may change its value abruptly from one catalyst to another. This is an essential contribution to the selectivity of a catalyst. R. B. King[125] has developed the idea of discrete variables to systematize organometallic reactions, but not catalytic reactions. An orbital symmetry consideration has been introduced into a catalytic reaction[126] following Hoffman and Woodward. Theoretical considerations relating the catalytic functions of a complex with its fundamental properties need to be made more extensively. Table 6 lists some of more important properties which relate to catalytic activity.

Note added in proof

(1) The autoxidation with the complexes of non-changeable valence (B, v (1)) was reasonably criticized by Beck[127].

(2) A monograph[128] covering the entire field of section D has been published, including detailed data.

(3) A complex which represents the intermediate in the butadiene oligomerization catalyzed by cobalt complex has been isolated and determined of its structure[129].

(4) X-ray crystallographic determination[130] of $[CoN_2(H)(PPh_3)_3]$ shows that the structure is essentially trigonal bipyramidal with N_2 (linear) and H^- on the apical positions.

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