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Organometallic Chemistry in Homogeneous Catalysis

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In most large-scale processes in the chemical industry catalysts are used to accelerate the desired reactions, both to increase productivity and to reduce the loss of starting materials in undesirable side reactions. Most commonly, the catalysts are insoluble metal oxides or metals, so-called heterogeneous catalysts. However, in an increasing number of processes, the catalyst is a transition metal complex that is soluble in the reaction medium. These homogeneous catalysts are used in about two dozen significant processes in the American chemical industry (*1*). Some of the varied applications are listed in Table 1. The total production by homogeneous catalytic processes in 1977 was nearly 10 million metric tons, worth over $5 billion. These totals are small compared to those associated with the heterogeneous processes of the petroleum industry but have provided a major incentive for research.

Summary. Many reactions catalyzed by soluble transition metal compounds proceed by way of organometallic intermediates, even though the original catalyst may be a simple salt. This generality is illustrated for three industrial syntheses of acetic acid that use homogeneous catalysts. Some developments in organometallic chemistry that may extend the utility of homogeneous catalysis are photoactivation of catalysts and the recognition of the importance of metallacyclic intermediates.

Many of these catalytic reactions proceed by way of organometallic intermediates (*2*), compounds that contain direct metal-carbon (M–C) bonds. Such organometallic species occur even with heterogeneous metallic catalysts or with soluble catalysts based on simple salts such as rhodium chloride, $RhCl_3$. This interrelation between organometallic chemistry and catalysis has stimulated extensive organometallic research in both university and industrial laboratories. The fundamental research that led to Nobel prizes for Karl Ziegler and Giulio Natta in 1963 and for Geoffrey Wilkinson and E. O. Fischer in 1973 has often underlain commercial development of processes similar to those listed in Table 1.

I will illustrate here the role of organometallic compounds in catalysis in terms of three processes for the production of acetic acid (CH_3COOH) (Fig. 1). All of these processes proceed through a series of organometallic intermediates, even though the catalyst precursor added to the reaction vessel is a simple metal salt with no C–M bonds. Because the catalysts are soluble in the reaction media, it has been possible to study these processes by the conventional techniques of physical organic chemistry. Consequently, much more is known about the mechanisms and reaction intermediates in these acetic acid syntheses than for classical heterogeneous catalytic processes.

The three acetic acid preparations of Fig. 1 also illustrate a trend toward the use of more economical starting materials or feedstocks. From the first commercial use of a soluble transition metal catalyst in 1913 until about 1950, nearly all industrial applications of homogeneous catalysis were based on reactions of acetylene. Much of the acetic acid made in this period was produced by a two-step process in which acetylene was hydrated to acetaldehyde, which was then oxidized to acetic acid (first reaction in Fig. 1). Both steps were catalyzed by soluble metal salts. This process had the disadvantage that acetylene is a hazardous chemical that requires large quantities of energy for its manufacture. These characteristics provided a major incentive to replace acetylene with safer, more economical feedstocks.

Research in Germany from 1940 to 1960 showed that olefins, especially ethylene, could be substituted for acetylene in the production of many industrial chemicals. Although much of this research was empirical, it provided the basis for much of homogeneous catalysis as we know it today. Wacker-Chemie developed an elegant process for the catalytic oxidation of ethylene to acetaldehyde (second reaction in Fig. 1), an acetic acid precursor as described above. This process began commercial operation about 1960 and is still used extensively.

The same German research also laid the basis for utilization of synthesis gas, a readily available mixture of carbon monoxide and hydrogen, as a feedstock for the chemical industry. A major virtue of synthesis gas is that it can be made from many carbon sources—natural gas, petroleum, coal, or biological wastes. This versatility commends it as a feedstock for the future just as it did in the petroleum-starved Germany of World War II. Both Badische Anilin und Soda Fabrik (BASF) and Monsanto have developed processes to convert methanol derived from synthesis gas to acetic acid by catalytic carbonylation reactions (third reaction in Fig. 1). These processes appear extremely useful in the energy

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and feedstock context of the next two decades.

