

Homogeneous Catalysis

Industrial Applications and Implications

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FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are refereed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Papers published in ADVANCES IN CHEMISTRY SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

Catalysis, according to the dictionary, derives from the same classic root as catastrophe and implies destruction or ruin. It, therefore, does not seem worthwhile to pursue this definition except to excuse it by noting that the word catalysis was first used by Berzelius in 1836 in discussing decomposition. The fact that catalysis of decomposition should be recognized before that of synthesis is quite reasonable in view of our present understanding of catalysis. Thus, if catalyzed synthesis implies a three-body collision, it is far less probable than the simple collision of a decomposing species with a catalytic center. This line of reasoning leads to the heart of catalysis which is primarily a probabilistic or thermodynamic phenomenon. Hence, a catalyst is an entity that alters the rate of a reaction by becoming intimately involved in the reaction sequence but without becoming a product. It must, therefore, be close to the reactants and usually in a well-defined geometric relationship to them. Such a relationship implies an unfavorable entropic transition on forming the activated complex. This transition must be more than offset by enthalpic considerations—*i.e.*, bond making—in order for catalysis to be effected. Thus, a catalyst alters the free energy of activation by becoming part of an activated complex which could not form in its absence. Hence, catalysis makes available an otherwise unavailable reaction path. Furthermore, a true catalyst must, on collapse of the activated complex, be returned to a state in which it can function again. This frequently is not the same state in which the catalyst was introduced.

A *homogeneous* catalyst is one so dispersed in the reactants that no gross interface exists between it and the reactants. This does not necessarily mean that catalyst and reactant, when alone under reaction conditions, must be in the same physical state. However, when they are not, some agent—*e.g.*, a solvent—must be present to bring them into the same phase, but the solvent is often more than a simple mutualizing agent. It is part, at least a thermodynamic part, of the reactants, of the catalyst, of the products, and of the activated complex. The lattice of heterogeneous catalysts can thus be thought of as a special case of solvent effect. Broadly speaking, solvents themselves are often homogeneous catalysts. Sometimes, if a transition state is less polar than its initial state, the reaction can be catalyzed by the entropy gain arising from the liberation of solvent when the transition state forms.

Working in a liquid medium involves not only heat and mass transfer problems that are different from those of heterogeneously catalyzed gas phase reactions, but also introduces solvent recovery and pollution problems. Since the catalysts are expensive and fugitive (because they are molecularly dispersed), their conservation also becomes important. Finally, in trying to contain the system, whole new areas of corrosion control are opened. Probably the largest titanium fabrication job ever done was recently done for a plant based on a homogeneously catalyzed oxidation. These problems notwithstanding, it does seem that most "breakthrough type" industrial processes developed during the last decade are homogeneously catalyzed ones; although industrial applications of homogeneous catalysts are young, these catalysts often seem better understood, more predictable—and if we include enzymes—more versatile than heterogeneous catalysts.

This volume concentrates on reactions in solution. In the first chapter, Halpern reviews the kinds of substances which can be used as homogeneous catalysts and the ways in which they function. In Chapter 2, Bond contrasts phenomena of homogeneous catalysis with those of heterogeneous catalysis. Gessner examines some of the implications of replacing the gross interface between catalyst and reactant, of heterogeneous catalysis, with the interfaces of homogeneous catalysis. Although the phenomena he discusses usually fall in the realm of the engineer, they should be thoroughly understood by chemists whose research must be tempered by economic considerations. Using the open literature, Szonyi has documented some of the industrial applications of homogeneous catalysis. The remaining papers treat specific subjects in depth; they are roughly grouped in terms of oxidation, reduction, and finally polymerization.

The papers in this volume were sponsored by the Division of Industrial and Engineering Chemistry with the exception of Tsuji's paper, which was read before the Petroleum Division.

Sincere appreciation is extended to each of the authors and particularly to Jack Halpern, and to Dolores Olson, whose help in organizing this symposium was invaluable.

B. J. LUBEROFF

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November 1967

Homogeneous Catalysis by Coordination Compounds

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Two classes of catalytic reactions of transition metal ions and coordination compounds are considered—i.e., those involving catalytic activation of inert saturated molecules and those involving addition to unsaturated molecules. Among the factors contributing to the catalytic activity are the existence of relatively stable but highly reactive complexes of transition metals which exhibit reactivities closely related to those of the “reactive intermediates” of organic chemistry; the ability of transition metal atoms to stabilize by coordination various reaction intermediates as relatively stable, but reactive complexes; and the ability of a transition metal atom to assemble and to orient appropriately within the framework of its coordination shell, several components of a reaction. The underlying principles of coordination chemistry which govern catalytic activity are developed and illustrated.

Among the most significant developments in the field of catalysis in recent years have been the discovery and elucidation of various new, and often novel, catalytic reactions of transition metal ions and coordination compounds (13, 34). Examples of such reactions are the hydrogenation of olefins catalyzed by complexes of ruthenium (36), rhodium (61), cobalt (52), platinum (3, 26, 81), and other metals; the hydroformylation of olefins catalyzed by complexes of cobalt or rhodium (Oxo process) (6, 46, 62); the dimerization of ethylene (1, 23) and polymerization of dienes (15, 64, 65) catalyzed by complexes of rhodium; double-bond migration in olefins catalyzed by complexes of rhodium (24, 42), palladium (42), cobalt (67), platinum (3, 5, 26, 81), and other metals (27); the oxidation of olefins to aldehydes, ketones, and vinyl esters, catalyzed by palladium chloride (Wacker process) (47, 48, 49,

Table I. Some Homogeneous Reactions of Olefins

Reaction	Typical Catalysts		
	d^6	d^7	d^8
Hydrogenation	Ru^{II} $RuCl_6^{4-}$	Co^{II} $Co(CN)_5^{3-}$	Fe^0 $Fe(CO)_5$
Hydroformylation	*RuCl_2L_4		
Double-bond migration			$FeH(CO)_4^-$
Dimerization			
Oxidation			

* Active form of catalyst uncertain.

76, 79, 82); the hydration of acetylenes catalyzed by ruthenium chloride (38); and many others. The catalytic reactions listed in Table I are illustrative of the subject but fall short of conveying its full scope.

This article will be concerned with the mechanisms of some of these reactions and with some of the general principles that underly this relatively new and rapidly developing field of chemistry. The subject in question has attracted much interest in recent years both because of the novelty of much of the chemistry it reveals and because of its potential practical applications, exemplified by at least two processes (the Oxo and Wacker processes) which have already achieved considerable industrial importance. The possible relevance of many of the catalytic reactions in this field as model systems for related heterogeneous and enzymic process also lends interest to the subject although attempts to exploit this theme have thus far met with only limited success.

Structure and Reactivity of Transition Metal Complexes

The majority of catalytic reactions to be considered (Table I) involve as catalysts coordination compounds of the metals near the end of each transition series—notably the platinum groups comprising Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, and Pt. The electron configurations of the metal atoms in question are generally in the range d^6 to d^{10} , with the configuration d^8 being especially widely represented. Furthermore, the catalytic complexes of interest are generally (although not invariably) of the spin-paired or low-spin type—*i.e.*, complexes in which the ligand field splittings are sufficiently large so that the d electrons first fill up (with pairing if necessary) the most stable orbitals available to them before occupying those of higher energy. Because of the relevance of this subject to an understanding of the catalytic properties of interest, some aspects of the electronic structures and chemical reactivities of this general class of complexes will first be considered.

Catalyzed by Transition Metal Complexes $(L = PPh_3)$

d^8				
Co^I	Rh^I	Ir^I	Pd^{II}	Pt^{II}
$CoH(CO)_4$	$RhClL_3$	$IrI(CO)L_2$		$^aPt(SnCl_3)_5^{3-}$
$CoH(CO)_4$	$RhCl(CO)L_2$			
$CoH(CO)_4$	$RhCl_3(olefin)^{2-}$		$PdCl_4^{2-}$	$^aPt(SnCl_3)_5^{3-}$
	$RhCl_2(C_2H_4)_2^-$		$PdCl_4^{2-}$	

The stable coordination numbers of spin-paired complexes of transition metals range from 8 to 2 and exhibit a systematic inverse dependence on the number of d electrons of the metal atom, which is illustrated by Table II.

Table II. Coordination Numbers of Some Transition Metal Complexes

<i>Coordination Number</i>	<i>Examples</i>	<i>Electron Configuration</i>	<i>Total Number of Valence Electrons</i>
8	$Mo(CN)_8^{3-}$, $Mo(CN)_8^{4-}$	d^1, d^2	17, 18
6	$M(CN)_6^{3-}$ ($M=Cr, Mn, Fe, Co$)	d^3, d^4, d^5, d^6	15–18
5	$Co(CN)_5^{3-}$, $Ni(CN)_5^{3-}$	d^7, d^8	17, 18
4 (square planar)	$Ni(CN)_4^{2-}$	d^8	16
4 (tetrahedral)	$Cu(CN)_4^{3-}$, $Ni(CO)_4$	d^{10}	18
2	$Ag(CN)_2^-$, $Au(CN)_2^-$	d^{10}	14

This trend has its origin in the fact that in general, the higher the coordination number, the fewer the d electrons that can be accommodated in stable (bonding or near nonbonding) orbitals of the complex. Configurations in which the valence shell of the metal atom contains 18 electrons tend to be particularly stable (inert gas rule), whereas those configurations in which this number is exceeded are generally unstable. For an octahedral complex, for example, reference to the simplified molecular orbital diagram in Figure 1 reveals that the three stable t_{2g} orbitals (non- σ -bonding or possibly slightly π -bonding in the case of π -acceptor ligands such as CO or CN^-) can accommodate up to six d electrons, any additional electrons being forced to occupy the e_g^* orbitals which are strongly anti- σ -bonding in the complexes of interest. This generally results in the destabilization of the coordination number 6, in favor of a lower coordination number which permits a larger number of d electrons to be accommodated in stable orbitals (*see* Figure 2). Taking account of ligand π -orbitals leads to some modification of this molecular orbital

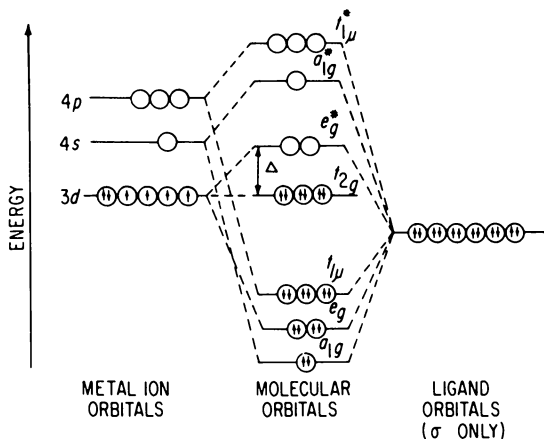
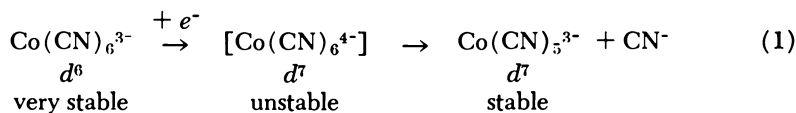


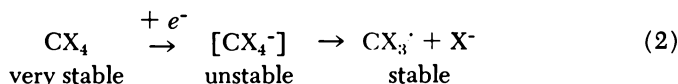
Figure 1. Molecular orbital (ligand field) diagram for octahedral complex (schematic)

scheme, but essentially the same conclusion is generally reached. (The symbols a_{1g} , e_g , and the like in the energy level diagrams in this article refer to the group theoretical designations of the orbital symmetries; starred orbitals, i.e., e_g^* , a_{1g}^* etc., are antibonding.)

