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Homogeneous Hydrogenation

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The present review examines catalytic systems which activate molecular hydrogen. Particular attention is paid to catalysis by compounds of transition metals. These systems are discussed in the following order: catalysis by salts of transition metals; catalysis by salts of transition metals in the presence of reducing agents (complex-forming reagents); and catalysis by individual complexes. General problems relating to the activation of hydrogen and the mechanism of the hydrogenation of organic compounds are also discussed. A separate section is devoted to the activation of molecular hydrogen by enzymatic systems. The bibliography contains 282 references.

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I. INTRODUCTION

Increasing attention is now being paid to homogeneous reactions involving complexes of transition metals: hydrogenation, hydroformylation, the polymerisation and oxidation of alkenes, the fixation of nitrogen, etc. A number of factors, for example the mode of activation of the substrate, the nature of the active species, etc., are common to these processes. Many hydroformylation catalysts are also effective hydrogenation catalysts; various Ziegler–Natta polymerisation catalysts are also active catalysts for hydrogenation and the fixation of nitrogen, etc. The investigation of the systematic features of these processes is therefore of general importance.

The problem of homogeneous hydrogenation is also of practical interest. For example, the use of molecular hydrogen in the polymerisation of alkenes by means of Ziegler–Natta catalysts makes it possible to control the molecular weight of the polymers formed[1], and homogeneous hydrogenation catalysts are used in fuel cells[2].

Research workers have long recognised the advantages of homogeneous over heterogeneous catalytic hydrogenation; the most important advantages are the ease of regeneration of the catalyst and the milder conditions of the process, combined with high efficiency, selectivity, and stereospecificity, and convenience for kinetic studies. In the last ten years the number of known homogeneous hydrogenation catalysts has increased considerably, and this has made possible a deeper and more complete study of a number of problems relating to the mechanism of hydrogenation.

In general, homogeneous hydrogenation with the participation of molecular hydrogen involves two inter-related stages: 1) the activation of molecular hydrogen; and 2) the actual hydrogenation, including activation of the substrate and the transfer of activated hydrogen to the substrate.

In the activation stage, molecular hydrogen reacts with the active compound with rupture of the H–H bond and the eventual formation of a hydrido complex, which may undergo further reactions (isotopic exchange, hydrogenation, etc.). Proof of the intermediate formation of these hydrides is an important task in the study of the mechanism of hydrogenation.

The activation of hydrogen has been the subject of an extensive review by Halpern[3], various papers[4–10], and individual chapters in other reviews[11–13]. The amount of work in this field has increased considerably since then, and the number of known homogeneous hydrogenation catalysts has increased significantly.

The present review covers data published up to 1967 and part of the data published in 1968; particular attention has been paid to the latest developments in the study of the mechanism of the activation of molecular hydrogen and homogeneous hydrogenation. Catalytic systems are classified as follows: a) systems without transition metal compounds; b) systems with transition metal derivatives; and c) biological systems.

It seemed convenient to consider isotopic exchange and the ortho-para conversion of hydrogen separately from hydrogenation.

II. ISOTOPIC EXCHANGE AND CONVERSION OF HYDROGEN

The isotopic exchange of molecular hydrogen and the conversion of ortho-hydrogen into para-hydrogen, which unavoidably involve rupture of the H–H bond, can be used successfully to study the activation of hydrogen. A significant advantage of these reactions compared with hydrogenation is their convenience for kinetic studies and their relative simplicity, since there is no need for the activation of a substrate, and the chemical changes in the system are minimal. Comparison of the results of studies of the exchange and conversion of hydrogen with data on hydrogenation for the same catalytic system provides an extremely fruitful method for investigating the mechanism of the activation of hydrogen and hydrogenation.

1. ACID–BASE SYSTEMS

Available data indicate the possibility of heterolysis of the H–H bond, primarily under the influence of various bases.

As early as 1936, Witz and Bonhoeffer[14] established that a 1 *N* aqueous solution of alkali at 100°C catalyses the exchange of molecular hydrogen with D_2O. The catalysis of the exchange and conversion of hydrogen by bases in aqueous solutions was subsequently studied by various groups of workers[15–19].

The kinetic studies of Wilmarth and coworkers[16] and Shindewolf[19] showed that the rate-determining stage of the reaction is the activation of H_2O by one hydroxide ion. In alcoholic solutions, the RO^- anion may act as hydrogen activator[19,20].

The activation energy for rupture of the H–H bond depends to a marked extent on the basic nature of the catalyst. Thus for the KNH_2–NH_3 catalytic system[19,21–25] this energy is 15 kcal mole^{-1} lower, and for the sodium acetate–acetic acid system 10 kcal mole^{-1} higher, than that for the reaction in aqueous alkali solutions[19]. The lowest activation energy for rupture of the H–H bond was observed when C_2H_5NHK–$C_2H_5NH_2$, that is the least basic catalytic system, was used[20]. Dilute and concentrated acids[16,17], and the BF_3–HF system[6], do not catalyse the exchange and conversion of hydrogen.

2. SYSTEMS CONTAINING SALTS OF TRANSITION METALS

The homogeneous isotopic exchange and ortho-para conversion of hydrogen in the presence of salts of transition metals was first observed by Calvin[26]. To explain these results he assumed a scheme involving the intermediate formation of the transition metal hydride:

$$n\,Cu^{I} + H_2 \rightleftarrows Cu^{I}_n \cdot H_2$$
$$Cu^{I}_n \cdot H_2 + 2\,Cu^{II} \rightleftarrows (n+2)\,Cu^{I} + 2\,H^+$$

It was found that in the presence of Cu^{II} acetate, neither conversion nor isotopic exchange of hydrogen takes place, and the molecular hydrogen is used up only in the reduction of the bivalent copper acetate; it is only when this reaction is complete that the Cu^{I} acetate formed begins to catalyse the exchange and conversion of H_2. It has also been reported[27], however, that the competing reactions of reduction and the isotopic exchange (or conversion) of hydrogen take place simultaneously under these conditions.

The rate of the ortho-para conversion is greater than the rate of the isotopic exchange of hydrogen. This is due to the fact that the conversion of hydrogen generally involves the recombination of two hydrogen atoms on a single metallic centre, whereas the exchange of hydrogen also requires interaction between the metal–hydrogen bond and the solvent. The isotopic exchange and ortho-para conversion of hydrogen are catalysed not only by copper salts but also by salts of silver, ruthenium, cobalt, etc. Both heterolytic and homolytic rupture of the H–H bond may take place. Thus homolytic rupture of the bond in the hydrogen molecule apparently takes place when the $CoCl_2$–KCN catalytic system is used[19,28,29], and also in the presence of copper acetate in quinoline[30]. On the other hand, detailed study of the kinetics of the exchange and conversion of hydrogen in the presence of $RuCl_3$–HCl–H_2O [19,31,32] showed that the hydrogen in this system undergoes heterolytic splitting according to the scheme:

$$Ru^{III}Cl^- + D_2 \rightarrow Ru^{III}D^- + D^+ + Cl^-$$
$$Ru^{III}D^- \xrightarrow{HCl} Ru^{III}Cl^- + HD$$
$$Ru^{III}D^- \xrightarrow{H_2O} Ru^{III}H^- + HOD$$
$$Ru^{III}H^- \xrightarrow{HCl} Ru^{III}Cl^- + H_2$$

where $Ru^{III}Cl^-$ represents the active chloro-complex of ruthenium.

According to this scheme, the exchange and conversion of hydrogen are accompanied by the intermediate formation of hydride (and deuteride) complexes of ruthenium. Of particular interest in this connection are the recently prepared iridium complexes $IrHD(CO)(PPh_3)_3$, which contain H and D attached simultaneously to the same metal atom, and which are active in hydrogenation[33]. It may be assumed that the study of the properties of these mixed hydrides will make it possible not only to reach a deeper understanding of the individual stages in the exchange, but also to reach definite conclusions regarding the structures of the intermediate hydride complexes.

III. HYDROGENATION

1. SYSTEMS WITHOUT COMPOUNDS OF TRANSITION METALS

a. Hydrogenation Under Conditions of Acid-base Catalysis

Systems of basic character, capable of catalysing the isotopic exchange and ortho-para conversion of hydrogen, can be regarded as potential hydrogenation catalysts. Basic systems of this kind were first used for hydrogenation by Walling and Bolliki[34,35], who showed that in the presence of potassium t-butoxide in butanol, benzene, or diglyme under fairly severe conditions (170–200°C, H_2 pressure 90–140 atm), benzophenone is hydrogenated with the formation of benzhydrol. The authors cited consider that in this instance the hydrogen undergoes heterolytic splitting with the formation of a hydride ion, which takes part in the first stage of the hydrogenation:

$$RO^- + H_2 \rightleftarrows ROH + H^-$$
$$H^- + R_2C{=}O \rightleftarrows R_2CH{-}O^-$$
$$R_2CH{-}O^- + ROH \rightleftarrows R_2CHOH + RO^- .$$

Aniline could be obtained from nitrobenzene under the same conditions; an attempt to hydrogenate cyclohexene was unsuccessful, and an attempt to hydrogenate acetone led to an aldol condensation.

The same authors also studied the possibility of acid-catalysed hydrogenation with activation of the hydrogen by means of a carbonium ion:

$$R^+ + H_2 \rightleftarrows RH + H^+ .$$

Thus when Lewis acids were used to obtain the carbonium ion (16% solution of $AlBr_3$ in cyclohexane at 150°C and 82 atm H_2), appreciable absorption of hydrogen was observed. A small quantity of hydrogen was also absorbed by benzene in the presence of $AlBr_3$, but neither cyclohexane nor methylcyclopentane were detected in the reaction products. In the hydrogenation of 2-methylpropene and cyclohexene in the presence of $AlCl_3$ in $CHCl_3$ at 140°C and 120 atm H_2, traces of saturated hydrocarbons were detected.