These three processes are described individually below with emphasis on the nature of the organometallic chemistry that underlies the technology.

$$HC{\equiv}CH + H_2O \longrightarrow CH_3CHO \xrightarrow{O_2} CH_3COOH$$

$$H_2C{=}CH_2 + O_2 \longrightarrow CH_3CHO \xrightarrow{O_2} CH_3COOH$$

$$CO + 2H_2 \longrightarrow CH_3OH \xrightarrow{CO} CH_3COOH$$

Fig. 1. The basic reactions in acetic acid syntheses of successive "feedstock eras."

Acetylene Hydration

In 1916, under pressure of feedstock shortages brought about by World War I, plants in Germany and Canada began to produce acetic acid from acetylene (Fig. 1) (*3*). This technology was widely used for 50 years.

The catalysis of acetylene hydration by mercury salts was discovered in 1881 and was used as a laboratory synthesis of acetaldehyde for many years. The commercial process was a scaled-up version of the laboratory method in many ways. Acetylene was blown through a hot, dilute sulfuric acid solution that contained small amounts of mercury and iron salts as catalysts. The acetylene was added at such a rate that unchanged acetylene swept the acetaldehyde product out of the solution before it could undergo undesirable side reactions. The yield was high and the process was simple, two characteristics that kept this technology economically viable until recently.

The chemistry of this seemingly simple process is quite complex. Even though the nominal catalyst mercuric sulfate ($HgSO_4$) is a classical inorganic salt, organometallic intermediates participate in the catalytic cycle. The nature of the catalysis is not as well defined as one would like because most of the research on the process was done before the development of modern kinetic and spectroscopic techniques.

Figure 2 illustrates one reasonable proposal (*4*) for the mechanism of this process. The sequence of reactions is depicted in Tolman's cyclic convention (*5*) to emphasize the cyclic nature of the catalytic reaction. In the initial step, starting from the top of the cycle, an acetylene molecule coordinates to Hg^{2+}. This coordination involves mixing of the π and π^* acetylenic molecular orbitals with both filled and unfilled orbitals of the metal ion. Overall, the interaction produces a fairly strong bond with some net transfer of electron density from the organic molecule to the metal. This depletion of electron density on the coordinated acetylene in structure **1** makes acetylene susceptible to attack by nucleophilic reagents such as water. Reaction with water and dissociation of H^+ forms a 2-hydroxyvinylmercury complex (structure **2**). Cleavage of the labile C-Hg bond by acid regenerates the Hg^{2+} ion for another catalytic cycle. The vinyl alcohol liberated in this step rearranges to its more stable isomer, acetaldehyde, under the usual reaction conditions.

The activation of the acetylene molecule by interaction with the metal ion illustrates a major characteristic of catalytic reactions. The mixing of molecular orbitals of the organic compound with those of the metal complex provides a low-energy pathway for reactions of the organic molecule. Although the overall reaction could occur in the absence of the catalyst, its rate is greatly enhanced by reduction of its normal activation energy. If the catalyst favors only one of several possible reactions of the organic compound, the catalyst improves the yield as well as the rate of the reaction.

Table 1. Catalytic processes based on organometallic chemistry.

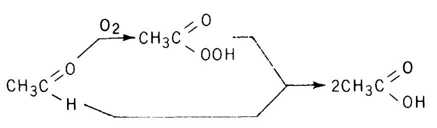
Catalytic process	1977 U.S. production ($\times 10^3$ metric tons)
Soluble organometallic catalysts	
Acetic acid from CO and H_2 or ethylene	590
Alcohols from CO-H_2 and olefins	780
Long-chain olefins from ethylene	177
Adiponitrile from hydrogen cyanide and butadiene	200
Chloroprene from chlorine and butadiene	166
Polybutadiene, polyolefins	845
Surface-supported organometallics	
Polyethylene (high density)	1,140
Polypropylene	1,230
Total organometallic	5,128
Soluble nonorganometallic catalysts	
Acetic acid from butane oxidation	986
Terephthalic acid from *p*-xylene oxidation	2,277
Adipic acid from cyclohexane oxidation	698
Polyester polymerization	1,655
Polyurethane polymerization	1,500
Total nonorganometallic	7,116
Total organometallic and homogeneous	12,244

Acetaldehyde Oxidation

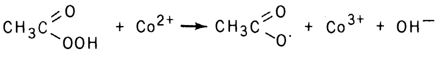
The catalytic reactions of acetylene, olefins, and carbon monoxide usually involve prior coordination of the organic reactant to the metal catalyst through C-M bonds. In contrast to these organometallic processes, another major family of catalytic reactions is not based on C-M bonds in the intermediates. The most common of these are Co^{2+}-catalyzed air oxidations of organic compounds. The oxidation of acetaldehyde to acetic acid is typical.