The loss of a CN^- ligand when an electron is added to the very stable d^6 complex, $\text{Co}(\text{CN})_6^{3-}$, to give the pentacoordinated spin-paired cobalt(II) complex, $\text{Co}(\text{CN})_5^{3-}$, can be understood in these terms,

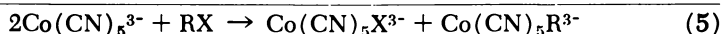
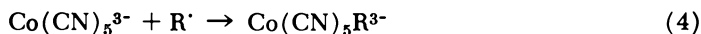
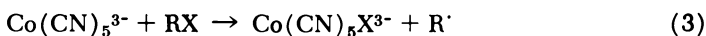


This process is analogous to that which accompanies the addition of an electron to a saturated carbon compound CX_4 (e.g., CCl_4), represented by the simplified molecular orbital diagram in Figure 3. Here, again, because all the stable bonding orbitals are filled, the extra electron is forced into a strongly antibonding orbital, with the result that the coordination number 4 is destabilized and a species of lower coordination number (a free radical or, in some cases, a carbanion depending on the relative electron affinities of X and CX_3) is generated,

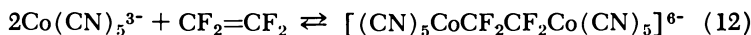
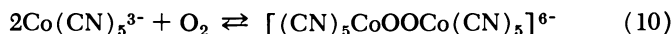
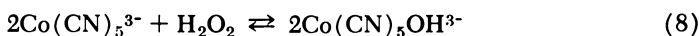
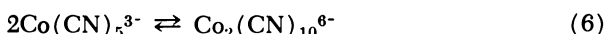


The purpose of developing this analogy is to provide a basis for the expectation that the chemical reactivities of $\text{Co}(\text{CN})_5^{3-}$ and related

pentacoordinated d^7 complexes will resemble those of typical organic free radicals, and indeed this is found to be the case. This is illustrated, for example, by the general reaction which $\text{Co}(\text{CN})_5^{3-}$ undergoes with organic halides to form stable organocobalt complexes (39, 40, 51, 54).



With respect to this and many other reactions such as Reactions 6–12,



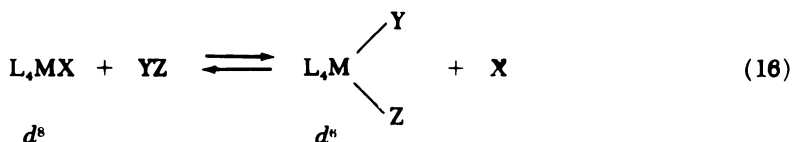
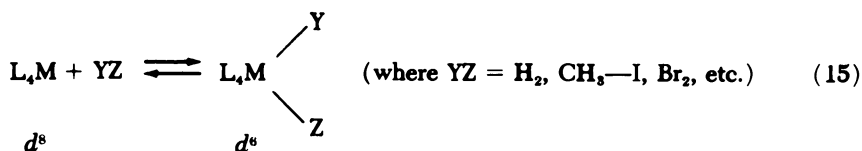
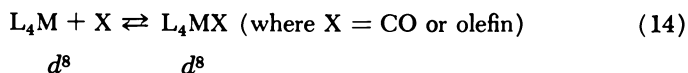
the reactivity of $\text{Co}(\text{CN})_5^{3-}$ resembles, to a remarkable degree, that of a typical reactive organic free radical. The basis for this marked parallelism is that in each case the characteristic reactivity pattern is dominated by the tendency to go from the open-shell configuration of the species in question to the more stable closed-shell configuration (CX_4 for the organic compound and the octahedral d^6 configuration for the coordination compound). The types of reactions which achieve this are the same in both cases. One such reaction which is of particular importance for the catalytic applications to be considered is that involving the reductive homolytic cleavage of covalent single bonds—*i.e.*,



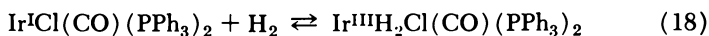
where $\text{YZ} = \text{H}-\text{H}$, $\text{HO}-\text{H}$, $\text{HO}-\text{OH}$, CH_3-I , etc.

The analogy developed above between pentacoordinated d^7 complexes and organic free radicals is capable of meaningful extension to coordination compounds of other electron configurations and coordination numbers (*see* Table III). Thus, similar reasoning leads to the expectation of similarities between the reactivity patterns of tetraordinated d^8 complexes and carbenes, pentacoordinated d^8 complexes and carbanions, and pentacoordinated d^6 complexes and carbonium ions. In each case the stoichiometries of the reactions which restore the stable closed-shell configurations are the same for both species; hence the similarity of reactivity patterns.

Many of the novel reactions of d^7 and d^8 complexes which contribute to the widespread roles of these complexes in homogeneous catalysis and which reflect reactivity patterns that are relatively unfamiliar in inorganic chemistry, are thus seen to be closely related to reactivity patterns that have in fact long been familiar in organic chemistry. For d^8 complexes in particular, the following general classes of reactions generally should be recognized:



The first two reactions—namely the addition to an unsaturated molecule and the insertion into a single bond—are also generally characteristic of carbenes. The last reaction is essentially a combination of the first two. The following specific reactions of $\text{Ir}^{\text{I}}\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (84, 87), and $\text{Ru}^0(\text{CO})_3(\text{PPh}_3)_2$ (21), are illustrative.



Catalytic Activation of Hydrogen and Other Saturated Molecules

The ability to catalyze certain reactions of molecular hydrogen homogeneously in solution has been demonstrated for many transition metal ions and complexes (34)—among them complexes of Cu^{II} , Cu^{I} , Ag^{I} , Hg^{II} , Hg^{I} , Co^{I} , Co^{II} , Pd^{II} , Pt^{II} , Rh^{I} , Rh^{III} , Ru^{II} , Ru^{III} , and Ir^{I} . In each case it appears that H_2 is split by the catalyst with the formation of a reactive transition metal hydride complex (which may or may not be detected) as an intermediate. Three distinct mechanisms by which this can occur have been recognized (34), which are exemplified by the following reactions.

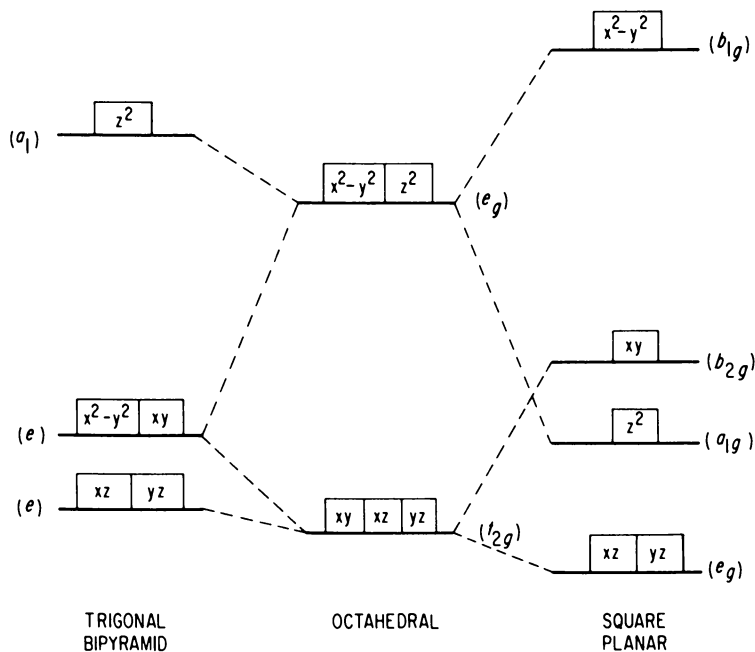
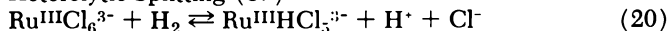
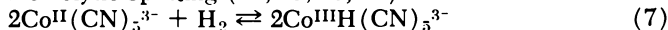


Figure 2. Energy level diagrams depicting orbital splitting in complexes of various symmetries. Only the orbitals involved in accommodating the d electrons of the metal are depicted. Note that the octahedral configuration with only three stable (t_{2g}) orbitals is most favorable for accommodating six d electrons, whereas the two configurations of lower coordination number, each with four stable orbitals, are more favorable for accommodating seven or eight d electrons. The orbital symmetries are described by the symbols xz , yz , x^2-y^2 . . . , as well as by the group theoretical designations a , e , t_{2g}

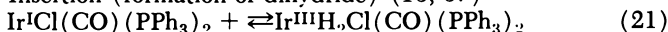
I. Heterolytic Splitting (37)



II. Homolytic Splitting (11, 29, 50, 52)



III. Insertion (formation of dihydride) (18, 87)

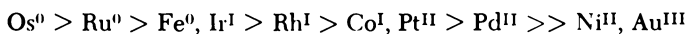


The assignment of oxidation numbers to the metal atoms in these and other hydride complexes is based on the generally accepted convention which assigns the oxidation number (-1) to the hydride ligand.

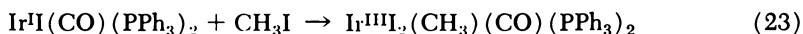
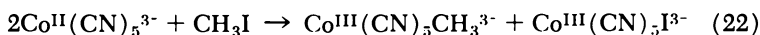
The characteristic reactivities of hexa-, penta- and tetraordinated complexes exemplified by these reactions follow readily from the general principles developed above. The first mechanism (heterolytic splitting), which is of widespread occurrence, involves essentially a substitutional

process (replacement of a chloride ligand by a hydride derived from H_2) without change in the formal oxidation number of the metal. Reactivity is thus governed by the substitution lability of the complex, by the stability of the hydride formed, and by the presence of a suitable base (which may be the solvent or the displaced ligand) to stabilize the released proton (41).

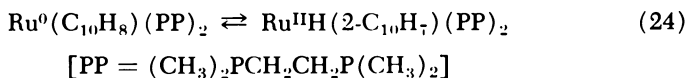
In the other two mechanisms (homolytic splitting and insertion) hydride formation is accompanied by formal oxidation of the metal, and reactivity is closely linked to the susceptibility of the latter to oxidation. Thus, the high reactivity of $Co(CN)_5^{3-}$ toward H_2 , compared with that of $Co(CNCH_3)^{2-}$, reflects the tendency of CN^- to stabilize preferentially the higher oxidation state, and $CNCH_3$ the lower oxidation state, of cobalt. For square planar d^8 complexes the expected order of the tendency toward oxidation, and hence of reactivity toward H_2 , is (subject to some modification by ligand variation),



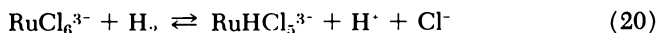
Analogous mechanisms are applicable to the splitting of other saturated molecules and are realized in the following examples involving the reductive cleavage of carbon-halogen bonds (39, 40, 45, 51, 54).