Thus even if acid catalysis of hydrogenation is possible, it takes place with much greater difficulty than base catalysis.

b. Hydrogenation Catalysed by Systems Based on Compounds of Boron and Aluminium

Köster and coworkers[36,37] showed that homogeneous hydrogenation of alkenes takes place in the presence of alkylboranes at temperatures greater than 200°C and a hydrogen pressure of 70 atm. DeWitt and coworkers[38,39], using boranes as catalysts, hydrogenated cyclohexene, oct-1-ene, polymers of butadiene, etc. With the trialkyl derivatives of boron, the first stage of the reaction gives a hydride, which subsequently reacts with the substrate:

$$BR_3 + H_2 \rightleftarrows R_2BH + RH$$
$$R_2BH + RCH{=}CH_2 \rightleftarrows RCH_2CH_2BR_2$$
$$RCH_2CH_2BR_2 + 2H_2 \rightarrow RCH_2CH_3 + RH + RBH_2 .$$

The same authors also made a detailed study of the influence of added Lewis acids on the hydrogenating power of alkylboranes. Lewis acids catalyse the addition of boron hydrides to alkenes, but in the present instance it was found that Lewis acids do not lower the hydrogenation temperature. In the opinion of the authors cited, this shows that the rate-determining stage of the reaction is the hydrogenolysis of the B–C bond.

The use of aluminium hydrides as catalysts for homogeneous hydrogenation was described in the patent literature[40]. Recently, Slaugh[41] showed that $LiAlH_4$ may act as a selective catalyst for the homogeneous hydrogenation of conjugated dienes (cyclo-octa-1,3-diene, cyclopentadiene) and dialkylacetylenes (pent-2-yne) to monoalkenes (hydrogenation takes place above 150°C in an atmosphere of H_2). A reaction scheme involving the formation and subsequent hydrogenolysis of an Al–C bond was proposed:

$$CH_3{-}CH{=}CH{-}CH{=}CHCH_3 + LiAlH_4 \rightarrow LiAlH_3(n\text{-}C_5H_9) \xrightarrow{n\text{-}(C_5H_9)} LiAlH_3(n\text{-}C_5H_9)_2 \text{ etc.}$$
$$LiAlH_3(n\text{-}C_5H_9) \xrightarrow{H_2} n\text{-}C_5H_{10} + LiAlH_4$$

Tracer studies showed that the hydrogenation of a conjugated diene involves one hydrogen atom from the hydride and another from the gaseous phase.

2. SYSTEMS CONTAINING COMPOUNDS OF THE TRANSITION METALS

Calvin's work[26,42] laid the foundation for the study of an extensive branch of homogeneous catalysis—the activation of molecular hydrogen by salts of transition metals. These systems, of which the great majority have been studied by Halpern and his school, can activate hydrogen under mild conditions, and their study has played an important part in the development of the theory of the activation of hydrogen and homogeneous hydrogenation.

The activation of hydrogen by transition metal complexes has been the subject of recent successful studies. It is difficult to make a sharp distinction between these two types of catalyst. For example, a polarographic study[43] of solutions of univalent copper salts in pyridine showed that the solution contains the ionic complexes $CuPy_2^+$, $CuPy_3^+$, $CuPy_4^+$, and $CuPy_6^+$. The ligands may be negative ions (Cl^-, CH_3COO^-, etc.) or uncharged molecules (amines, water, etc.). For convenience in the subsequent discussion, however, we shall divide catalysts of homogeneous hydrogenation involving transition metal compounds into three classes: a) salts of transition metals (in this instance the reaction of the salts with the solvent leads to the formation of a complicated system of ionic complexes); b) two-component systems (in this instance the transition metal salt reacts with organometallic compounds or with complex-forming reagents); and c) individual transition metal complexes with known composition.

a. Salts of Transition Metals

The catalytic activity of solutions of transition metal salts in water and in ammonia has been most widely studied. Reactions of three types have been studied: 1) the exchange and conversion of hydrogen, examined above; 2) the reduction of inorganic ions ($Cr_2O_7^{2-}$, IO_3^-, etc.) by hydrogen; and 3) the hydrogenation of organic compounds.

Of the salts studied, those of copper[2,44–54], silver[55–64], and mercury[65–67], and compounds of manganese (MnO_4^-),[68] molybdenum (MoO_4^{2-}),[69] and metals of the platinum group[70–73] were found to be active in aqueous solutions. Salts of copper[26,42,74–78] and silver[76,79] were also found to be active in solutions of amines. Salts of copper[80,81], silver, and mercury[82] are active in solutions of heptanoic acid and in biphenyl.

We shall not discuss these systems in the present review, since they have been examined in detail elsewhere[3,69,83,84]. It should be emphasised, however, that transition metal salts capable of catalysing the exchange and conversion of hydrogen and also the reduction of inorganic ions, may nevertheless not act as catalysts for the hydrogenation of organic compounds. Examples of such systems are provided by aqueous solutions of Cu^{II}, Ag^{I}, and Hg^{II} salts; in Halpern's opinion[85], there are two possible reasons for this: 1) these ions activate hydrogen but do not activate alkenes; 2) the ions themselves are reduced by hydrogen.

In some instances, however, reduction of transition metal salts by hydrogen does not take place in the presence of alkenes, and homogeneous hydrogenation of the alkenes takes place. Thus Flynn and Hulburt[86] observed the homogeneous hydrogenation of ethylene in the presence of the complex $C_2H_4.PtCl_2$. Precipitation of metallic platinum was observed as the ethylene was used up. In the present instance, complex formation with the alkene stabilises the valency state of the metal. An analogous picture is apparently observed in the homogeneous hydrogenation of maleic acid in the presence of $RuCl_3$ in an acidic aqueous solution[85] and in the hydrogenation of ethyl crotonate by means of palladium salts[87].

A curious feature is that in the catalytic reduction of oxidising ions $Cr_2O_7^{2-}$, IO_3^-, etc. by hydrogen in the presence of transition metal salts, the precipitation of metal is observed only after the oxidant is completely used up.

On the other hand, various transition metal ions which are not capable of activating hydrogen in ortho-para conversion or isotopic exchange may catalyse the hydrogenation of organic compounds. For example, aqueous solutions of Ni^{II} do not activate hydrogen[3], but hydrogenation of pent-2-ene and benzene takes place in aqueous $NiSO_4$ solution[88]. The apparent explanation is that the substrate first forms a complex with the metal salt, and this complex subsequently reacts with hydrogen. A large number of hydrogenating systems of this type involving transition metal salts was studied by Tulupov, who showed that solutions of the stearates and adipates of Ni^{II}, Fe^{III}, Co^{II}, Mn^{II}, Cr^{III}, and Zn^{II} in ethanol, liquid paraffin, and n-heptane catalyse the hydrogenation of cyclohexene and benzene (to cyclohexane), cyclohexanone (to cyclohexanol), and pentenes (to pentanes).[69,88-94] The rate of hydrogenation in the presence of transition metal salts under ordinary conditions is extremely low.

In the presence of copper and cadmium oleates under severe conditions (H_2 pressure 250–275 atm, temperature 260°C), unsaturated aliphatic acids are hydrogenated to the corresponding unsaturated aliphatic alcohols[95]. The hydrogenation of benzoquinone by means of copper acetate in quinoline[26] and of copper heptanoate in heptanoic acid solution[80] has been described. Rylander and coworkers[96] hydrogenated dicyclopentadiene, quinone-1,2, and naphthoquinone-1,4 by means of salts of metals of the platinum group in dimethylformamide (or dimethylacetamide) solution.

Finally, rhodium chloride in alcoholic solutions catalyses the homogeneous hydrogenation of hex-1-ene[97] and the hydrogenation of maleic acid to succinic acid[98] in acetamide.

b. Two-component Systems

Systems formed by the reaction of transition metal salts with reducing agents or with complex-forming reagents are much more effective catalysts for homogeneous hydrogenation than the transition metal salts themselves. This section deals with the $CoCl_2$–KCN system and catalysts of the Ziegler–Natta type. The investigation of the reaction mechanism and the nature of the active intermediate compound in these systems is an extremely complicated problem.

$CoCl_2$–KCN System. The absorption of hydrogen when potassium cyanide is added to an aqueous cobalt(II) chloride solution was first observed by Iguchi[99] in 1942, but this system only attracted special attention after the work of King[100] and Kwaitek[101,102].

Table 1. Hydrogenation of various substrates by means of the $CoCl_2$–KCN system in aqueous solutions (25°C; H_2 pressure = 1 atm).

Substrate	Reaction product	References
$[Fe(CN)_6]^{3-}$	$[Fe(CN)_6]^{4-}$	102
H_2O_2	H_2O	102
Ethylene	not hydrogenated	102
Propene	ditto	102
Cyclohexene	ditto	102,104
Styrene and substituted styrenes	ethylbenzene etc.	101,102,104
Propenylbenzene $CH_3CH=CHPh$	not hydrogenated	101
1,1-Diphenylethylene	not hydrogenated	101
Cyclohexene oxide	cyclohexanol	101
Styrene oxide	phenylethanol	101
Allyl chloride	propene	119
Butadiene	mixture of butenes	101,102,119–124,138
Isopropene	2-methylbut-2-ene	
	2-methylbut-4-ene	101,102,125,126
Cyclopentadiene	cyclopentene	102
1,3-Cyclohexadiene	cyclohexene	101,102
Unsaturated aldehydes (acrolein, tiglaldehyde, cinnamaldehyde)		101,102
Acrylic acid and its derivatives		101,102
Sorbic acid	2-hexenoic and 3-hexenoic acids	101,104,126–128
Cinnamic acid	phenylpropionic acid	101,104,118,129
Keto-acid *oximes*[a]		104,130–134
Keto-acids and keto-esters[a] (reductive amination)		104
Acetaldehyde[b]		102
Benzaldehyde	benzyl alcohol	102
$t\text{-}C_4H_9NO_2$	t-butylamine	136
Nitrobenzene and its derivatives	azoxy-, azo-, and hydrazobenzenes, aniline	102,135,139
Nitrophenols	*aminophenols*	136
Benzonitrile[c] etc.		136
Acrylonitrile[c]		136
Benzoquinone	hydroquinone	102
Azoxybenzene	azobenzene	101
Benzil	benzoin	101,104
Methylene Blue etc.		137

[a]Temperature 30–100°, H_2 pressure 50–100 at. [b]Condensation accompanied by absorption of hydrogen. Temperature of reaction 100°. [c]Reduction products not isolated, because they are hydrolysed.