The oxidation of acetaldehyde is the second step in the production of acetic acid from acetylene or ethylene (*6*). A similar reaction has also been used to oxidize grain alcohol to acetic acid, a process that may become significant if natural products again become major feedstocks for the organic chemicals industry. Typically, acetaldehyde that contains a trace of the acetate of Co^{2+} is heated with air or oxygen at 65°C and atmospheric pressure. The yield of acetic acid approaches 90 percent, and the technology is relatively simple.

The chemistry consists of two basic steps (*7*):



The first step, oxidation of acetaldehyde to peracetic acid, is a free-radical process that does not involve the metal ion except perhaps as an initiator. The metal ion catalyzes the second step in which the peracetic acid oxidizes another molecule of acetaldehyde. The chemistry of this step is less well understood. One of the many reactions in the catalytic cycle is the oxidation of the cobalt ion:



$$CH_3C(=O)OOH + Co^{2+} \longrightarrow CH_3C(=O)O\cdot + Co^{3+} + OH^-$$

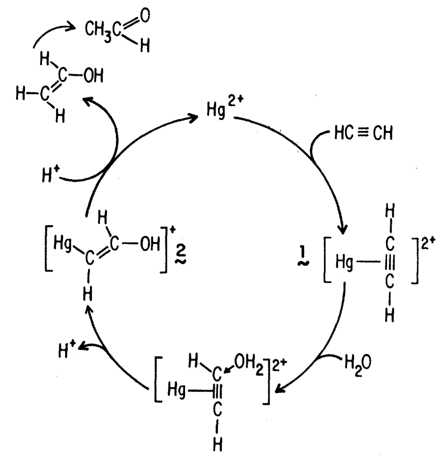


Fig. 2. A likely mechanism for the catalysis of acetylene hydration by Hg^{2+}.

The acetoxy radical thus formed yields acetic acid by abstracting a hydrogen atom from acetaldehyde. The oxidation of the metal ion almost certainly begins with formation of a coordination complex with peracetic acid. This chemistry includes the formation of organic complexes of the metal ion, although not organometallic compounds which contain C-M bonds as required by a strict definition.

Ethylene Oxidation

A major step in the replacement of acetylene by olefins as a feedstock was development of the Wacker process for the oxidation of ethylene to acetaldehyde (*8*). Chemists at Wacker-Chemie applied the fact, known since 1894, that ethylene is stoichiometrically oxidized by a palladium salt:

$$C_2H_4 + Pd^{2+} + H_2O \rightarrow CH_3CHO + Pd^0 + 2H^+$$

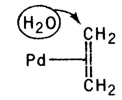
This reaction was combined with a copper-catalyzed reoxidation of palladium by air to effect a catalytic air oxidation of the olefin:

$$C_2H_4 + 1/2\ O_2 \rightarrow CH_3CHO$$

The process was commercialized in 1960 and was soon adopted worldwide because it avoided the expense and the hazards associated with acetylene as a starting material.

The chemistry of ethylene oxidation is more complex than that of acetylene hydration. Like hydration, ethylene oxidation involves an extended sequence of organometallic intermediates. One proposed mechanistic scheme (*9*) is depicted in Fig. 3. This catalytic cycle illustrates the variety of chemistry that can occur within the coordination sphere of a metal ion. Curiously, almost every step in this scheme is controversial in spite of careful study with modern kinetic and spectroscopic techniques.

One major aspect of this scheme, the activation of the olefin by coordination to a metal ion, is unchallenged. As in acetylene hydration, the mixing of ethylene π and π^* orbitals with the orbitals of the metal cation in structure **3** forms a stable bond and withdraws electron density from the olefin. This electron withdrawal facilitates nucleophilic attack of the olefin by water:



The controversial aspect of this step is whether the water molecule is coordinated to the palladium ion. Under some conditions, it is clear that the attacking water molecule is not activated by coordination (*9*).