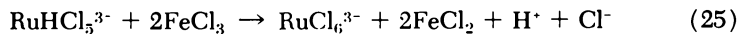
In principle it should also be possible to accomplish the reductive cleavage of C—H and C—C bonds by similar mechanisms, but this has not yet been realized except in a few special cases such as the tautomeric equilibrium described by Chatt and Davidson (17) (Reaction 24).



The reactive nature of the hydrido complexes formed in many of the above reactions permits them to function as intermediates in homogeneous catalytic hydrogenation reactions. Thus, the reversible reaction,



provides a mechanism for the homogeneous exchange of H_2 with D_2O (37) and for the homogeneous catalytic oxidation of H_2 by $FeCl_3$ since the latter oxidizes $RuHCl_5^{3-}$ rapidly (43) according to Reaction 25.

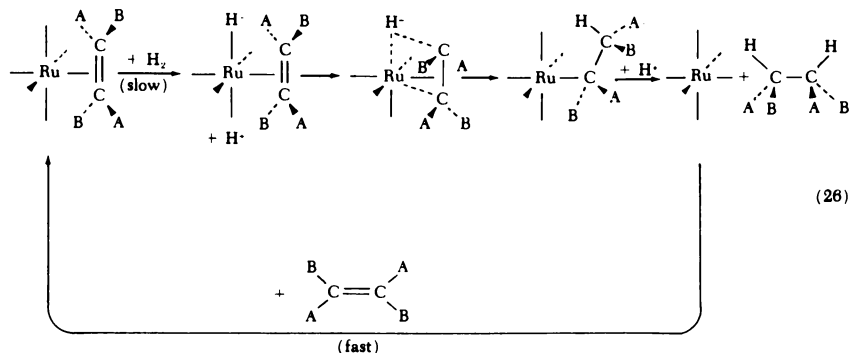


The reactivity of the hydride intermediate in such reactions is generally high so that its formation is the rate-determining step in the over-all catalytic reaction.

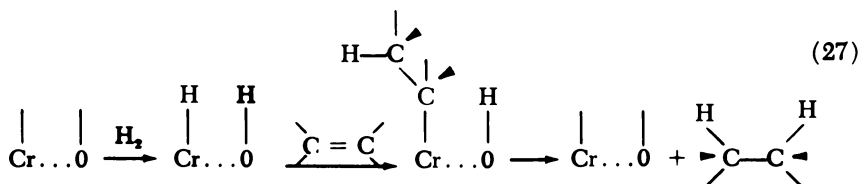
Catalytic Hydrogenation of Olefinic Compounds

In favorable cases, homogeneous catalytic hydrogenation of organic substrates such as olefins also may be achieved by transfer of hydrogen from the hydrido-transition metal complex. The following examples, all discovered within the last few years, illustrate how this can be realized for each of the three mechanisms of splitting of hydrogen (heterolytic, homolytic, and insertion) described above.

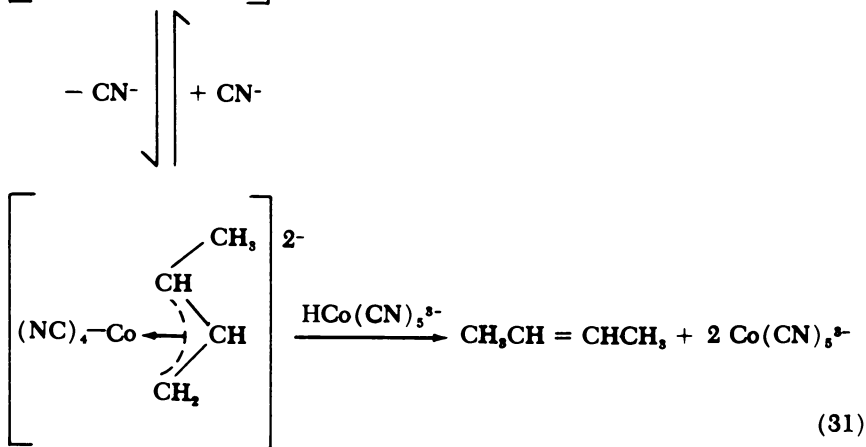
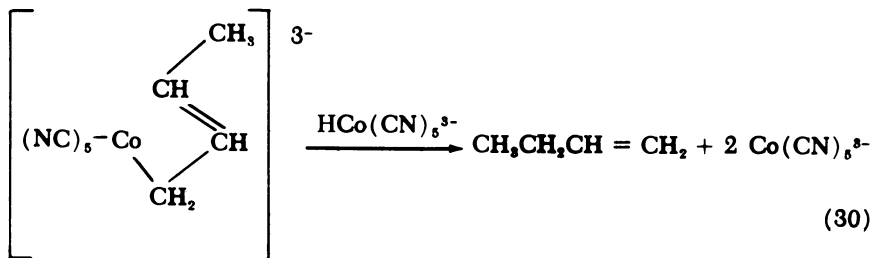
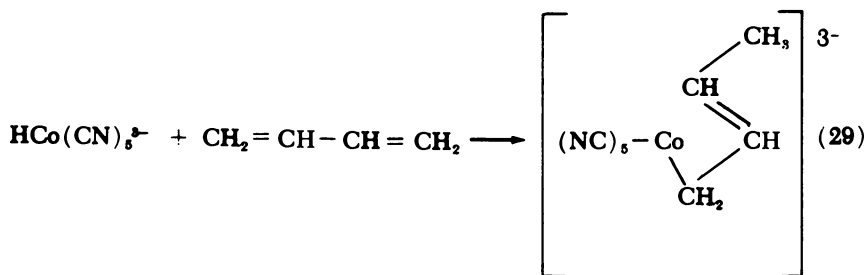
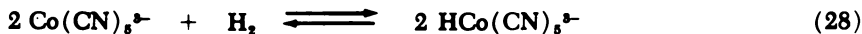
Ruthenium(II) Chloride. The homogeneous catalysis of the hydrogenation of fumaric acid in aqueous solution by ruthenium(II) chloride has been interpreted (36) in terms of the following mechanism in which the heterolytic splitting of H_2 by a Ru^{II} -olefin complex is the rate-determining step.



This mechanism has many features in common with that proposed by Burwell (12) for the heterogeneous catalytic hydrogenation on a chromia gel catalyst (Reaction 27).



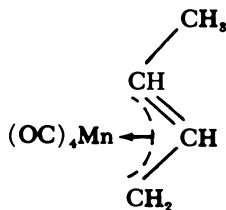
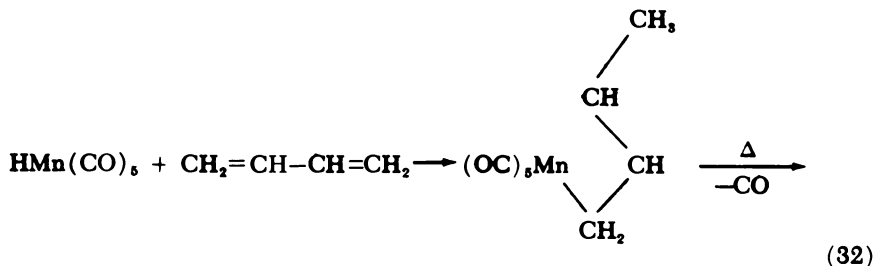
Pentacyanocobaltate(II). The homogeneous catalytic hydrogenation of an olefin by a mechanism involving the homolytic splitting of hydrogen is illustrated by the $Co(CN)_5^{3-}$ -catalyzed hydrogenation of butadiene in aqueous solution. Detailed studies by Kwiatek and his co-workers (51, 52, 54) suggest that this reaction proceeds by the following mechanism.



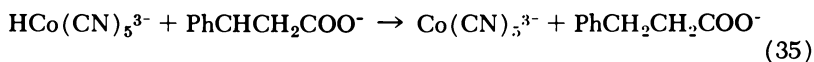
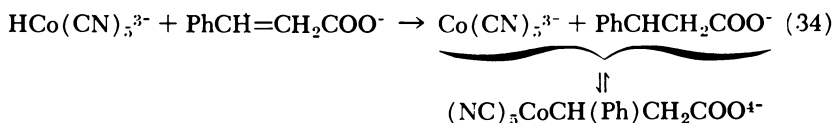
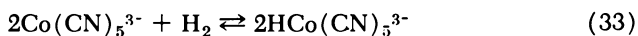
The CN^- -dependent equilibrium between the σ - and π -allyl intermediates accounts for the observation that hydrogenation at high CN^- concentrations yields predominantly 1-butene and at low CN^- concentrations predominantly *trans*-2-butene.

Some features of the above mechanism find close parallels in the reaction (58) of $\text{HMn}(\text{CO})_5$ (isoelectronic with $\text{HCo}(\text{CN})_5^{3-}$) with butadiene—*i.e.*, Reaction 32.

$\text{Co}(\text{CN})_5^{3-}$ also catalyzes the hydrogenation of other conjugated olefins, among them styrene and α,β -unsaturated aldehydes and acids.



A mechanism, somewhat different from that for the hydrogenation of butadiene, has been proposed (77) for the hydrogenation of cinnamate—*i.e.*,



Kwiatek and Seyler (53) consider these and other relevant aspects of catalytic hydrogenation and hydrogenolysis by pentacyanocobaltate(II) in greater detail.

Tris(triphenylphosphine)chlororhodium(I). The homogenous catalysis of the hydrogenation of ethylene and other olefins by $\text{RhCl}(\text{PPh}_3)_3$, recently discovered by Wilkinson and co-workers (61), probably involves a dihydride intermediate. A plausible mechanism for this reaction, involving steps of the type already described, is shown in Reaction 36.