The $CoCl_2$–KCN system can be used for the ready reduction of inorganic oxidising agents [H_2O_2, $Fe(CN)_6^{3-}$], benzoquinone, conjugated alkenes, unsaturated acids etc., and aliphatic and aromatic aldehydes (the reduction of aliphatic aldehydes is accompanied by condensation). Reductive amination of keto-esters also takes place in the presence of $CoCl_2$–KCN (see Table 1).

Monoalkenes[102-104] and non-conjugated dienes[102] are not hydrogenated under these conditions, however. α,β-Unsaturated acids and aldehydes show different behaviour on hydrogenation in the presence of the $CoCl_2$–KCN system[102]. Thus it was found that α-substituted acrylic acids—methacrylic, itaconic, and atropic acids—are hydrogenated quantitatively, but the corresponding aldehydes are not hydrogenated. On the other hand, crotonaldehyde is partly hydrogenated, and tiglaldehyde is quantitatively hydrogenated, whereas tiglic acid [*trans*-2-methyl-2-butenoic acid] is not hydrogenated at all. In the hydrogenation of acrylic acid at elevated temperature, it was unexpectedly found that α-methylglutaric acid is formed in addition to propionic acid.

The study of the extremely complicated process of complex formation in the $CoCl_2$–KCN system was begun by the work of Hume and Kolthoff[105] and Adamson[106]. Research workers have paid most attention to the problem of the nature of the complex activating the hydrogen (see for example Refs. 107–111). It has now been shown that the active species in the $CoCl_2$–KCN system is the complex $[Co^{II}(CN)_5]^{3-}$. The partial replacement of CN^- ligands in the complex $[Co(CN)_5]^{3-}$ by ethylenediamine produces new hydrogenation catalysts[112].

Griffith and Wilkinson[113,114] used the NMR method to detect the formation of a Co–H bond during the reduction of a solution of cobalt(II) chloride and KCN by sodium hydridoborate. A curious feature is that the hydrido-complex is present in the solution in concentrations of 3% even without treatment with $NaBH_4$.

King and Winfield[108] studied the ultraviolet spectra of cyanide solutions of cobalt salts after their reduction by hydrogen, $NaBH_4$, or electrolysis, and showed that in all instances a hydrido-complex with probable structure $[CoH(CN)_5]^{3-}$ ($\lambda = 305$ mμ) is formed. The formation of a hydridopentacyano-complex of cobalt was confirmed by De Vries[115], Burnett and coworkers[116], and others. This hydrido-complex was recently isolated in the form of the salt $NaCs_2CoH(CN)_5$.[117]

A number of authors[19,28,29,100,108] hold the view that the formation of the hydrido-complex $[CoH(CN)_5]^{3-}$ involves the simultaneous reaction of a hydrogen molecule with two molecules of the complex $[Co(CN)_5]^{3-}$ according to the scheme:

$$[Co] + [Co] \rightleftarrows [Co]_2; \quad [Co]_2 + H_2 \rightleftarrows 2H[Co]$$

where $[Co] = [Co(CN)_5]^{3-}$.

Simandi and Nagy[118] recently showed, however, that the activation of hydrogen is a two-stage process: a complex of H_2 with one molecule of the cyano-compound $[Co(CN)_5]^{3-}$ is formed first, after which rupture of the H–H bond in the complex takes place with the participation of a second $[Co(CN)_5]^{3-}$ anion:

$$[Co] + H_2 \rightleftarrows H_2 \cdot [Co]$$
$$H_2 \cdot [Co] + [Co] \rightleftarrows 2H[Co] \ .$$

CoF_2–NaF System. It has been reported[140] that the CoF_2–NaF system in water catalyses the hydrogenation of ethylene and butadiene.

Ziegler–Natta Catalysts. The reaction of compounds of transition metals (acetylacetonates etc.) with organometallic reducing agents (Alk_3Al, Et_3B, RMgBr, etc.) leads to the formation of soluble systems capable of catalysing the hydrogenation of various alkenes[141-148] at 30–50°C and a hydrogen pressure of 3–5 atm. The rate of hydrogenation by means of these systems is greater by several orders of magnitude than that for salts of transition metals without a reducing agent.

The metals can be arranged in the following order of decreasing activity in these systems[141,147]: Ni ≥ Co > Cu ≥ Fe > Mn ≥ Cr > V, and that the activity of the catalyst decreases with increase in the acceptor power of the ligands[147]. The rates of hydrogenation of mono- and disubstituted alkenes are approximately the same, but much greater than the rates of hydrogenation of trisubstituted and more particularly tetrasubstituted alkenes. Compounds containing a carbonyl group (ketones and aldehydes), and also compounds containing nitrile, nitro, azo, and other functional groups are not hydrogenated in the presence of these catalysts.

The hydrogenation of alkenes by means of these catalysts involves the initial formation of a compound with a transition metal–carbon bond, and hydrogenolysis of this compound gives the final product and the transition metal hydride[141,142,147] according to the scheme:

$$R_3Al + MX_n \rightarrow R_3AlX + RMX_{n-1}$$
$$RMX_{n-1} + H_2 \rightarrow RH + HMX_{n-1}$$
$$\text{>C=C<} + HMX_{n-1} \rightarrow \text{>HC–C–}MX_{n-1}$$
$$\text{>HC–C–}MX_{n-1} + H_2 \rightarrow \text{>HC–CH} + HMX_{n-1}$$

or

$$\text{>HC–CH}X_{n-1} + HMX_{n-1} \rightarrow \text{>HC–CH<} + (MX_{n-1})_2$$
$$(MX_{n-1})_2 + H_2 \rightarrow 2\,HMX_{n-1} \ .$$

Systems of this type can also be used for the hydrogenation of aromatic compounds. Thus Lapport and Schuett[149] showed that a solution of Et_3Al and Ni^{II} 2-ethylhexanoate in heptane or in benzene is an excellent catalyst for the hydrogenation of various aromatic compounds (150°C, 70–80 atm H_2).

The hydrogenation of aromatic derivatives by means of catalysts of the Ziegler–Natta type is apparently accompanied by the intermediate formation of a π-complex. In the opinion of Kalechits and coworkers[150], evidence of this is provided by the fact that hydrogenation takes place under conditions in which π-complexes are formed.

Catalysts of the Ziegler–Natta type also hydrogenate compounds with conjugated double bonds[151] and oils[152].

Individual Transition Metal Complexes

A large number of individual transition metal complexes capable of catalysing homogeneous hydrogenation are now known; the activities of some of these are greater than that of the most active of the catalysts examined in previous sections. The use of these catalysts has played an exceptionally important part in the investigation of the mechanism of hydrogenation, since the compositions and structures of these complexes have in most instances been reliably established.

Metal Carbonyls and Their Derivatives. Hydrogenation by means of metal carbonyls is closely related to hydroformylation. Hydrogenation generally takes place under the same conditions as hydroformylation (a high pressure of "synthetic" gas—a mixture of CO and H_2—ensures the presence of carbonyls in the reaction mixture). The hydrogenating power of various carbonyl hydrides has been briefly discussed by Davydov[153].

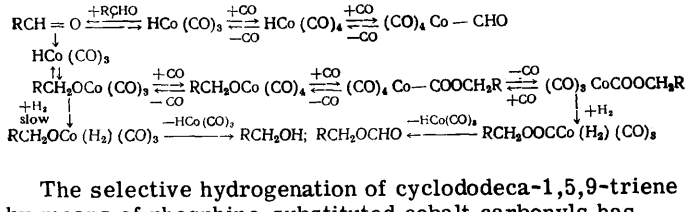
The hydrogenating power of cobalt carbonyl has been most extensively studied[154]. The ratio of the rates of the parallel reactions of hydroformylation and hydrogenation depends on the structure of the substrate. Thus simple alkenes give saturated aldehydes and the corresponding alcohols[155-159]; α,β-unsaturated ketones and aldehydes are hydrogenated to saturated carbonyl derivatives[155,160,161]; and conjugated alkenes give both hydrogenation products and hydroformylation products[154].

Cobalt carbonyl has been used for the hydrogenation of aldehydes[154,155,157,158,162-164], ketones[155,165], alcohols[155,160,165-169], aromatic compounds[155,166,170], azobenzene[171], poly-unsaturated acids[172], etc.

Two possible routes for the activation of hydrogen during hydrogenation by means of cobalt carbonyl have been discussed[154,160,162]: a) $Co_2(CO)_8 + H_2 \rightleftharpoons CoH(CO)_4$, that is the formation of cobalt hydride as homogeneous catalyst, and b) heterogeneous hydrogenation on metallic cobalt, formed by decomposition of the carbonyl:

$$Co_2(CO)_8 \rightleftarrows 2Co^0 + 8\,CO.$$

It may be taken that the homogeneous nature of catalytic hydrogenation by means of $Co_2(CO)_8$, in which the hydrogenating agent is $CoH(CO)_4$, has now been proved. This scheme involving the participation of $CoH(CO)_4$ was adopted, for example, by Marko[164] to explain the formation of alcohols in the hydrogenation of aldehydes. The same scheme explains the presence of a certain amount of formates in the reaction mixture.