The product of the hydration step is a 2-hydroxyethylpalladium species (structure **4**). Transfer of a hydrogen from the β-carbon of the ethyl group to palladium yields complex **5** in which a vinyl alcohol molecule is coordinated to a palladium hydride. This transfer of a β-hydrogen is a prevalent reaction in organometallic chemistry. Typically, the transfer is readily reversible. If the palladium-bonded hydrogen in structure **5** transfers to C-2 instead of C-1, the 1-hydroxyethyl complex (structure **6**) forms. (This reaction can also be viewed as an addition of the Pd-H bond to the C=C bond.) Dissociation of the O-bonded proton from structure **6** yields acetaldehyde and a palladium atom. The effectiveness of the Wacker process depends on reoxidation of this zerovalent species before it can agglomerate as palladium metal, which is difficult to reoxidize. The Cu^{2+} ion readily oxidizes the palladium to Pd^{2+}, which can begin another catalytic cycle.

Methanol Carbonylation

At the same time that Wacker-Chemie began to make acetic acid from ethylene, BASF in Germany started commercial production of acetic acid from methanol (*6*). The process evolved from World War II research that demonstrated that combinations of cobalt salts and iodides catalyze the reaction of methanol with carbon monoxide. Since methanol itself is derived from synthesis gas (CO plus H_2), this reaction sequence uses exceptionally cheap and abundant starting materials. The process is clean and simple and gives good yields of acetic acid. The major drawback is that it requires severe reaction conditions (210° to 250°C and pressures of about 500 atmospheres). This problem was overcome in a Monsanto process, commercialized in 1970, in which rhodium replaces cobalt as the catalyst. The precious metal catalyst gives almost quantitative yields of acetic acid at about 175°C and 15 atmospheres.

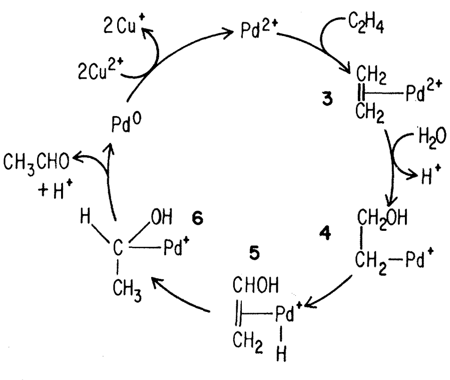


Fig. 3. Major features of the oxidation of ethylene by palladium salts in water.

In both the BASF and Monsanto processes, the iodide component of the catalyst reacts with methanol to form methyl iodide:

$$CH_3OH + HI \rightleftharpoons CH_3I + H_2O$$

The methyl iodide, in turn, reacts with the cobalt or rhodium component of the catalyst to form an organometallic compound with a CH_3-M bond. The catalyst cycle for the rhodium-catalyzed process is shown in Fig. 4 (*10*).

The rhodium source for the catalyst may be simple salt such as $RhCl_3 \cdot 3H_2O$, but it is reduced by CO and iodide to form a complex anion (structure **7**). The metal center in this anion is formally Rh^+. Despite this formalism, the metal is an electron-rich nucleophile that readily reacts with methyl iodide. By the customary electron-counting procedures of organometallic chemistry (*5*), the addition of methyl and iodide fragments to the metal to form structure **8** is an oxidative process and the metal in structure **8** is Rh^{3+}. Such oxidative addition reactions are characteristic of many organic transformations catalyzed by soluble transition metal complexes.

The most important feature about the formation of structure **8** is that methyl and CO ligands are brought together in the coordination sphere of the metal ion. This proximity facilitates the migration of methyl from rhodium to a CO carbon to form an acetyl ligand in structure **9**. The formation of a C–C bond is the key step in this acetic acid synthesis.