Numerous other examples of homogeneous catalytic hydrogenation of olefins, dienes, acetylenes, aldehydes, and aromatic compounds have been reported, involving a variety of catalysts—among them $\text{PtCl}_2\text{-SnCl}_2$ (26); $\text{PtCl}_2(\text{PPh}_3)_2\text{-SnCl}_2$ (3, 81); $\text{IrI}(\text{CO})(\text{PPh}_3)_2$ (86); $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ (85); $\text{RuCl}_2(\text{PPh}_3)_4$ (31); $\text{HCo}(\text{CO})_4$ (56, 57); $\text{Fe}(\text{CO})_5$, or $\text{Fe}(\text{CO})_3(\text{diene})$ (32, 33, 60); $\text{Ni}(\text{OOCR})_2\text{-Al}(\text{C}_2\text{H}_5)_3$ (55, 78), and others. Not uncommonly, such catalysts exhibit a higher degree of selectivity than can be realized with heterogeneous catalysts,

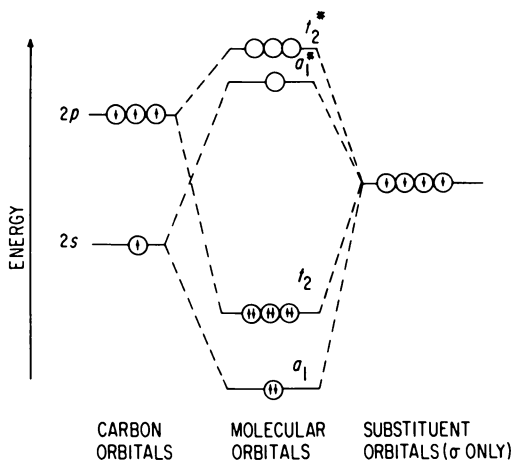
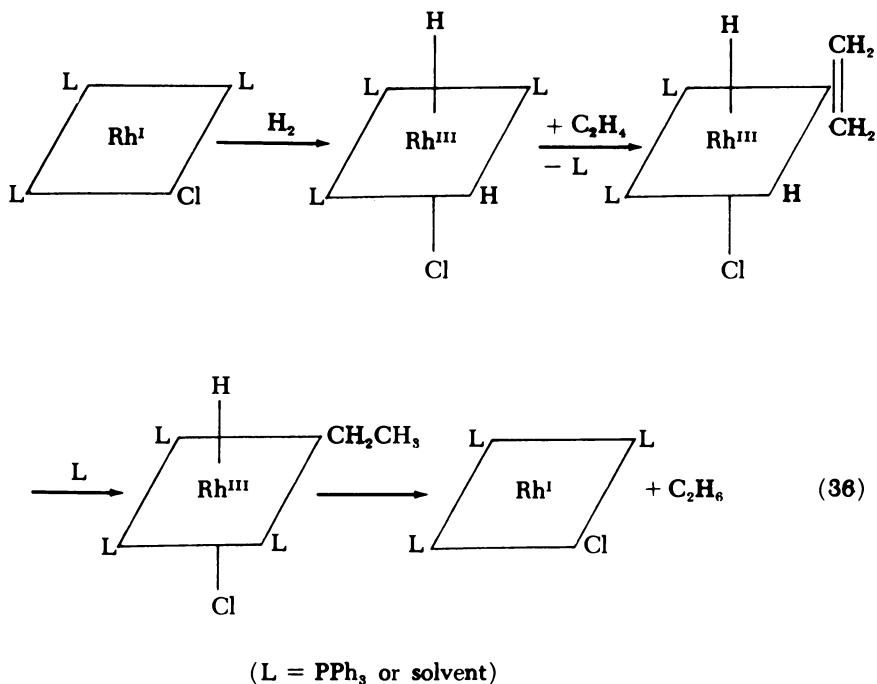


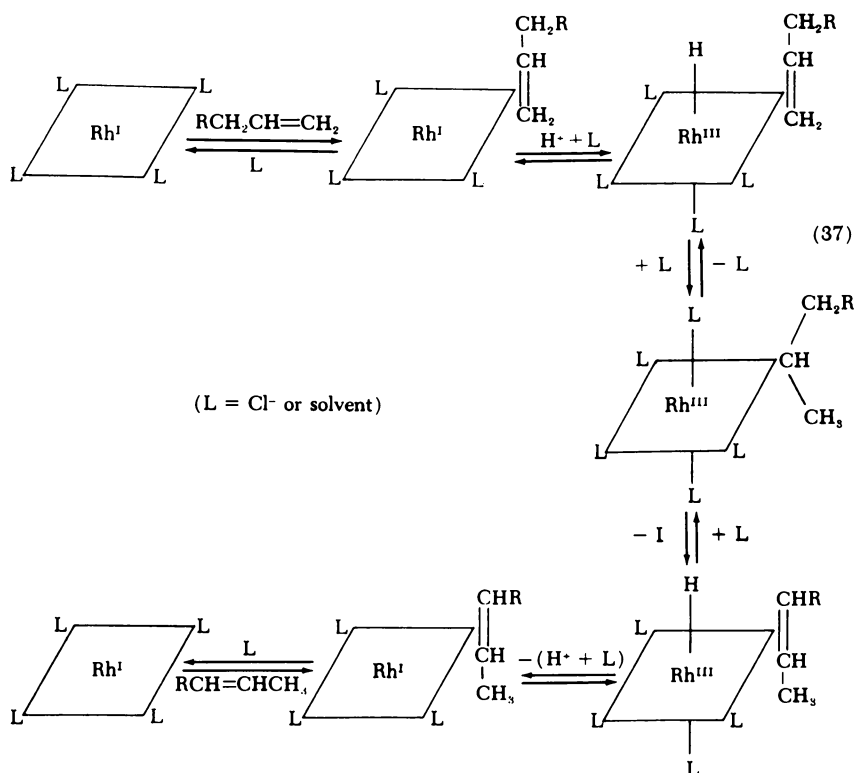
Figure 3. Molecular orbital diagram of a tetrahedral carbon compound (schematic)

as exemplified by the several catalysts ($\text{Co}(\text{CN})_5^{3-}$; $\text{PtCl}_2(\text{PPh}_3)_2$ – SnCl_2 , etc.) which effect the hydrogenation of dienes exclusively to monoenes. In many of the above cases, the precise constitution of the catalyst and

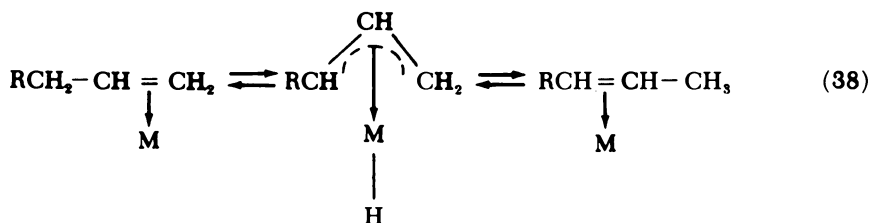
the mechanism of catalytic hydrogenation are still incompletely understood and remain to be elucidated.

Isomerization of Olefins

Complexes of many transition metals including cobalt, rhodium, iridium, iron, nickel, palladium, and platinum have been found to catalyze double-bond migration in terminal olefins. Evidence for a mechanism of the following type, which is probably also applicable to some of the other catalysts, has been obtained by Cramer (24, 27) for the rhodium chloride-catalyzed reaction (Reaction 37).



An alternative mechanism of olefin isomerization, involving rearrangement through an intermediate π -allyl hydride—*i.e.*, Reaction 38, has also been proposed (28, 66) and may operate in the case of some of the other catalysts.

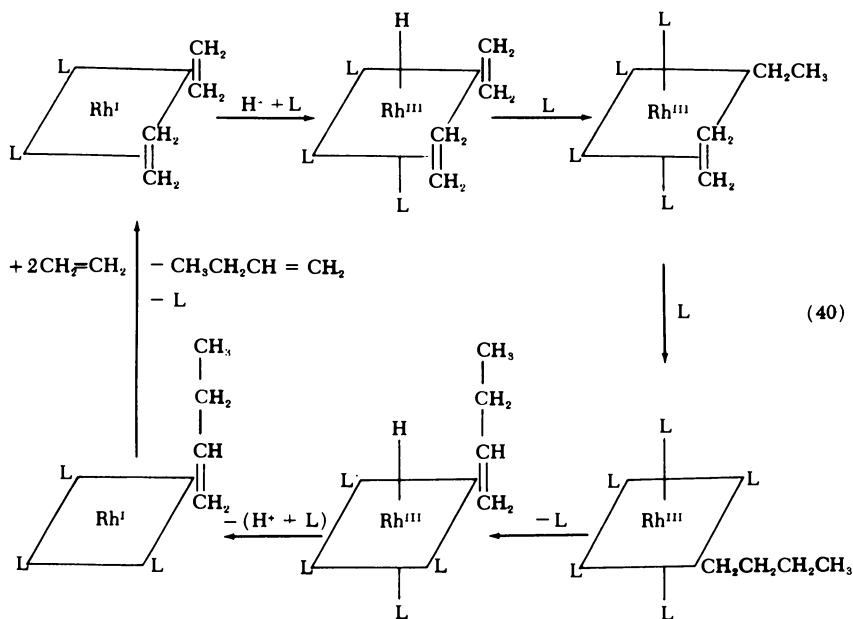


Dimerization and Polymerization of Olefins

Another olefin reaction catalyzed by rhodium chloride is the dimerization of ethylene to 1-butene (1),



A detailed study of this reaction (23) suggests the following mechanism which is closely related to the earlier mechanism of olefin isomerization.



Rhodium chloride also catalyzes a number of other olefin-to-olefin addition reactions, including the addition of ethylene to dienes (1, 25),

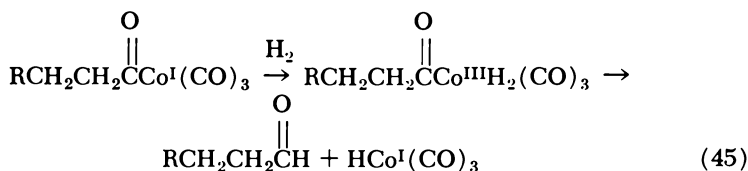
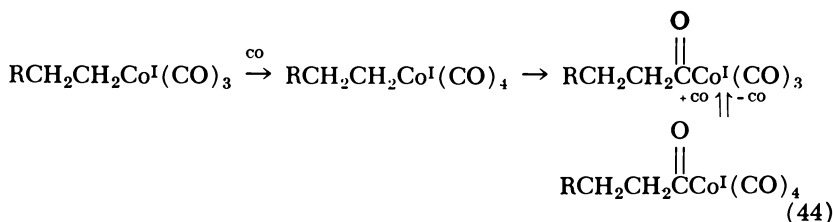
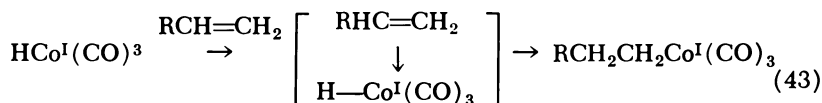
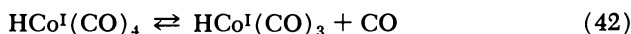
the dimerization of 1,3-dienes to linear trienes and the highly stereospecific polymerization of dienes (15, 64, 65). The mechanisms of these reactions remain to be fully elucidated.

Hydroformylation of Olefins

The addition of H₂ and CO to olefins to form aldehydes—*i.e.*,



in the presence of HCo(CO)₄ as catalyst, constitutes a reaction of great scientific and practical interest. The results of many investigations on this reaction, including the observation of inhibition by CO, are plausibly interpreted in terms of the following mechanism suggested by Heck and Breslow (6, 46).