The selective hydrogenation of cyclododeca-1,5,9-triene by means of phosphine-substituted cobalt carbonyls has also been described[173].

Recent work has shown that not only cobalt carbonyls, but also the carbonyls of other metals, can act as catalysts for homogeneous hydrogenation. Thus Imyanitov and Rudkovskii[174] studied the hydrogenation of alkenes in the presence of rhodium and iridium carbonyls. Hydroformylation takes place in parallel.

Heil and Marko[175], under the conditions of formation of rhodium carbonyl from $RhCl_3$, hydrogenated aliphatic aldehydes and benzaldehyde to the corresponding alcohols. Hept-1-ene and cyclohexene under these conditions first undergo hydroformylation, and are then hydrogenated to octanol and cyclohexylcarbinol.

The iron carbonyl $Fe(CO)_5$ is an effective catalyst for the homogeneous hydrogenation of poly-unsaturated fats. The hydrogenation of soya-bean oil in the presence of iron carbonyl at 180°C and 7–70 atm H_2 has been reported by Frankel and coworkers[176-178].

A complex of iron carbonyl with linoleate was isolated in the hydrogenation of methyl linoleate[177], and this complex was found to be a better hydrogenation catalyst than the original $Fe(CO)_5$.

The selective hydrogenation of unsaturated esters by means of π-complexes of $Fe(CO)_5$ [179-181] and by means of π-complexes of chromium carbonyl[182] has been described. In both instances the authors cited suggest that during the reaction these π-complexes dissociate with the formation of the species $Fe(CO)_3$ and $Cr(CO)_3$ respectively. The reaction of these species with hydrogen gives the hydrides $FeH_2(CO)_3$ and $CrH_2(CO)_3$, which then react with the substrate. Frankel[182] showed that the two hydrogen atoms are transferred to the substrate simultaneously.

Japanese workers[183] studied the mixed cyclopentadienylcarbonyl complex $Cp_2Ti(CO)_2$ as hydrogenation catalyst. They used this catalyst to hydrogenate various acetylenic derivatives in a hydrocarbon medium under comparatively mild conditions (50–65°C and H_2 pressure 50 atm). It was found that the rates of hydrogenation depend on the nature of the substituents R, decreasing in the order Ph > t-butyl > n-alkyl for the monosubstituted acetylenes RC≡CH or in the order Ph > n-alkyl for the disubstituted RC≡CR. Conjugated dialkenes have been hydrogenated by means of the π-complexes of iron, nickel, and cobalt carbonyls[151].

Complexes of Group VIII Metals with P-containing Ligands. In 1962, Vaska and coworkers[184] found that iridium complexes of the type $IrCl(CO)(Ph_3P)_2$ absorb molecular hydrogen reversibly at room temperature and atmospheric pressure with the formation of hydrides stable in air. Later, they also showed that hydrido-complexes of the type $IrH(CO)(Ph_3P)_3$ are effective catalysts for the homogeneous hydrogenation of ethylene[185,186]. The hydrogenation of alkenes is also catalysed by complexes of the type $IrHX_2L_3$, where X = Hal, L = PPh_3, Ph_3As, or Ph_3Sb;[187] alkenes with a terminal double bond are hydrogenated more rapidly than disubstituted alkenes, and further branching of the alkene chain leads to an even more marked decrease in the rate of hydrogenation. The use of iridium complexes as hydrogenation catalysts is also described in the patent literature[188,189]. In the presence of $IrH_3(PPh_3)_3$, aldehydes are hydrogenated with the formation of alcohols[190]. Unlike the iridium complex $IrCl(CO)(Ph_3P)_3$, the rhodium complex $RhCl(CO)(Ph_3P)_3$ was found to be inactive under the same conditions[185]. In a study of the hydroformylation of alkenes by means of $RhCl_3(Ph_3P)_3$, Osborn and coworkers[191,192] found that at high temperatures and pressures of the CO + H_2 mixture (1 : 1) the aldehyde obtained is converted into the alcohol. The complex $RhCl(Ph_3P)_3$ is an even more effective hydrogenation catalyst[193]. This catalyst has been used to hydrogenate a number of alkenes and alkynes (see Table 2); the rate of hydrogenation of the triple bond was found to be less than that of the double bond. As in the hydrogenation of alkenes, steric hindrance has a significant influence on the rates of hydrogenation of alkynes and the duration of the induction period.

Organic compounds with functional groups—ketones (aldehydes), alcohols, carboxylic acids, nitriles, chlorides, and nitro-compounds—are not hydrogenated in the presence of $RhCl(Ph_3P)_3$.[193] Butadiene and cyclo-octa-1,3-diene are hydrogenated only at 60°C, but are not hydrogenated at room temperature.

Non-conjugated dienes with double bonds in terminal positions (octa-1,7-diene) are hydrogenated more rapidly than hex-1-ene, which in turn is hydrogenated more rapidly than hex-2-ene; cis-alkenes are hydrogenated more rapidly than the trans-isomers. Unlike propene, ethylene is not hydrogenated under these conditions. The rate of hydrogenation depends on the concentration of substrate and catalyst, the H_2 pressure, and temperature, and increases considerably when a polar solvent is used. The addition of such complex-forming reagents as triphenylphosphine, thiophen, 8-quinolinol, pyridine, and acetonitrile decreases the reaction rate; ethylene, conjugated dienes, and O_2 poison the catalyst.

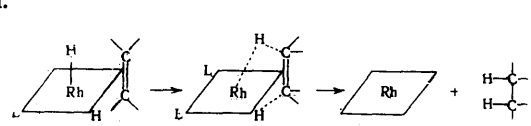
It has been shown that in the hydrogenation of alkenes in the presence of $RhCl(Ph_3P)_3$ the active compound is the dihydride $Rh(H_2)Cl(Ph_3P)_2$; one molecule of catalyst takes part in the transfer of hydrogen to the alkene.

Table 2. Hydrogenation of organic compounds in the presence of phosphine complexes of transition metals (25°C, H_2 pressure 1 atm).

Complex	Compound hydrogenated	Reaction product	References
$RhX(Ph_3P)_3$, where X = Cl, Br, or I	Ethylene	not hydrogenated	193, 194
	Alkenes (propene, butenes, hexenes, stilbene, etc.)	alkanes	193, 194, 202, 203, 206, 207
	Dienes	alkanes	193
	Maleic and fumaric acid	succinic acid	193
	Alkynes	alkenes + alkanes	193, 203
	Acetylenedicarboxylic acid		193
	Aliphatic-aromatic and higher aliphatic unsaturated acids; higher aldehydes, etc.	not hydrogenated	202, 203
	Steroids		203, 204
	Quinones		205
$RhCl_3(Ph_3P)_3$[a]	Heptaldehyde	heptyl alcohol	191
$RhH(CO)(PPh_3)_3$	Ethylene	ethane	185, 208
	Hex-1-ene	hexane	
$IrH(CO)(PPh_3)_3$	Ethylene	ethane	185
	Acetylene	ethylene + ethane	
$Ir(H)Cl_2(Ph_3P)_3$ $Ir(H_2)Cl(Ph_3P)_3$	Norbornadiene	not hydrogenated	148
$RhX(CO)(Ph_3P)_2$	Ethylene	ethane	209
$IrX(CO)(Ph_3P)_2$	Propene	propane	209
	Acetylene[b]	ethylene + ethane	
	Alkenes	alkanes	
	Alkynes	alkenes + alkanes	
$[Ir(Ph_2PCH_2CH_2PPh_2)_2]Cl$	Butyraldehyde	butanol	210
$[Rh(Ph_2PCH_2CH_2PPh_2)_2]Cl$	Acetylenes	olefins + paraffins	210
$H_3Ir(PPh_3)_3$[b]	Butyl aldehyde	Butyl alcohol	190
$RuCl_2(Ph_3P)_4$ $RuCl_2(Ph_3P)_3$	Hept-1-ene	heptane	195
$RuHCl(Ph_3P)_3$	Cyclopentene	cyclopentane	196, 211
	Cyclohexene	cyclohexane	
	Cyclo-octene	cyclo-octane	
	Tolane	cis-stilbene	
$OsHCl(CO)(Ph_3P)_3$	Acetylene[c]	ethylene + ethane	185

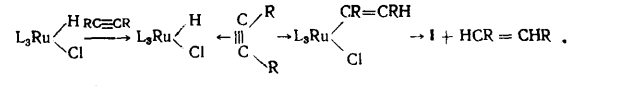
[a]Temperature 100°, H_2 pressure 50 atm. [b]Temperature 60°. [c]Temperature 50°; solvent—acetic acid.

The following hydrogenation scheme with simultaneous transfer of two hydrogen atoms to the substrate was proposed:



Complexes of rhodium with Ph_3As and more particularly Ph_3Sb ligands were found to be much less effective catalysts[194].

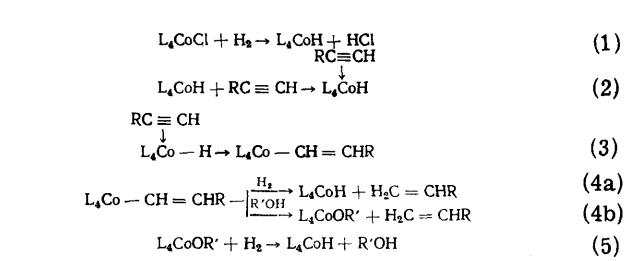
Evans and coworkers[195] showed that hept-1-ene and hex-1-yne are readily hydrogenated in the presence of ruthenium complexes of the type $RuCl_2L_4$ and $RuCl_2L_3$, where L = Ph_3P (at 25°C and 1 atm). A mechanism involving the formation and subsequent hydrogenolysis of an Ru–C bond was proposed for this reaction[196].