Subsequent steps are less well defined, but addition of another CO molecule to a vacant coordination site in structure **9** is likely. The product (structure **10**) is formally a Rh^{3+} species that can reduce spontaneously by elimination of acetyl and iodide ligands. This reductive elimination (the inverse of oxidative addition) produces acetyl iodide and regenerates structure **7** for another reaction cycle. The acetyl iodide can hydrolyze to form the desired acetic acid product:

$$CH_3COI + H_2O \rightleftharpoons CH_3COOH + HI$$

The hydrogen iodide coproduct reacts with methanol to form methyl iodide as described above. Overall, this complex organometallic sequence provides a facile, low-energy route to acetic acid.

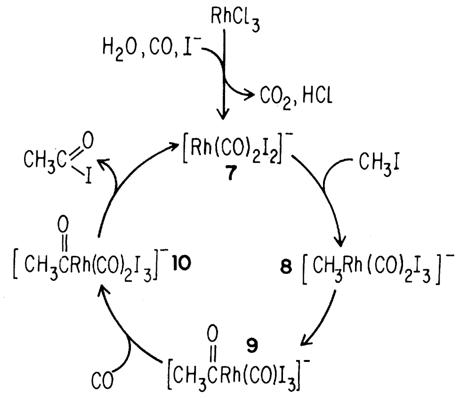


Fig. 4. The catalytic cycle for rhodium in the Monsanto acetic acid synthesis. An analogous iodine cycle (not shown) interacts with the rhodium cycle.

New Organometallic Catalysts

The catalysts used in the acetic acid processes described above are simple metal salts that transform to organometallic compounds in the catalytic reactor. This situation is typical of most of the large-scale commercial processes that have been used for many years. Recently, however, more sophisticated methods have been used to generate organometallic species that are catalytically active. For example, photochemical activation of a transition metal complex can greatly enhance its catalytic activity.

Irradiation of a metal carbonyl can produce an unstable but highly active catalyst for reactions of olefins (*11*). With $Cr(CO)_6$, near-ultraviolet light gives a catalyst for the selective hydrogenation of a diolefin to a monoolefin:

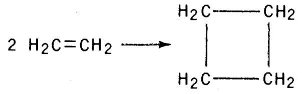
$$H_2C{=}CHCH{=}CHCH_3 + H_2 \rightarrow CH_3CH{=}CHCH_2CH_3$$

The photocatalytic reaction occurs at 25°C and 1 atmosphere in contrast to the severe conditions (200°C and 35 atmospheres) required normally. The irradiation seems to create vacancies in the coordination sphere of the metal atom by expulsion of carbon monoxide:

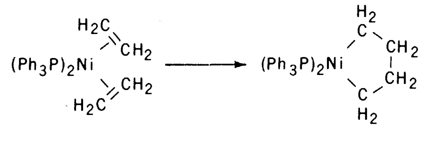
$$Cr(CO)_6 \rightleftharpoons Cr(CO)_5 + CO$$

These vacant coordination sites permit interaction of the olefin and H_2 with the metal ion.

Recent work has also shown that metallacyclic intermediates participate in homogeneous catalytic reactions such as olefin metathesis and olefin dimerization (*2*). An elegant example is the cyclodimerization of ethylene to form cyclobutane (*12*), a compound that is very difficult to prepare ordinarily:



A key step in the catalytic process is the conversion of a bis(ethylene) complex (structure **11**) to a nickelacyclopentane (structure **12**):



11 12

where Ph is the phenyl group. Phosphine-promoted reductive elimination of the two Ni–C bonds in structure **12** forms cyclobutane and regenerates $(Ph_3P)_3Ni$, which can react with more ethylene.

Other new developments in homogeneous catalysis have been reviewed in *Science*. These include the following:

1) Catalysts for asymmetric syntheses, that is, stereochemically selective catalysts that cause nonchiral reagents to combine to form optically active products such as the drug L-dopa (3-hydroxy-L-tyrosine) (*13*).

2) Metal clusters that mimic the effect of a metal surface in the catalysis of complex organic reactions (*14*).

3) "Anchored" catalysts, which contain metal complexes bound to the surfaces of metal oxides or to polymers. These catalysts combine the virtues of homogeneous and heterogeneous catalysts (*15*).

These new concepts broaden the utility of homogeneous catalysis through application of our basic knowledge of organometallic chemistry. In turn, the applications research exposes deficiencies in our basic knowledge that challenge our understanding. The synergism of fundamental and applied research is characteristic of this area of chemistry.

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