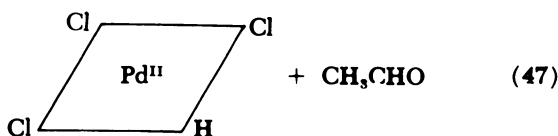
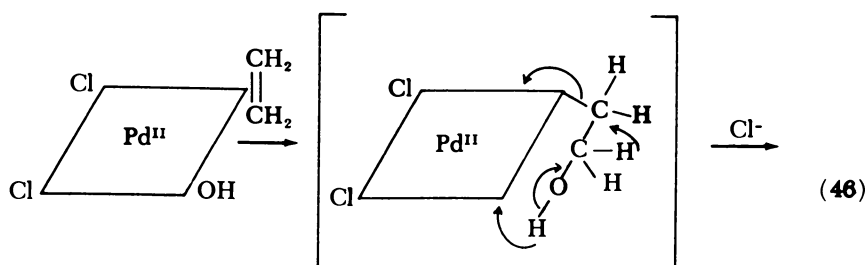
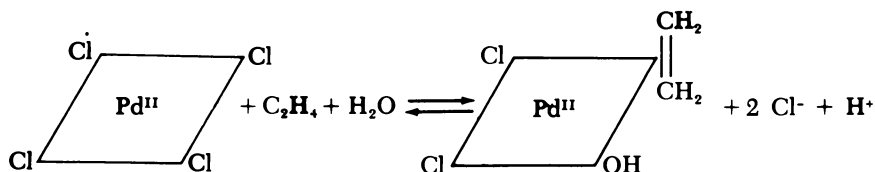
Extensions of this mechanism also may account for the hydrogenations of olefins and of aldehydes which generally accompany hydroformylation (56, 57).

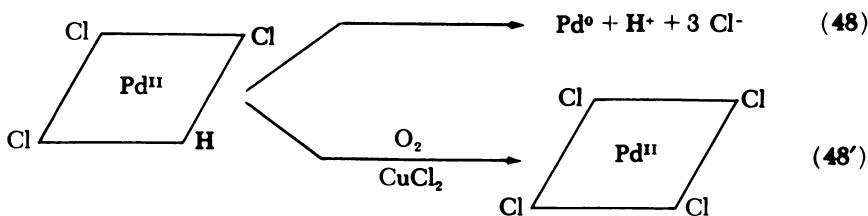
Many other addition reactions of olefins, dienes, and acetylenes are known, which are catalyzed by metal carbonyls including Ni(CO)₄, Fe(CO)₅, and Co₂(CO)₈ and by carbonyl derivatives such as hydrocarbons or phosphine-substituted carbonyls. Among these are the hydrocarboxylation, hydroesterification, and hydrocyanation of olefins; the synthesis of hydroquinones from acetylenes, carbon monoxide, and water;

the cyclooligomerization of acetylene to benzene, cyclooctatetraene, etc.; the carbonylation of acetylenes and olefins to acids, etc. (70). The mechanisms of most of these reactions remain to be elucidated.

Oxidation of Olefins and Related Substrates

The oxidation of ethylene in aqueous solution by palladium(II) chloride, or by oxygen in the presence of palladium(II) chloride as catalyst, is a reaction of considerable novelty and great practical interest (Wacker process). It is unique in that ethylene is oxidized exclusively to acetaldehyde (and other olefins to ketones), whereas oxidation of olefins by other metal ions such as thallium(III) and lead(IV) generally yields glycol derivatives as well as carbonyl products. The mechanism of this interesting reaction has not been fully elucidated, but the results of detailed equilibrium, kinetic, and isotopic tracer studies by several workers including Smidt (79) in Germany, Moiseev (82) in Russia and Henry (47, 48, 49) in the United States, are plausibly accommodated by the following scheme.



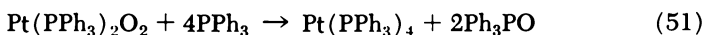
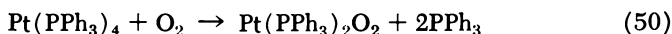


In the presence of oxygen and cupric chloride the reduction of palladium (II) is prevented so that a homogeneous catalytic cycle is established in which PdCl_4^{2-} and CuCl_2 serve as catalysts for the reaction,



The corresponding oxidations of substituted olefins yield ketones, while oxidation in acetic acid medium yields vinyl acetates. Various alternative suggestions concerning the mechanisms of these reactions are considered in the papers by Henry (47) and by Schulz (76) in this volume.

The ability of certain transition metal compounds—*e.g.*, $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (83) and $\text{Pt}(\text{PPh}_3)_4$ (22, 35, 80, 90) to form complexes with molecular oxygen (in some cases reversibly, in a manner analogous to that of haemoglobin) has aroused interest in the possible effectiveness of such compounds as oxidation catalysts. This possibility appears to have been realized in at least one case—namely the catalysis by $\text{Pt}(\text{PPh}_3)_4$ of the oxidation of triphenylphosphine (22, 35, 80, 90). A plausible mechanism which accommodates the essential features of this reaction is,



Further possibilities for catalytic oxidation are realized in the well-known catalysis of the autoxidation of hydrocarbons and other substrates by salts of transition metals such as copper, cobalt, and manganese which exhibit more than one stable oxidation state and which catalyze oxidation through free radical chain mechanisms (16).

Other Catalytic Reactions and General Observations

Many of the areas of chemistry touched upon in this article are of comparatively recent origin, and nearly all of the reactions described have been discovered and elucidated within the past decade. The selection of examples has been conditioned to some degree by the author's own interests as well as by emphasis on those reactions whose mechanisms are best, although not always fully understood. Consequently, the reactions

Table III. Species of Related Configurations and Organic Species

<i>Species</i>	<i>Coordination Number^a</i>	<i>Nonbonding Electrons</i>	<i>Characteristic Reactions</i>
Saturated molecule (R_3C-X)	4	0	Substitution
Free radical ($R_3C\cdot$)	3	1	Dimerization Abstraction Addition
Carbene ($R_2C:$)	2	2	Addition Insertion
Carbonium ion (R_3C^+)	3	0	Addition of nucleophile
Carbanion (R_3C^-)	3	2	Addition of electrophile

^a Intermediate in S_N1 substitution reactions of $Co(CN)_5OH_2^{2-}$.

^b Note that the change in coordination number and in the number of nonbonding electrons in going from one species to the next is the same in each series. This results

described are illustrative of the field of homogeneous catalysis by coordination compounds but fail to do justice either to its scope or variety. Among the many other relevant topics not considered are catalysis of electron-transfer and redox (including autoxidation) reactions by metal ions of variable oxidation state (16); nucleophilic catalysis of decarboxylation and hydrolysis reactions owing to activation of the (coordinated) reactant by the positive charge of the metal ion (4); the extensive array of cyclooligomerization, polymerization, and carbonylation reactions of acetylenes and olefins catalyzed by nickel carbonyl and its derivatives (Repe chemistry) (69); the cyclotrimerization of butadiene and related reactions catalyzed by π -complexes of nickel, recently discovered by Wilke (89); the polymerization of olefins by soluble catalysts of the Ziegler-Natta type (7, 8, 63); the catalytic hydration of acetylenes (38); and numerous other catalytic reactions. The mechanisms of many of these are still incompletely understood.

Several factors contribute the great catalytic versatility of transition metal complexes in these and related reactions. Among these are the factors listed below.

(1) The existence of relatively stable but highly reactive complexes of transition metals which, by virtue of their electron configurations and

Reactivities in Organic and Coordination Chemistry*Transition Metal Counterpart*

<i>Coordination Number^b</i>	<i>Nonbonding Electrons</i>	<i>Examples</i>	<i>Reactions</i>
6	6	RhCl_6^{3-}	$\text{RhCl}_6^{3-} + \text{H}_2\text{O} \rightleftharpoons \text{RhCl}_5\text{OH}_2^{2-} + \text{Cl}^-$ $\text{RhCl}_6^{3-} + \text{H}_2 \rightleftharpoons \text{RhHCl}_5^{3-} + \text{HCl}$
5	7	$\text{Co}(\text{CN})_5^{3-}$	$2\text{Co}(\text{CN})_5^{3-} \rightleftharpoons \text{Co}_2(\text{CN})_{10}^{6-}$ $\text{Co}(\text{CN})_5^{3-} + \text{CH}_3\text{I} \rightarrow \text{Co}(\text{CN})_5\text{I}^{3-} + \text{CH}_3\cdot$ $2\text{Co}(\text{CN})_5^{3-} + \text{CH}\equiv\text{CH} \rightarrow (\text{NC})_5\text{CoCH}=\text{CHCo}(\text{CN})_5^{6-}$
4	8	$\text{IrI}(\text{CO})(\text{PPh}_3)_2$	$\text{IrI}(\text{CO})(\text{PPh}_3)_2 + \text{C}_2\text{H}_4 \rightleftharpoons \text{IrI}(\text{CO})(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ $\text{IrI}(\text{CO})(\text{PPh}_3)_2 + \text{H}_2 \rightleftharpoons \text{IrH}_2\text{I}(\text{CO})(\text{PPh}_3)_2$
5	6	$^o\text{Co}(\text{CN})_5^{2-}$	$\text{Co}(\text{CN})_5^{2-} + \text{I}^- \rightleftharpoons \text{Co}(\text{CN})_5\text{I}^{3-}$
5	8	$\text{Mn}(\text{CO})_5^-$	$\text{Mn}(\text{CO})_5^- + \text{H}^+ \rightleftharpoons \text{Mn}(\text{CO})_5\text{H}$

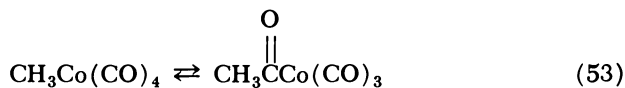
in correspondingly similar changes in the reactivity patterns of the two series of compounds since the reactivity pattern in each case is dominated by the tendency to return to the stable closed-shell configuration of the first member of the series.

coordination numbers, exhibit reactivities closely related to those of the "reactive intermediates" of organic chemistry namely, free radicals, carbenes, and carbanions. As noted earlier, the prominence of d^7 and, particularly, of d^8 complexes in homogeneous catalysis is related to this theme.

(2) The ability of transition metals to stabilize a variety of otherwise unstable reaction intermediates through coordination as ligands in relatively stable but reactive complexes. Among these are σ -bonded ligands such as hydride and alkyl groups and π -bonded species such as allyl, cyclobutadiene, etc. Reaction mechanisms involving such intermediates, which are prohibitively endothermic in the absence of catalysts, are thus rendered feasible. The ability of certain complexes to dissociate molecular hydrogen and other stable molecules is related to this property.