(I)

Alkyl phosphite complexes of univalent cobalt $CoXL_3$ and $CoXL_4$, where L = $(EtO)_3P$ and X = Cl, Br, or I, absorb hydrogen under mild conditions and act as catalysts for the hydrogenation of alkynes and various alkenes with activated double bonds (vinyl ethyl ether, vinyl acetate, etc.).[198,199]

The following scheme was proposed for the hydrogenation of alkynes by phosphite complexes of cobalt (in alcohol):



To determine whether hydrogenation takes place with hydrogenolysis (4a) or alcoholysis (4b) of the intermediate compound with the Co–C bond, C_2H_5OD was used as solvent. It was found that the hydrogenation product did not contain deuterium. Thus the molecular hydrogen is the source of both hydrogen atoms in the hydrogenation of alkynes (scheme 4a). An interesting feature is that an alkyl phosphite complex of zero-valent cobalt[200] did not catalyse hydrogenation even at 150°C and a hydrogen pressure of 120 atm.

It was recently found[201] that the complex $CoH_2(Ph_3P)_3$ catalyses the hydrogenation of ethylene.

Complexes Containing the $SnCl_3$ Ligand. Cramer and coworkers[212] were the first to carry out the homogeneous hydrogenation of ethylene in an alcoholic solution of K_2PtCl_4 and $SnCl_2$ (H_2 pressure 1 atm, 25°C). This system also catalyses the hydrogenation of pent-1-ene[213], cyclohexene[214], and other alkenes[215]. In the hydrogenation of acetylene[212], a mixture of ethylene and ethane is formed. Cramer and coworkers[212] were able to isolate a compound containing a Pt–$SnCl_3$ bond and to show that $SnCl_2$ plays a dual role in complex formation in this system: 1) it promotes the coordination of ethylene to platinum; and 2) it stabilises the valency state of platinum relative to reduction by hydrogen.

Bailar and coworkers[216–219] showed that complexes of the type MX_2L_2 (where L = R_3P, R_3As, etc., X = Hal, and M = Ni, Pd, or Pt) in the presence of $SnCl_2$ are capable of catalysing the selective hydrogenation of compounds with two or more double bonds to compounds with a single isolated bond.

Khrushch and coworkers[220,221] studied the reaction kinetics and isotopic composition of the products of the hydrogenation of ethylene by means of platinum complexes of this type in the $C_2H_4 + D_2 + CH_3OH$ and $C_2H_4 + H_2 + CH_3OD$ systems, and found that in both instances the chief product is C_2H_5D. This shows that in the hydrogenation,

one of the hydrogen atoms is provided by the H_2 molecule and the other by the alcohol, according to the scheme:

$$[Pt] + C_2H_4 \rightleftarrows Pt(C_2H_4)$$

$$Pt(C_2H_4) \overset{H_2}{\rightleftarrows} \left[\begin{matrix} H \\ H \end{matrix}\!\!>\!PtC_2H_4\right] \rightleftarrows [^-HPtC_2H_4] + H^+$$

$$[^-HPtC_2H_4] \rightleftarrows PtC_2H_5^-$$

$$PtC_2H_5^- + H^+ \rightarrow [Pt] + C_2H_6$$

where [Pt] represents the active complex.

The complex $PtHCl(Ph_3P)_2$ in the presence of $SnCl_2$ catalyses the hydrogenation of norbornadiene and hex-3-yne-2,5-diol. The complex $Ir(H_2)(SnCl_3)(Ph_3P)_3$ does not exhibit hydrogenating power[196].

Complexes with Other Ligands. The influence of nitrogen-containing ligands (ammonia and amines) on the activity of hydrogenation catalysts has been studied.

Iguchi[222] observed the precipitation of metal in the hydrogenation of quinone, cinnamic acid, and other compounds in the presence of complexes of rhodium with ammonia.

A number of authors[8,62] have studied the influence of amines as ligands on the reduction of Ag^+ by hydrogen. It was found that the reactivity of the corresponding ionic complex decreases in the following order of ligands:

$$R_3N > R_2NH > RNH_2 > NH_3$$

The reaction of hydrogen with the complex $RhCl_3Py_3$ gives a hydride with assumed composition $RhHCl_2Py_3$, which hydrogenates hex-1-ene[223].

A number of effective catalysts for homogeneous hydrogenation have been prepared by Khidekel' and coworkers. Thus solutions of complexes of transition metals (Rh, Ru, Ir, or Mo), stabilised by π-donor quinonoid and aromatic ligands (duroquinone, mesitylene, etc.) in dimethylformamide (25°C, H_2 pressure 1 atm) catalyse the hydrogenation of alkenes; the activity of these catalysts is greater by several orders of magnitude than that of heterogeneous catalysts (rhodium on carbon, etc.).[224,225]

The reduction of rhodium salts in the presence of aminoacids (L-tyrosine, α-phenylalanine, etc.) and peptides leads to the formation of Rh^I complexes, which are extremely effective catalysts for the hydrogenation of unsaturated compounds under mild conditions[226-228]. An important property of the complexes of rhodium with aminoacids is their ability to catalyse the hydrogenation of aromatic compounds under mild conditions (anthracene > benzene > naphthalene).[229] When the ligand has an asymmetric centre (the complex with L-tyrosine), acetoacetic ester undergoes asymmetric hydrogenation to ethyl β-hydroxybutyrate[229]. According to the data obtained, these catalysts show a marked similarity to the enzyme hydrogenase.

The study of the structures of these complexes has shown that they are of the half-sandwich type, the aromatic ring of the aminoacid acting as π-ligand.

IV. GENERAL SYSTEMATIC FEATURES AND MECHANISM OF THE ACTIVATION OF HYDROGEN AND HOMOGENEOUS HYDROGENATION

Comparison of the results of the study of a number of catalytic systems makes it possible to distinguish various common regular features of homogeneous hydrogenation and the activation of hydrogen in the presence of transition metal complexes and to examine the part played by the transition metal and the ligands, the influence of solvents, the stereospecificity and selectivity of the catalysts, etc.

1. ACTIVATION OF MOLECULAR HYDROGEN BY TRANSITION METAL COMPLEXES

a. The Part Played by the Transition Metal

The H_2 molecule is a fairly inert molecule with a closed electron cloud, and its dissociation energy is 104 kcal mole^{-1}.

The activation of H_2 by transition metal compounds involves the reaction of the hydrogen molecule with the ion (or complex) of the metal; the H–H bond in the transition state (or in the intermediate compound) is weakened and then broken.

There are thus two possibilities in the activation of hydrogen. According to the first, the H_2 acts as electron donor, that is the bonding electrons of the hydrogen are partly transferred to vacant orbitals of the metal ion (donor–acceptor bond).[230] The other possibility in the activation of H_2 is that an electron is transferred from the metal atom rich in electrons to an antibonding orbital of the hydrogen molecule (dative bond), that is H_2 acts as an electron acceptor (in Halpern's opinion[230], this process may involve the $2p$ orbitals of the hydrogen). Dative bond formation makes it possible to explain the activation of hydrogen not only by ions (or complexes) of metals rich in electrons[193], but also by such ions as OH^-, NH_2^-, R^-, etc.[231]

Thus the transition states (or intermediate compounds) of these two extreme types, depending on whether hydrogen acts as electron donor or electron acceptor, can be represented as $M.....H_2^+$ and $M.....H_2^-$. The energies of rupture of the H–H bonds in the corresponding molecular ions H_2^+ and H_2^- are not the same and have the values 62 kcal mole^{-1} and 3.4 kcal mole^{-1} (or 18.6 kcal mole^{-1} according to other data) respectively[232].

Syrkin[233] suggested that in the activation of H_2 with the formation of a bond of the donor–acceptor type, a three-centre transition state with two electrons in the field of three nuclei may be realised:

$$M^+ : \begin{matrix} \cdot\,H \\ \vdots \\ \cdot\,H \end{matrix}$$

For a transition state of the type $M.....H_2^+$ to be realised in the activation of hydrogen, the M atom must have suitable vacant orbitals with sufficiently low energy. For transition metals these are primarily d orbitals.

In the earliest reviews of the homogeneous activation of hydrogen it was noted that the active species are primarily transition metal ions with a filled or almost filled d electron level[3]:

$$Cu^{II} - 3d^9;\ Cu^I - 3d^{10};\ Pd^{II} - 4d^8;\ Ag^I - 4d^{10};\ Hg^{II} - 5d^{10}$$

It is significant that for ions with a filled d level the difference in the energies of the d orbitals and the next vacant s and p orbitals is comparatively small, and the ease of the $d \rightarrow s$ and $d \rightarrow p$ transitions leads to the production of vacant d orbitals. It is interesting in this connection to note that although the ions Zn^{2+}, Cd^{2+}, and Hg^{2+} have similar d^{10} electronic configurations, only the Hg^{2+} ion is effective in the activation of hydrogen, since the difference in the energies of the d orbitals and the higher s orbital is much smaller for this ion than for the other ions of this series[8].

On the other hand, the formation of a dative M.....H_2^- bond, that is transfer of the electrons of the M atom to an antibonding molecular orbital of hydrogen, is favoured by a minimal positive charge on the metal. This explains the higher activating power of Cu^I compared with Cu^{II} in the reaction with hydrogen. A large proportion of catalysts for homogeneous hydrogenation known at present are compounds of transition metals with a low oxidation state.