(3) The ability of certain transition metal complexes to promote rearrangements within their coordination shells by virtue of the existence of two or more stable configurations of the complex differing in coordination number and/or oxidation number. An example of this effect, which is probably of widespread importance in catalytic reactions, is the existence of two stable configurations, corresponding to the coordination

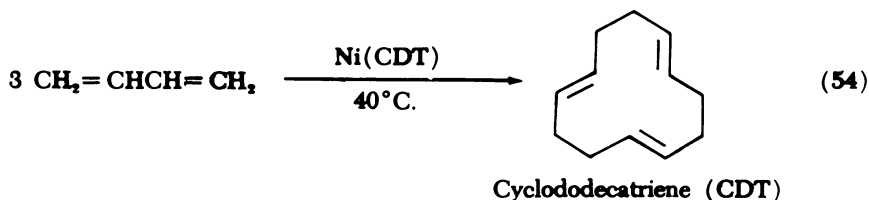
numbers 4 and 5, for d^8 complexes. This facilitates such rearrangements as the proposed step in the hydroformylation reaction:



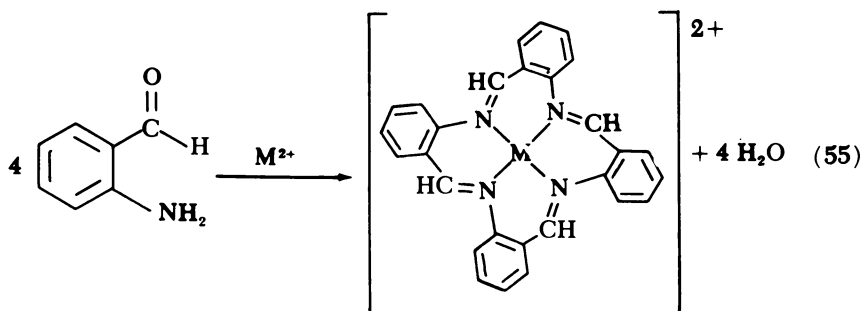
and related "insertion" rearrangements which are believed to play important roles in many catalytic addition reactions.

(4) The ability of a transition metal atom to assemble and/or to orient within the framework of its coordination shell several components of a reaction (template effect). Some examples of reactions in which this effect is probably important are:

(1) the catalysis of the cyclotrimerization of butadiene to 1,5,9-cyclododecatriene (CDT) by cyclododecatrienenickel(0), reported by Wilke (89),

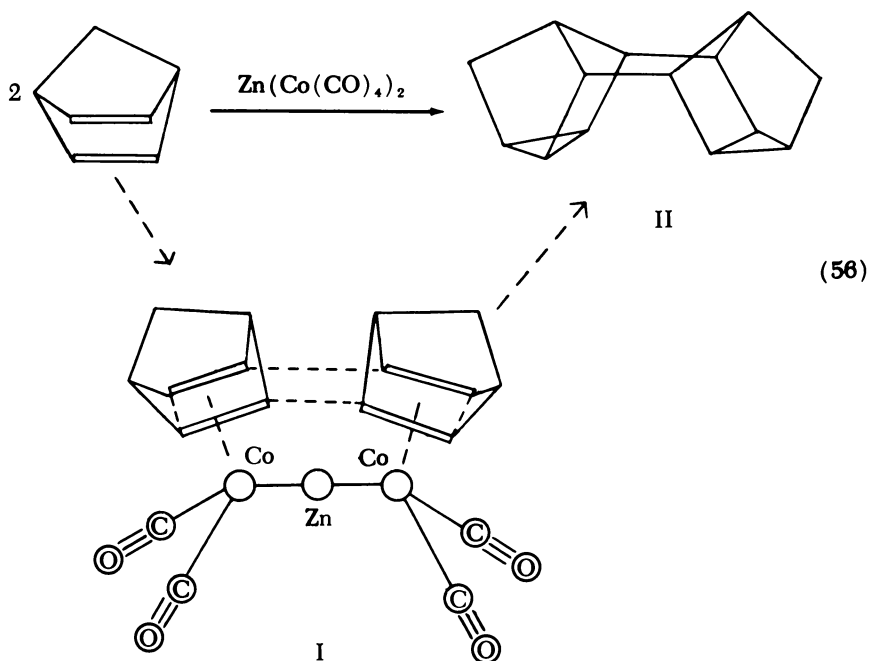


(2) the metal-ion promoted synthesis of macrocyclic ligands, such as the reaction described by Melson and Busch (14, 59).

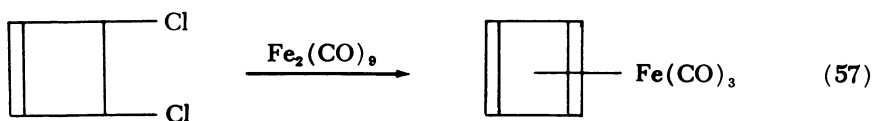


(M = Cu, Ni, or Co)

(3) the stereospecific dimerization of norbornadiene to "Binor-S" (II) by the binuclear catalyst, $\text{Zn}[\text{Co}(\text{CO})_4]_2$ via the proposed intermediate (I), described by Schrauzer *et al.* (71),



Also closely related to this theme are certain reactions involving the metal ion-promoted synthesis of (otherwise unstable) coordinated ligands such as cyclobutadiene, which are stabilized through coordination —*e.g.*, the reaction described by Emerson, Watts, and Pettit (30),



Current and Future Trends

Homogeneous catalysis by coordination compounds continues to be an active and fruitful field of research. Currently important lines of research are concerned particularly with the search for and discovery of new catalytic reactions, the more detailed elucidation of the mechanisms of the many reactions which are as yet incompletely understood, and the discovery and characterization of new coordination compounds, often containing novel ligands, which are of interest as potential catalysts or catalytic intermediates, or whose study might contribute to a better understanding of related catalysts or catalytic intermediates. Recent

progress in all three of these areas has been impressive, and there is every indication that the present pace of research and discovery will continue for some years to come.

Many important problems, both of understanding and of application, remain to be solved. Among these is attaining objectives such as the homogeneous catalytic activation of saturated hydrocarbons and the catalytic fixation of molecular nitrogen, which still await major breakthroughs. The hope that attainment of at least the latter objective is at hand is reinforced by the recent success of Vol'pin and Shur (88) in fixing nitrogen stoichiometrically with transition metal complexes of the Ziegler-Natta type, as well as the recent discovery of several transition metal complexes containing coordinated nitrogen—*i.e.*, $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$ (2), $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$ (19, 20), $\text{Co}(\text{PPh}_3)_3\text{N}_2$ (91, 92) and $\text{CoH}(\text{PPh}_3)_3\text{N}_2$ (68). Although several of these complexes have been prepared from molecular nitrogen, the effectiveness of such complexes in *catalytic* nitrogen fixation remains to be demonstrated.

There is also some reason to hope and to expect, although the complexity and difficulty of this objective should not be underestimated, that the detailed understanding which is emerging of catalytic mechanisms in these relatively simple homogeneous systems will ultimately make a meaningful contribution to our understanding of related catalytic phenomena in heterogeneous and enzymic systems. In specific instances this already has occurred, one such instance being the insight that has been gained into certain aspects of vitamin B₁₂ chemistry through studies on related cobalt complexes such as the carbonyl (44), cyanide (37, 39, 40, 51, 54) and dimethylglyoxime (72, 73, 74, 75) complexes.

Acknowledgment

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Homogeneous and Heterogeneous Catalysis by Noble Metals

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Many of the significant reactions of unsaturated hydrocarbons (hydrogenation, isomerization, carbonylation, oxidation, polymerization) are catalyzed heterogeneously by metals in or near Group VIII or homogeneously by salts and complexes of these elements. Those reactions effected in both systems are discussed in terms of probable common intermediates; anomalies, where they occur, are ascribed either to the ability of surfaces to form intermediate species which cannot be stabilized by single metal atoms or to the ability of the latter to coordinate simultaneously more than one hydrocarbon molecule.

Serious study of heterogeneous catalysis has proceeded with ever-increasing intensity for some 70 years; by contrast, serious study of homogeneous catalysis by transition metal salts and complexes began only a decade ago. It is scarcely surprising therefore that heterogeneous catalysis has achieved a cardinal position in chemical industry, whereas the application of homogeneous catalysis (although not slow to start) has yet to achieve a similar prominence. Among the considerations discussed in this volume is the question of whether homogeneous catalysis may in a generation have relegated many heterogeneous catalytic operations to the lumber-rooms of chemical technology. Some thoughts on this are presented below.

Although heterogeneous catalysis has a good head start in its applications and usefulness because of its chronological advantage, theoretical understanding of its phenomena has not progressed as rapidly. It is no exaggeration that some homogeneously catalyzed reactions are understood as well after five years study as some heterogeneously catalyzed

ones are after 50. The reasons for this are not hard to find: the application of modern physical methods (particularly spectroscopic ones) to detecting intermediates, and the simplicity and reproducibility of homogeneous systems, permits the specification of reaction mechanisms with a facility which is the envy of those who are restrained to multiphase systems. Those so restrained have hoped, not unreasonably, that the rapid advances we are witnessing in understanding homogeneous mechanisms will assist the resolution of some of the seemingly intractable problems in the heterogeneous field. One of the objects of this paper will be to explore how well founded this hope is.

Hence, there are two aspects to consider—the theoretical and the applied. Consideration of the former logically precedes the latter.

Descriptive Chemistry of Catalysis

It is now clearly recognized that elements exhibiting the phenomenon of catalysis, either in the zero-valent (*i.e.*, metallic) or some other oxidation state, occur in or adjacent to the transition series. For all practical purposes we may confine our attention to the elements and compounds of Groups VI, VII, VIII and IB of the Periodic Table; by doing so of course we ignore some technically important acidic and other oxides (*e.g.*, alumina, silica, zinc oxide) which are not within the terms of reference here.

If we merely compare the heterogeneous catalytic properties of the elements of these groups with the homogeneous catalytic activity shown by solutions of their salts and complexes, we find a broad and striking correlation—*i.e.*, in both systems the catalytic phenomena are most apparent in Group VIII. We therefore direct our attention to the elements of Group VIII and their compounds, with only passing reference to elements of other Groups.

Heterogeneous Catalytic Properties of the Group VIII Metals

In addition to their ability to atomize molecular hydrogen (an ability widely shared by other *d* metals although not to the same extent by *sp* metals), the Group VIII metals are outstanding in their propensity to catalyze the hydrogenation of unsaturated functions, for example $C\equiv C$, $C=C$, $C=O$, $C\equiv N$, $N\equiv N$, $O=O$, NO_2 etc. (5). Between the metals there are however considerable differences in activity, selectivity, and stereospecificity shown; thus, all the Group VIII metals catalyze the hydrogenation of oxygen, olefins, and acetylenes, while the facility to synthesize ammonia is limited to the Fe, Ru, Os Group. Hydrogenolysis of carbon-halogen bonds and, under more vigorous conditions, of $C-C$ bonds is also catalyzed by these metals. A practical difficulty often encountered

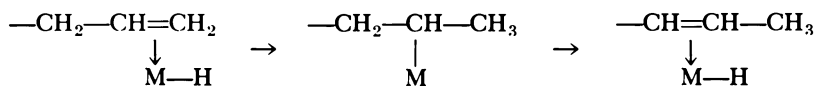
is the lack of specificity shown by heterogeneous catalysts; for example, supported palladium catalysts will convert a chloronitrobenzene to a mixture of chloroaniline and aniline, and undesirable selective poisoning procedures often must be adopted to obtain the desired result.

Some of the Group VIII metals have uses as oxidation catalysts (5). All except platinum do however tend to oxidize under vigorous conditions, such as are used in ammonia oxidation and the Andrussov process, for which only platinum and its alloys are acceptable catalysts. Under milder conditions both platinum and palladium have somewhat limited applications in liquid-phase oxidation processes, as for example in the carbohydrate field.