Another factor facilitating the formation of dative bonds is the presence of electron-donating ligands on the metal atom. Thus the activation of hydrogen may be favoured by the presence of vacant orbitals and by a low degree of oxidation of the metal in the complex.

b. The Part Played by the Ligands and Solvent

A significant influence on the catalytic activity of a complex is shown by the nature of the ligands attached to the metal atom. The ability of various ligands to form both donor–acceptor bonds and dative bonds leads to the stabilisation of low valency states of the metal. Thus for example ligands of the type PR_3 can use the unshared pair of electrons of the tervalent phosphorus to form a donor–acceptor bond, and can use vacant *d* orbitals with comparatively low energy to accept electrons from the metal atom. Ligands of this type stabilise rhodium complexes[193] which absorb hydrogen reversibly and catalyse the homogeneous hydrogenation of organic compounds. With the analogous complexes formed by rhodium with amines, which are not capable of forming dative bonds, hydrogenation is accompanied by the formation of a metallic precipitate. The preferential formation of bonds of a given type by different ligands makes it possible to increase or decrease the electron density at the metal atom in the reaction with hydrogen or the substrate and thus to ensure the optimal conditions for the manifestation of catalytic properties by the complex. An interesting feature here is that the catalytic activity of rhodium complexes which absorb hydrogen readily and reversibly is extremely sensitive to small changes in the donor–acceptor properties of the ligand: the replacement of a phenyl group in triphenylphosphine by an ethyl group reduces considerably the activity of the rhodium complex[206] in hydrogenation.

A decrease in the positive charge of a metal ion is also brought about by its reaction with an anion acting as ligand. It is important, however, that the bond between this ligand and the metal ion be sufficiently labile to ensure the ready liberation of a coordination position for the H_2 molecule in the reaction with hydrogen. Thus for example silver acetate and sulphate are catalytically active, whereas the trifluoroacetate, chloride, and other silver salts are inactive. The catalytic activity of copper acetate and chloride, and also of $HgSO_4$, is greater than that of the corresponding salts with less nucleophilic anions.

A coordination position may also be vacated by dissociation of a complex, as shown by the complexes $RhCl(Ph_3P)_3$,[193] $RuCl_2(Ph_3P)_4$,[195] etc. This vacant position is apparently occupied by a solvent molecule, which is readily displaced by hydrogen. An attempt by Halpern[3] to correlate the catalytic activities of various metals with their stability constants is of interest in this connection.

The importance of a vacant (or readily liberated) coordination position for the catalytic activity of a complex in homogeneous hydrogenation can be demonstrated by a number of other examples. Thus the Cu^{2+} ion is active in aqueous medium, but its catalytic activity is decreased by the addition of chelating reagents which "screen" the orbitals accessible to hydrogen, and the catalytic activity may disappear completely at high concentrations of the chelating agent[52].

The catalytic activity of the complexes of rhodium and iridium with bidentate ligands $[Rh(Ph_2PCH_2CH_2PPh_2)_2]Cl$ and $[Ir(Ph_2PCH_2CH_2PPh_2)_2]Cl$ is much smaller than that of the corresponding complexes with unidentate ligands $RhCl(Ph_3P)_3$ and $IrCl(CO)(Ph_3P)_2$.[220] In the opinion of the authors cited, the chelate complexes form a very stable adduct with hydrogen, and this prevents further hydrogenation.

Triphenylphosphine complexes of rhodium react with such compounds as CO, $CH_2{=}CH_2$, $CF_2{=}CF_2$, and tolane to form complex compounds which are so stable that they do not activate hydrogen[193]. This explains the "poisoning" of rhodium catalysts by ethylene and carbon monoxide.

Thus in homogeneous hydrogenation the part of ligands may be played not only by groups introduced beforehand, but also by molecules of the substrate, reaction products, hydrogen, and the solvent.

The functions of the solvent in catalytic systems may be extremely varied. Thus the solvent takes direct part in complex formation. With strong electrolytes, such as aqueous solutions of perchlorates, the metal ion is solvated by water. (The absence of a perchlorate salt effect when copper perchlorate is used as hydrogenation catalyst indicates that it is the Cu^{II} ion, and not a perchlorato-complex of copper, which is active in this reaction.) Measurements of the molecular weight of copper acetate in pyridine and dodecylamine led Wright and coworkers[76] to suggest that the copper salt exists in the form of a complex in solutions of effective complex-forming reagents such as amines. This complex formation with the solvent explains the marked influence of substituents in quinoline and pyridine on the catalytic activity of Cu^{II} in these solvents[27,77]. Thus the introduction of a methyl group into the pyridine molecule leads to a significant increase in the activity of copper acetate compared with the activity of this salt in pyridine.

It has been suggested[193] that the rhodium complex $RhCl_3(Ph_3P)_3$, which dissociates readily in benzene, subsequently reacts with hydrogen and a substrate in the form of a solvated four-coordinated complex $RhCl(Ph_3P)_2(Sol)$, where Sol represents a solvent molecule. In the opinion of the authors cited, this is confirmed by the fact that hydrogenation does not take place in solvents which are more powerful complex-forming reagents. An interesting feature is that a fairly stable complex with the composition $Rh(H_2)Cl(AsPh_3)_2.0.5CH_2Cl_2$ was isolated from solutions of the analogous complex of rhodium with Ph_3As in CH_2Cl_2.[194]

The nature of the solvent has a significant influence on the nature of the rupture of the H–H bond in the hydrogen molecule. Thus in the activation of hydrogen by solutions of copper and silver salts in amines, heterolytic splitting of the hydrogen predominates over homolytic splitting in the absence of aqueous solutions of these salts. In Halpern's opinion, this is partly due to the fact that a solvent more basic than water combines with the H^+ ions formed.

Heterolytic rupture of the H_2 is facilitated not only by greater basic strength of the solvent but also by dilution of the solution and increase in temperature[56].

There is no doubt that the stability and hence the activity of the hydride formed by the reaction of hydrogen with the transition metal complex also depends to a marked extent on the nature of the solvent. In many instances the hydrogen atom of the hydride takes part in exchange reactions with the solvent, and this may have a significant influence on the kinetics and yield of reaction products.

In some instances it has been shown that a solvent containing labile hydrogen can take direct part in one of the hydrogenation stages by acting as a source of one of the H atoms, as for example with platinum complexes [221]:

$$^{-}H[Pt] + C_2H_4 \rightarrow PtC_2H_5^-$$
$$PtC_2H_5^- + ROH \rightarrow C_2H_6 + [Pt] .$$

The part played by ethanol in the catalytic reactions of complexes of Group VIII metals is considerable, and many of its aspects are not clear. The rhodium complexes mentioned above are more active when ethanol is introduced into the non-polar solvent; the efficiency of the $CoCl_2$–KCN system is greatly increased in alcoholic solutions; phosphite complexes of cobalt are also active only in the presence of alcohols [197]; and ruthenium complexes do not catalyse hydrogenation in the absence of traces of alcohol [195]. It should also be noted that side reactions involving alcohols may also deactivate a catalytic system: at elevated temperatures, the complex $RhCl(Ph_3P)_3$ may decarbonylate alcohol and be converted into the inactive $RhCl(CO)(Ph_3P)_3$. [193]

c. Mode of Activation of Molecular Hydrogen

The various possible reactions involved in the activation of hydrogen can be represented schematically as follows:

1) Heterolysis: $RuCl_6^{3-} + H_2 \rightleftharpoons RuHCl_5 + H^+ + Cl^-$
2) Homolysis: $2Co(CN)_5^{3-} + H_2 \rightarrow 2CoH(CN)_5^{3-}$
3) Insertion: $IrCl(CO)L_2 + H_2 \rightarrow IrCl(H_2)(CO)L_2$
4) Electron transfer: $Hg^{2+} + H_2 \rightarrow Hg^0 + 2H^+$.

Insertion, which is of independent interest, may also apparently be an intermediate stage in the homolytic or heterolytic splitting of hydrogen, for example:

$$MXL_n + H_2 \rightarrow M(H_2)XL_n \rightarrow MHL_n + HX \text{ etc.}$$

Published data indicate that activation of hydrogen may take place on a single metallic centre or on two such centres. In the latter instance the metal atoms may be the same, as in $Co_2(CO)_8$, [154] or different, as in complexes with a Pt–Ge bond [234]; the lowest value for the activation of rupture of the H–H bond (9 kcal mole^{-1}) was observed when these complexes were used. In some instances, ligands such as amines may act as second centre for the activation of hydrogen, for example:

$$(L{-}Ag{-}L)^+ + H_2 \rightarrow \begin{bmatrix} L{-}Ag^+{-}L \\ \vdots \quad\quad \vdots \\ H^{-\delta} \ldots H^{+\delta} \end{bmatrix} \rightarrow AgHL + H^+$$

where L represents an amine.

2. TRANSITION METAL HYDRIDES TAKING PART IN CATALYTIC REACTIONS OF HOMOGENEOUS HYDROGENATION

The intermediate formation of a hydride in the reaction of hydrogen with an active complex is the most important stage in catalytic hydrogenation. The study of the properties of hydride complexes of transition metals and their behaviour under the conditions of hydrogenation is of considerable assistance in reaching an understanding of the reaction mechanism.

In the earliest work on the activation of hydrogen, the intermediate formation of hydrides was assumed merely on the basis of kinetic and thermodynamic data (with the exception of CuH, which was actually prepared), but the position has now altered significantly. It has been possible to isolate a number of hydrides in the form of individual compounds. To confirm the formation of hydrides in the reaction mixture and to obtain information on their structures, extensive use is made of infrared spectroscopy and proton magnetic resonance spectroscopy [235,236].

The stability of hydride complexes depends to a marked extent on the nature of the metal, the ligand, and the solvent; the nature of the H atom in these complexes varies from strongly acidic in $CoH(CO)_4$ to labile hydrido in $PtHCl(Ph_3P)_2$.

The hydrogen in the hydride complex should be sufficiently labile to take part in hydrogen transfer with subsequent regeneration of the complex, capable of activating hydrogen again.

Hydride complexes with one, two, or three hydrogen atoms on one metallic centre are now known. In the discussion of reaction mechanisms, allowance must be made for the fact that with di- and tri-hydrides the hydrogen atoms may not be transferred to the substrate molecule simultaneously, since the properties of these H atoms may be different. Osborn and coworkers [193] discuss the alternative possibilities of simultaneous or consecutive transfer of hydrogen for the rhodium dihydride $Rh(H_2)Cl(Ph_3P)_2$.