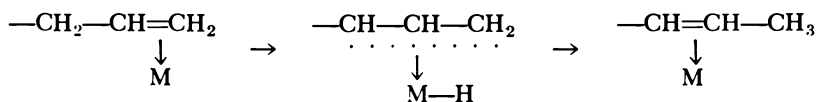
Homogeneous Catalytic Properties of Group VIII Salts and Complexes

The main areas which have commanded attention to the present are olefin isomerization, hydrogenation, oxidation, carbonylation, and polymerization.

Olefin isomerization has been widely studied, mainly because it is a convenient tool for unravelling basic mechanisms involved in the interaction of olefins with metal atoms (10). The reaction is catalyzed by cobalt hydrocarbonyl, iron pentacarbonyl, rhodium chloride, palladium chloride, the platinum-tin complex, and by several phosphine complexes; a review of this field has recently been published (12). Two types of mechanism have been visualized for this reaction. The first involves the preformation of a metal-hydrogen bond into which the olefin (probably already coordinated) inserts itself with the formation of a σ -bonded alkyl radical. On abstraction of a hydrogen atom from a different carbon atom, an isomerized olefin results.

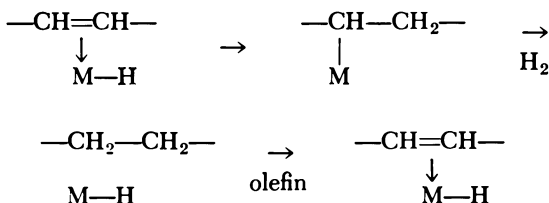


This mechanism, which appears to be well-established in certain systems (10), has close analogies with suspected mechanisms for heterogeneous hydrogenation and isomerization of olefins (6). The second suggested mechanism involves hydrogen abstraction from the olefin with the reversible formation of a π -allylic species.



This also has analogies with some proposed heterogeneous mechanisms (14).

The ability of solutions of salts and complexes of the Group VIII metals to catalyze homogeneous hydrogenation is also widespread; once again hydridic species probably play an important role. For olefins, the general mechanisms may be written as follows.



Among the complexes which may function in this way are pentacyanocobaltate ion, iron pentacarbonyl, the platinum-tin complex, and iridium and rhodium carbonyl phosphines. It has been suggested that with trisphenylphosphine Rh(I) chloride, a dihydride is formed and that concerted addition of the two hydrogen atoms to the coordinated olefin occurs (16). There are few examples of the homogeneous reduction of other functional groups besides C=C, C=C, and C=C—C=C; pentacyanocobaltate incidentally is specific in reducing diolefins to monoolefins.

Among the several types of homogeneously catalyzed reactions, oxidation is perhaps the most relevant and applicable to chemical industry. The well-known Wacker oxidation of ethylene to ethylene oxide is the classic example, although this is not a true catalytic process since the palladium(II) ion becomes reduced to metallic palladium unless an oxygen carrier is present. Related to this is the commercial reaction of ethylene and acetic acid to form vinyl acetate, although the mechanism of this reaction does not seem to have yet been discussed publicly. Attempts to achieve selective oxidation of olefins or hydrocarbons heterogeneously do not seem very successful.

Unsaturated compounds have been carbonylated by their reaction with carbon monoxide under pressure in the presence of palladous chloride, but supported palladium catalysts will also perform this function (15). This is perhaps the clearest illustration of a class of reactions which proceeds both homogeneously and heterogeneously with apparent comparable facility.

Rhodium chloride catalyzes the polymerization of butadiene with high stereospecificity to *trans*-poly(1,4-butadiene) (4) and also the dimerization of ethylene and other olefins (2). Although certain oligomerizations are catalyzed by solid palladium and rhodium catalysts (9), polymerization to high molecular weight products is not generally observed.

Catalytic Properties of Group VIII Elements and Their Compounds

We can now say (a) that optimum catalytic activity for a number of systems, both homogeneous and heterogeneous, resides in the Group VIII elements and their compounds; (b) that particularly where activation of carbon-carbon multiple bonds is involved, compounds of the second row elements (Ru, Rh, Pd) in solution are generally the most active; and (c) that while hydrogenation and the associated isomerization of olefins, and carbonylation, are encountered in both homogeneous and heterogeneous systems, certain processes (especially oxidation and polymerization) which are homogeneously catalyzed have no close heterogeneous counterpart. We must now consider some of the theoretical principles which may form the basis for understanding these generalizations.

We can restrict our thinking to the behavior of olefins and other unsaturated hydrocarbons because these represent the area of greatest practical and theoretical interest. The fact that their reactions are predominantly catalyzed by the Group VIII metals and their salts and complexes must mean that the metal atoms in whatever environment have certain common properties. It is most important to establish beyond doubt that an individual metal atom has catalytic properties; the catalytic properties of a metal surface cannot therefore *solely* be caused by a large number of metal atoms in concert but must at least be caused partly by certain qualities of each metallic surface atom. It has been proposed (8) that these common properties reside in the molecular orbitals associated with the metal atoms. It is well-known that for a square-planar d^8 complex (e.g., Rh^I , Pd^{II}), the four ligands are bound to the metal atom by using the latter's $d_{x^2-y^2}$ orbitals, the d_{xy} (or t_{2g}) family of orbitals being filled and the d_{z^2} orbital empty. It is possible to describe the structure of a face-centered cubic metal analogously (11). The 12 near neighbors are bonded to the central atom by overlap of the 12 lobes of t_{2g} orbitals, thus forming a continuous d band, accounting for communal electronic properties; the six next-nearest neighbors are weakly bonded by overlap of the six lobes of e_g orbitals, thus forming essentially localized levels accounting for magnetic properties. It is then possible to evaluate the way in which the two types of orbital emerge at the three low index crystal planes and then examine and compare the local symmetry with that existing in complexes (8).

It is not possible here to elaborate this hypothesis or its potential usefulness in understanding the detailed mechanisms of surface reactions; for our purpose it is important that the model permits us to consider that olefins and other reactive hydrocarbons may be chemisorbed

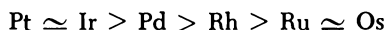
in a way closely analogous to their coordination to single metal atoms. In the light of this we may briefly examine the trends which exist in the metals of Group VIII which may serve to adjudicate the hypothesis.

A generally valid rule in catalysis is that the stronger the binding of the substrate to the catalytic center, the less efficient the catalysis becomes, until the point is reached where the concentration of the substrate-catalyst complex falls below the maximum. Discussion of the binding of olefins to Group VIII metals and complexes is hampered by the almost total absence of quantitative information on bond strengths in metal-olefin complexes; nevertheless, certain qualitative trends are emerging. The stability of monoolefin complexes increases from Ni^{II} to Pd^{II} to Pt^{II} , although Cu^{I} complexes are stabler than those of Ag^{I} . Olefin complexes of Rh^{I} are probably stabler than those of Pd^{II} since, for example, two ethylene molecules are comfortably coordinated by the former but not by the latter. The differences in C=C stretching frequencies in ethylene complexes supports this view. There is little quantitative information on the effect of olefin structure on complex stability, although ethylene complexes are undoubtedly the most stable. Only for Ag^{I} complexes are any quantitative stability measurements available (3), but the situation is confused by a combination of steric and electronic effects.

This somewhat incomplete picture can be coordinated with known facts of homogeneous catalysis. We may say that the monoolefin complexes of Ni^{II} are too unstable to be reactive, while the simple analogues of Pt^{II} are too stable; optimum reactivity therefore resides in complexes of Pd^{II} and Rh^{I} where these opposing effects balance properly. We must defer for the present a discussion of the effects which other coordinated groups (*e.g.*, PR_3 , CO, SnCl_3^-) have on the reactivity of coordinated olefins since much more systematic information is needed for this to be feasible. The limited catalytic activity of d^{10} olefin complexes (*e.g.*, Cu^{I} , Ag^{I}) is presumably caused by the absence from these complexes of any vacant orbitals at which attack by another reactant can occur.

When olefins chemisorb on metal surfaces (in the absence of hydrogen), substantial disruption of the molecules usually occurs; measurements of heats of adsorption or of infrared spectra of adsorbed species are therefore of limited utility in establishing behavioral patterns, and more reliance should perhaps be placed on indirect assessments of chemisorption strengths arising from kinetic analysis of reacting systems. This information is of two kinds: (a) the sequence of chemisorption strengths of an olefin on a series of metals, and (b) the sequence of chemisorption strengths of different unsaturated hydrocarbons on one metal.

The sequence for ethylene at 50°C. on several alumina-supported metals has been derived from a detailed analysis of the products of the ethylene-deuterium reaction (7) and is:



Pd and Rh reverse positions below room temperature. The positions of Fe, Co, and Ni relative to these metals is uncertain, but on their general characteristics (6) they would be placed in the neighborhood of Pd and Rh; Cu would fall at the end of the sequence. This sequence is quite reminiscent of the coordination strength sequence, particularly in the relative placings of Pt and Ir, followed by Pd and Rh, with Cu at the end. What is however anomalous is the position of the base metal triad; in fact, Fe, Co, and Ni are better catalysts for olefin hydrogenation than would be expected on the basis of their ability to form olefin complexes. We will return to this point.

It is well known that alkynes and diolefins are more strongly chemisorbed during their hydrogenation on metal surfaces than are olefins, although the effect can arise from quite small differences in heats of chemisorption (5). The analogy with organometallic complexes is quite close, but the stronger coordination of diolefins compared with mono-olefins is almost entirely an entropy effect.

There is one further area in which the properties of olefin-metal complexes and adsorbed olefins show common behavior. The olefin is often readily displaced by diolefins and alkynes; many other ligands, including phosphines, amines, nitriles, cyanide ion, and carbon monoxide, can however cause olefin displacement, and these include molecules which are notorious catalyst poisons. Again no quantitative information is available, but a causal connection is strongly suggested.

Differences between Homogeneous and Heterogeneous Catalytic Systems

In one field, although restricted, there is a reasonably close analogy between the reactivity of olefins under reducing conditions in both homogeneous and heterogeneous catalytic systems. We now turn our attention to possible explanations of the observed anomalies and to the causes of the different behaviors shown by the two systems in oxidation and polymerization.

The major anomaly in olefin reactions is the superior ability of Fe, Co, and Ni to act as hydrogenation catalysts in comparison with expectations based on the strength of olefin bonding in complexes. Olefins are quite strongly chemisorbed by these metals (5); we must therefore infer that the presence of several metal atoms in proximity sometimes confers a binding ability not possessed by single atoms. Whether this effect is of particular importance with these metals or whether it will prove to

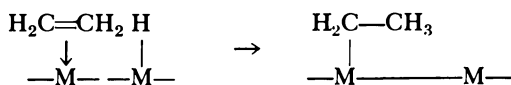
have general significance is not certain at this time and will clearly be a matter for future debate. Structure determinations of organometallic complexes performed in recent years have vastly widened our concepts of chemical bonding, and of particular relevance to our problem are the recently investigated complexes of alkynes with multiatom clusters (13). It will be interesting to see whether such multiatom clusters have catalytic properties.