Some authors regard the reaction of hydrogen with a transition metal complex as formal oxidation of the metal by hydrogen [184]:

$$Ir^{I}Cl(CO)(Ph_3P)_2 + H_2 \rightleftharpoons Ir^{III}(H_2)Cl(CO)(Ph_3P)_2$$
$$2[Co^{II}(CN)_5]^{3-} + H_2 \rightleftharpoons 2[Co^{III}H(CN)_5]^{3-} \text{ (Ref.108)}$$

With increase in the valency of the metal there is an increase in its coordinating power, and both these factors have a direct influence on the stability of the resulting hydride [235]. Vaska [185] suggests that in homogeneous hydrogenation by means of the hydrido-complex $IrH(CO)(Ph_3P)_3$ this monohydrido-compound reacts with H_2 with the formation of the even more active seven-coordinated trihydrido-compound $IrH_3(CO)(Ph_3P)_3$, which subsequently reacts with the substrate.

In the reaction of H_2 with the osmium complex $OsHL_5$ (where L represents a ligand), the 8-coordinated OsH_3L_5 is formed [185]. Complexes of this kind with an unusual coordination number are unstable and should give up hydrogen readily. In Vaska's opinion, it is necessary in the prediction of the catalytic activity of complexes to consider the relative stabilities of their electronic and stereochemical configurations, and also the stabilities of their potential active adducts with hydrogen, such as OsH_3L_5, $IrH_3(CO)L_3$, [185] or the proposed unstable 5-coordinated complex $[PtHCl_2(SnCl_3)(C_2H_4)]^{2-}$. [221]

Most catalysts of homogeneous hydrogenation absorb hydrogen reversibly. This property of complexes (or salts) is not essential, however, for the manifestation of catalytic power. Thus the complex $RhH(CO)(Ph_3P)_3$ does not absorb H_2, but it catalyses the hydrogenation of ethylene [208]. This is apparently due to the fact that the complex (in the present instance a hydrido-complex) first reacts with the substrate, and then activates hydrogen (hydrogenolysis of the metal–carbon bond).

3. ACTIVATION OF THE SUBSTRATE AND TRANSFER OF HYDROGEN

In hydrogenation it is possible to distinguish stages involving the activation of hydrogen, the activation of the substrate, and the transfer of hydrogen to the substrate.

In general, the sequence of these stages can be represented by the following basic schemes[69] (M represents the transition metal complex, and S the substrate):

Scheme I:

$$M + H_2 \rightleftarrows M\cdot H_2 \quad (a)$$
$$M\cdot H_2 + S \rightleftarrows S\cdot M\cdot H_2 \quad (b)$$
$$S\cdot M\cdot H_2 \rightarrow S\cdot H_2 + M \quad (c)$$

According to scheme I, activation of hydrogen takes place first with formation of a hydride, which then reacts with the substrate and hydrogen is transferred to the substrate.

Scheme II:

$$M + S \rightleftarrows M\cdot S \quad (a)$$
$$M\cdot S + H_2 \rightleftarrows H_2\cdot M\cdot S \quad (b)$$
$$H_2\cdot M\cdot S \rightarrow S\cdot H_2 + M \quad (c)$$

According to scheme II, the complex with the substrate is formed first, and this complex then activates hydrogen.

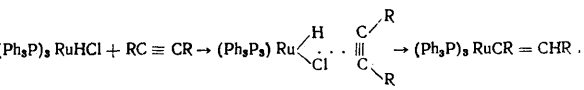
Scheme III:

$$M + S \rightleftarrows M\cdot S \quad (a)$$
$$M' + H_2 \rightleftarrows M\cdot H_2 \quad (b)$$
$$M\cdot S + M'\cdot H_2 \rightarrow M' + S\cdot H_2 + M \quad (c)$$

According to scheme III, the complex activates hydrogen and the substrate separately, and in the general case the activation of these reagents may be brought about by different complexes. Examples of reactions of this kind are provided by various reactions of enzymatic catalysis, in which the substrate and hydrogen are activated by different centres[237].

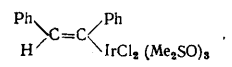
Activation of the substrate has been studied in most detail for the homogeneous hydrogenation of alkenes and alkynes. A theory of complex formation by alkenes and alkynes with transition metal compounds was put forward in 1952 by Dewar. A fairly large number of alkene and alkyne complexes have now been described, and a number of interesting reviews[238,239] have been devoted to these compounds. There is no doubt that the formation of a complex with the substrate is not sufficient for catalytic hydrogenation, which also requires that the bond between the substrate and the transition metal be fairly labile. Homogeneous hydrogenation is usually undergone only by those alkenes which react reversibly with the transition metal compound in solution[193]. Attempts to correlate the tendency of alkenes to undergo hydrogenation with the stability constants of the complex formed by the transition metal with these alkenes are extremely interesting in this connection[193,240]. According to the data of Osborn and coworkers[193], the equilibrium constant for the reaction of propene with the rhodium complex $RhCl(Ph_3P)_3$ is smaller by a factor of 2000 than that for ethylene, so that propene, unlike ethylene, is hydrogenated by means of this catalyst. The higher activity of $RhBr(Ph_3P)_3$ and $RhI(Ph_3P)_3$ compared with the corresponding chloride is in agreement with the lower stability of the complexes formed by the alkenes with the iodide and the bromide. The analogous complexes of rhodium with Ph_3As form more stable complexes with the alkene and are correspondingly less effective hydrogenation catalysts.

In the stage involving activation of the alkenes and acetylenes, both π- and σ-complexes with transition metal compounds may be formed. The hydride formed by the reaction of hydrogen with the transition metal compound according to scheme I (or introduced directly into the reaction mixture) may give a π-complex with the alkene (or alkyne), which is then converted into a σ-complex. This scheme was adopted, for example, by Jardine and McQuillin[196].

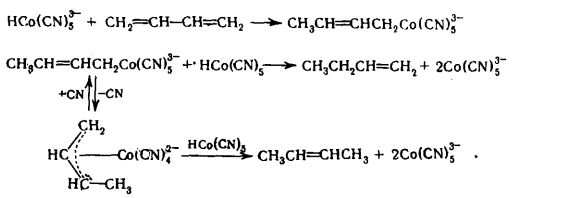


Examples of complexes containing both hydrogen and a π-bonded alkene on the same metallic centre are provided by the recently prepared complexes of iridium[241] $Ir_2HCl_2(C_8H_{12})_2$ and rhodium[242] $RhH_2(C_2H_4)(Ph_3P)_3$.

The organometallic σ-compound of iridium whose existence was assumed in the above scheme of Jardine and McQuillin was recently prepared[243]:

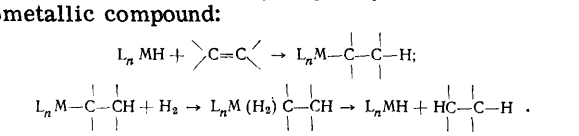


On acidification, this compound gives *cis*-stilbene. On the other hand, the reaction of the hydride with the substrate may involve the initial formation of a σ-complex, which is subsequently converted into a π-complex. Thus the following scheme was proposed to explain isomerisation during hydrogenation[119]:



The organometallic σ-compound formed may subsequently react with the transition metal hydride or undergo hydrogenolysis or hydrolysis (alcoholysis), depending on the conditions of the reaction. The hydrogenolysis of metal–carbon bonds is a fairly common phenomenon. Gilman[244] described the splitting of alkali metal compounds by hydrogen; Clauss and Bestain[245] described organometallic compounds of Mn and Ti, and Hein and Weiss[246,247] described compounds of chromium (the formation and properties of these derivatives have been reviewed[248,249]).

In a sense, the hydrogenolysis of a metal–carbon bond represents the activation of hydrogen by an intermediate organometallic compound:



A hydrogenation mechanism involving the formation of σ-alkyl complexes was assumed by Vaska[185] for an iridium complex, and has also been proposed for Ziegler–Natta catalysts[141,147], etc.

Although the formation of a σ-alkyl bond is widely encountered, this stage cannot always be observed in homogeneous hydrogenation. Thus in the hydrogenation of alkenes by means of a rhodium hydride, Osborn and coworkers[193], using the NMR method, were unable to detect the formation of a σ-C–Rh bond. In this instance, on the basis of the available experimental data, they put forward a hydrogenation scheme involving the simultaneous transfer of two hydrogens to the alkene.

The form in which the hydrogen is transferred to the compound being hydrogenated—ionic (see for example the review on hydride displacements[250]) or radical—depends to a large extent on the nature of the transition metal hydride, the substrate, the presence of a hydrogen carrier, the participation of the solvent, and other factors.

There is also the interesting possibility of carrying out catalytic hydrogenation without hydrogen transfer, by a mechanism involving electron transfer[251] (in this instance the solvent is the source of hydrogen):

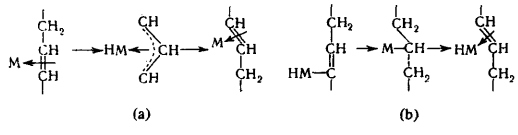
$$L_nM^{+m} + S \rightarrow L_nM^{+m+1}S^-$$
$$L_nM^{+m+1}S^- + H^+ \text{ (from solvent)} \rightarrow L_nM^{+m+1} + SH$$
$$L_nM^{+m+1} + H_2 \rightarrow L_nM^{+m} + 2H^+ \text{ etc.}$$

In most of the hydrogenating systems examined above, the activation of both hydrogen and the substrate was brought about by reaction with the same catalyst.

Complexes capable of activating hydrogen, however, are often not capable of simultaneously activating various substrates. On the other hand, the introduction, into a system containing a hydrogen activator, of substances capable of activating the substrate may extend considerably the range of application of the catalytic system. Khidekel'[229] points out that this method of activating the substrate differs fundamentally from the method of increasing the rate and specificity of homogeneous catalytic hydrogenation by modification of a catalyst activating molecular hydrogen. Thus organic compounds with carbonyl groups are not hydrogenated in the presence of the complex $RhCl(Ph_3P)_3$, which activates hydrogen. By adding zinc chloride, which forms complexes with carbonyl compounds, to the reaction mixture, however, Khidekel'[229] was able to hydrogenate carbonyl compounds under the same conditions.

4. ISOMERISATION OF THE SUBSTRATE DURING HOMOGENEOUS HYDROGENATION. THE SELECTIVITY AND STEREOSPECIFICITY OF HYDROGENATION CATALYSTS

Hydrogenation may be accompanied by a number of side reactions, depending on the nature of the substrate and the complex. One such reaction involving a transition metal hydride is the isomerisation of alkenes, described by many workers for complexes of Ir, Pt, Pd, Co, Ru, and Fe. It is now usual to consider "hydrido-σ-allyl" (a) and "hydrido-alkyl" (b) mechanisms of isomerisation, which can be represented schematically as follows[252-254]:



(a) (b)

Study of the distribution of isomers may give valuable information on the mechanism of homogeneous hydrogenation, since these processes involve the participation of a transition metal hydride with transfer of hydrogen by an "alkyl" or "allyl" mechanism. Work on the isomerisation of pent-1-ene in the presence of hydrogenation catalysts with a Pt–Sn bond is of interest in this connection[255].

In a number of instances, catalysts of homogeneous hydrogenation are extremely selective. Thus $LiAlH_4$ catalyses the homogeneous hydrogenation of pent-2-yne with the exclusive formation of pent-2-ene, and with conjugated alkenes, one C=C bond is preserved[41]; in the presence of the complex $Cp_2Ti(CO)_2$, hex-1-yne is hydrogenated to hex-1-ene[183]; the hydrogenation of sorbic acid by means of $[Co(CN)_5]^{3-}$ gives chiefly 2-hexenoic acid (see Table 1). The complex $Co_2(CO)_8$ can catalyse the hydrogenation of unsaturated aldehydes to saturated aldehydes, but at elevated temperature aliphatic aldehydes are hydrogenated to the corresponding alcohols. This property of the catalyst is extremely important for the control of hydroformylation. An important feature is that many catalysts of homogeneous hydrogenation, for example Ziegler–Natta systems[141] or the complex $RhCl(Ph_3P)_3$,[193] which are extremely active towards C=C and C≡C bonds, are incapable of reducing functional groups such as =CO, –CHO, –CN, –N=N–, $-NO_2$, etc.

Catalysts of homogeneous hydrogenation in a number of instances also show distinct stereospecificity. Thus in the hydrogenation of maleic acid by molecular deuterium in the presence of the complex $RhCl(Ph_3P)_3$, preferential cis-attachment of D_2 is observed, and the chief product is 1,2-dideuterosuccinic acid[193]. According to the observations of these authors, the quantity of *cis*-hex-2-ene obtained in the hydrogenation of hex-2-yne is twenty times the quantity of *trans*-hex-2-ene obtained.

The direction of hydrogenation sometimes depends on the conditions of the reaction. For example, the hydrogenation of butadiene by means of the $CoCl_2$–KCN system gives *trans*-but-2-ene at $CN^-/Co^{2+} \leqslant 5$, whereas but-1-ene is formed preferentially at $CN^-/Co^{2+} \geqslant 6$.[119]

V. ENZYMATIC CATALYSIS OF HYDROGENATION AND THE ISOTOPIC EXCHANGE AND CONVERSION OF HYDROGEN

Work by Stephenson, Strickland, and Green[256-259] laid the foundation for the study of a large class of micro-organisms capable of activating molecular hydrogen. This ability was ascribed to an enzyme or system of enzymes, named hydrogenase[260]. In the study of the catalytic power of hydrogenase, use is made of both the exchange and conversion of hydrogen[237,261-269] and hydrogenation[263-275].

Krasna and Rittenberg[264], on the basis of a study of the kinetics of these reactions, proposed the mechanism $H_2 + E \rightleftharpoons H:E^- + H^+$, where E represents hydrogenase, and the HE^- formed takes part in hydrogenation or the exchange or conversion of hydrogen.

When Methylene Blue or hexacyanoferrate(III) is added to an aqueous suspension of *Pr. vulgaris*, D_2–H_2O exchange is inhibited, and the rate of exchange increases to its previous value only after an induction period, during which hydrogenation of the substrate takes place[265,267]. In the opinion of the authors cited, this shows that the same intermediate compound is formed during hydrogenation and exchange.

The same opinion is held by Farkas and Fisher[237], who studied the hydrogenation of fumarate in the presence of inhibitors of two types (CN and urethane).

Peck and coworkers[266] cast doubt on the idea that the catalysis of isotopic exchange by hydrogenase is a necessary condition for hydrogenating power in hydrogenase, since the rate of exchange in the presence of *Az. vin.*[276,277] and *Rhod. rubrum*[278] is very low compared with the rate of hydrogenation. Study of the catalytic activity of a wide range of micro-organisms showed that the rate of reduction of Methylene Blue is also increased by enzymes which have no significant catalytic effect on exchange. The authors cited emphasise that these results do not agree with the mechanism of Krasna and Rittenberg[264], and they put forward a reaction scheme, according to which hydrogen is activated by an iron-containing enzyme; the reduced enzyme can be oxidised by Methylene Blue or by

other acceptors, with the participation of a flavine component:

$$H_2 + E(Fe^{3+}) \rightleftarrows E(Fe^{2+}) : 2H$$
$$\downarrow \text{flavine}$$
Methylene Blue

They do not, however, exclude an alternative mechanism, according to which a complex of the reduced enzyme may combine with flavine and be oxidised by one-electron acceptors such as viologen dyes, the reaction involving a second metal atom as a functional component of the hydrogenase:

$$E(Fe^{2+})\ \text{flavine} : 2H \xrightarrow{Mo} 2\ \text{viologen} \cdot + \bar{e} + 2H^+$$

The presence of iron in hydrogenase was established by Hoberman and Rittenberg[263], Peck and coworkers[266], and Gest[272]; Peck and coworkers[266] also discuss the part played by Mo.

The activation of hydrogen according to the scheme proposed by Rittenberg and Krasna is heterolytic[3]:

$$\overline{Fe^{3+}} + : B \rightleftarrows \overline{FeH^+} + H : B^+$$

whereas according to Gest and coworkers it is homolytic, the rupture of the H–H bond taking place on two metallic centres.

In heterolytic rupture of H_2, the reduction of two-electron acceptors such as Methylene Blue becomes possible, whereas one-electron processes, such as the reduction of viologen dyes and D_2–H_2O exchange, require the participation of a second metal. This explains the observation that *Az. vin.* and *Rhod. rubrum* catalyse the reduction of Methylene Blue but do not catalyse exchange.

The main features of the results obtained by Krasna and Rittenberg[265,267] in the study of the catalytic activities of various micro-organisms agree with those obtained by Peck and coworkers[266]. They found, however, that exchange is observed in all instances when reduction of Methylene Blue takes place.

Comparison of the hydrogenating power of the bacterium *Ph. vulgaris* with the activity of $[Co(CN)_5]^{3-}$ led King and Winfield[137] to the conclusion that the mechanisms of hydrogenation by hydrogenase and pentacyanocobaltate are the same.

The activation energy for D_2–H_2O exchange by means of the bacterium *Pr. vulgaris* suspended in a phosphate buffer is 7.7 kcal mole^{-1};[263] other authors give the value 14 kcal mole^{-1}.[237] Couper and coworkers[269] determined the activation energy for the exchange and conversion of hydrogen, catalysed by *Pr. vulgaris* and *E. coli*. According to their data, for *Pr. vulgaris*, the activation energy for $D_2 + H_2O$ exchange is 7.47 ± 1.11 kcal mole^{-1}, and that for the ortho-para conversion of hydrogen 7.35 ± 0.46 kcal mole^{-1}.

Thus the enzymatic catalysis of hydrogenation by means of hydrogenase involves an extremely complicated chain of catalytic processes, responsible for the exceptional activity and stereospecificity of the processes under mild conditions. In this connection, the study of transition metal compounds as catalysts of homogeneous hydrogenation gives extensive material for constructing models of biochemical processes. An exceptionally important feature is the presence of a transition metal in hydrogenase. The part played by cobalamin (an enzyme containing Co[279-281]) in hydrogen transfer is extremely important. One example of the construction of a model of this enzyme is the use of cobaloxime—a model of vitamin B_{12S}—as hydrogen carrier in a system containing a rhodium catalyst which brings about the homogeneous activation of molecular hydrogen[282].

It can confidently be stated that the study of the mechanism of action of enzymatic systems is giving valuable information for the creation of new and effective complex catalysts for homogeneous hydrogenation. The introduction, into catalytic systems, of hydrogen carriers and additives capable of activating the substrate, together with modification of the hydrogen activation catalysts themselves, is now making it possible to obtain highly effective hydrogenation catalysts.

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The number of known systems capable of activating hydrogen under the conditions of a homogeneous reaction—Lewis bases and acids, salts and complexes of transition metals—is now extremely large. Among compounds of these classes, the transition metal complexes show the greatest activity.

The catalytic action of transition metal complexes is observed under comparatively mild reaction conditions, and their activity in the hydrogenation of organic compounds in a number of instances is as high as or even greater than that of heterogeneous catalysts. An understanding of the mechanism of action of homogeneous hydrogenation catalysts is of assistance in the investigation of the mechanism of heterogeneous catalytic hydrogenation and also the mechanisms of polymerisation, hydroformylation, and other reactions.

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