We now consider homogeneously catalyzed oxidation and polymerization—both of which do not have strict heterogeneous counterparts. Taking the Wacker oxidation of ethylene to acetaldehyde as an example, it appears that the central role of the Pd atom is to act as an electron acceptor, permitting the first formed $(\text{HOCH}_2\text{CH}_2\text{PdCl}_3)^{2-}$ species to form the $\text{HOCH}_2\text{CH}_2^+$ carbonium ion, which subsequently rearranges to CH_3CHO and H^+ . The accumulation of negative charge on the PdCl_3 moiety is released only by disruption to Pd^0 and 3Cl^- . Strict analogy in a heterogeneous system is therefore not to be expected since surface metal atoms cannot similarly be reduced, and some alternative means of releasing the negative charge would have to be found.

The cause of the general inability of metallic surfaces to catalyze oligomerization or polymerization in the way complexes can is easy to see in principle. The usual mechanism at a complex will be the cis-ligand transfer of an alkyl radical to a coordinated olefin, giving a higher alkyl radical and a free coordination site; this is basically Cossee's mechanism for polymerization catalyzed by TiCl_3 . Thus a minimum of two coordination sites is required, but surface metal atoms have on the average only one site available; surface-catalyzed polymerization is therefore not expected to be a general phenomenon.

Conclusions

Three significant conclusions emerge: (a) there is a similarity between homogeneous and heterogeneous hydrogenation and isomerization of olefins, which suggests that mechanisms occurring at a complex are analogous to those operating at surfaces, and that hydrogen atom transfer steps on surfaces, for example:



occur with comparable ease to cis-ligand transfer steps at complexes. (b) Sometimes, if not always, the existence of many atoms at surfaces permits the formation of chemisorbed species having no analogy in simple complexes. (c) Reactions involving electron transfer and a change

in oxidation state of a metal atom are more readily accomplished by complexes than by surfaces.

Practical Considerations

Long years of experience lie behind the present state of catalytic technology which has been developed to a high level of sophistication, but the success in operating a catalytic process is limited by the skill with which the catalyst has been designed. The chief limitation lies in the lack of specificity of solid catalysts, and the design of a selective catalyst frequently taxes the competence and patience of the scientist. It is precisely in this area where homogeneous systems stand to gain. Because of the small size of the catalytic entity, only one functional group of a polyfunctional molecule is likely to be engaged at any one time; moreover the coordination requirements are likely to render such interactions quite specific. On surfaces, on the other hand, the simultaneous engagement of more than one function is frequently possible, resulting in nonselective behavior. The role of selective poisoning is at least sometimes to produce a catalyst having only isolated active sites to overcome this difficulty.

There is therefore every reason to hope that homogeneous catalytic processes will play a larger part in the future development of chemical industry. The two chief reasons are (a) the hope of greater specificity and (b) the expectation of a more efficient use of expensive elements such as Pd and Pt.

Some practical problems remain, however. When, as in the operation of the Wacker process, the product may be continuously distilled from the system, no insuperable problem exists; when, however, this is not possible, the problem of separating product from catalyst remains. A possible means of performing a continuous homogeneous process is to dissolve the active species or a precursor in an involatile solvent which is then supported on a porous solid, similar to gas-liquid chromatography; thus isomerization of 1-pentene occurs on passing the vapor through a column containing rhodium chloride in ethylene glycol on a suitable porous solid (1). The development of novel process methods will be required before homogeneous catalytic processes can take the place they undoubtedly merit by the side of the more conventional operations of chemical industry.

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Mass Transfer Effects on Liquid-Phase Chemical Reaction Rates

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The rate of liquid-phase chemical reactions involving transfer of reactants from another phase depends on the homogeneous liquid-phase kinetics, physical mass transfer rates of reactants, and their thermodynamic equilibria at the phase boundaries. The interaction among these phenomena produces four distinct types of behavior depending on chemical reaction velocity. These will be examined in this paper.

Many industrially important liquid-phase chemical reactions require the transfer of one or several reactants into a reactive liquid phase from a gas, from another liquid phase of limited miscibility with the reactive liquid, or from a solid. Reaction products accumulate in the liquid or leave by vaporization, migrate to another liquid phase, or precipitate as solids. The rate of chemical reaction in such systems is determined not only by the homogeneous liquid-phase reaction kinetics but also by the physical transfer rates of reactants and their thermodynamic equilibria at the phase boundaries. In reversible reactions, the chemical equilibrium constant and the rate of removal of reaction products are also important.

The reactive liquid phase may be brought into contact with gases and immiscible liquids in spray columns, packed columns, bubble trays, sparged columns or sparged mechanically agitated tanks, pipeline reactors, and, in the laboratory, in shaken flasks, liquid jets and falling film apparatus. Owing to the relatively slow motion of immiscible liquids relative to one another, centrifugal action is sometimes used in liquid-liquid systems. Solid-liquid contact is achieved by suspension of small solid particles in the liquid, which often is agitated mechanically to prevent settling of the solids. In laboratory studies, solids cast into flat slabs or mounted on rotating cylinders are sometimes used.

The factors of primary importance in such chemical reaction systems are:

- (a) The interfacial area between the reactive liquid phase and the phases supplying reactants and removing products.
- (b) The contact time of the reactive liquid phase with these other phases and the degree of backmixing of the phases in the reaction vessel.
- (c) The thermodynamic equilibria of reactants and products at the phase boundaries.
- (d) Physical mass transfer rates between phases.
- (e) Mass transfer rates with chemical reaction.

The first four will be examined only superficially in this work in order to permit a somewhat more detailed examination of the last topic—mass transfer rates with chemical reaction.

Interfacial Area

The interfacial area between the reactive liquid phase and the other phases is determined by the equipment configuration and the fluid flow rates and properties—density, viscosity, and surface tension. Interfacial area is usually given the symbol a and is specified on the basis of a unit volume. Its dimensions are thus area/volume or length⁻¹.

The interfacial area is known accurately only in some systems used in laboratory studies: falling laminar films, laminar cylindrical jets, undisturbed gas-liquid and liquid-liquid interfaces, and solid castings of known dimensions immersed in liquids. In all reactor systems used industrially such as packed towers, spray towers, and bubble trays, the interfacial area is relatively difficult to determine. Photographic, gamma-ray, light scattering and chemical methods have been used to determine a in bubble dispersions (5, 6, 7, 8, 10, 42). For an average bubble diameter d_B , a superficial gas velocity u_{SG} and a bubble rise velocity u_B ,

$$a = 6 u_{SG} / (d_B u_B) \quad (1)$$

In packed columns, the total packing surface is known (Table I), but the portion of the packing which is wetted by the liquid and thus available for mass transfer is widely variable, ranging from 5 to 70% of the packing surface, depending on the superficial liquid velocity through the packing, the packing dimensions, and the type of liquid distributor used (17, 30, 36, 38, 42).

Liquid Contact Time and Backmixing

The choice of reactor type is usually dictated by the liquid residence time required to attain the desired degree of reactant conversion and

Table I. Total Surface Area of Some Column Packings (33)

Packing	Nominal Size, inch	Total Surface Area	
		(ft. ⁻¹)	(cm. ⁻¹)
Metal Raschig Rings	$\frac{1}{2}$	118-128	3.9-4.2
	1	57-63	1.9-2.1
	2	31	1.0
	3	21	0.7
Ceramic Intalox Saddles	$\frac{1}{2}$	190	6.2
	1	78	2.6
	2	36	1.2
Metal Pall Rings	1	66	2.2
	2	37	1.2

Table II. Characteristics of Some Liquid-Phase Reactors

Equipment	Phases Contacted	Approximate Upper Limit of:		
		Interfacial Area cm. ⁻¹	Liquid Residence Time, sec.	Degree of Liquid Backmixing
Spray Tower	G/L	0.01	2	plug flow
Packed Column	G/L	3	12 sec./ft. of packed depth	plug flow
Bubble Tray Tower	G/L	8 sq. cm./cc. of froth	15 sec./ft. of liquid path	partly back- mixed on each tray
Sparged Column	G/L	5	unlimited	backmixed
Agitated Vessel	S/L, L/L,	10	unlimited	backmixed
	G/L	2		
Pipeline	G/L, L/L, S/L	10	unlimited	plug flow

by considerations of temperature and pressure control, susceptibility to plugging, safety, and cost. The average liquid residence time depends on the liquid feed rate and the reactor volume, but the residence time distribution and the average reactant concentration depend in addition on the degree of liquid mixing in the reactor. Mixing highly converted material with fresh feed lowers the average reactant concentration and thus the reaction rate. Table II summarizes some characteristics of common reactor types.

Interphase Equilibria of Reactants and Products

Reactants and products on both sides of phase boundaries are assumed to be at physical—not chemical—thermodynamic equilibrium.

This assumption is supported by many experimental studies. The concentrations of a component in two phases at equilibrium are related by equilibrium ratios, which remain approximately constant over a substantial concentration range.

The distinction between physical and chemical equilibrium is important. For example, when chlorine is absorbed into water, it first enters the water as dissolved chlorine and then undergoes a relatively slow chemical reaction with water to form HOCl, H⁺, and Cl⁻. Two equilibrium ratios may be written—one based on total chlorine in the liquid [Cl₂ + ½HOCl + ½Cl⁻], and the other based on dissolved Cl₂ only. It is the latter ratio which controls the mass transfer rate. As another example, when carbon dioxide is absorbed into alkaline aqueous solutions, it first dissolves as CO₂ and then reacts with OH⁻ to form bicarbonate ion. The equilibrium ratio controlling the mass transfer rate is $p_{\text{CO}_2}/[\text{CO}_2]$. This ratio is independent of pH and is affected only by changes in the ionic strength of the solution. The interphase equilibria of the reaction products are important only for reversible chemical reactions.

Mass Transfer Without Chemical Reaction

The mass transfer rate of a component, A, across a phase boundary has been found to be proportional to the concentration difference in A across a hypothetical fluid film between the bulk of each fluid phase and the phase boundary. Thus,

$$N_A = k(c_A - c_{A1}), \quad (2)$$

where N_A = rate of flow of reactant A across interface, gram-moles/sec./sq. cm.

c_A = concentration of A in the bulk of the phase, gram-moles/cc.

c_{A1} = concentration of A at the phase boundary, gram-moles/cc.

k = mass transfer coefficient, cm./sec.

This equation applies to both gases and liquids. In gases, the concentration is often expressed in terms of partial pressure or mole fraction, and the units of k are changed accordingly.

For the transfer of A from a gas into a liquid, we may write

$$N_A = k_G(p_A - p_{A1}) = k_L(c_{A1} - c_A) \quad (3)$$

At the phase boundary, it is assumed that equilibrium exists between dissolved and gaseous A. Thus,

$$p_{A1} = H_A c_{A1}, \quad (4)$$

where H_A is the Henry's law constant for A, expressed in atm-cc./gram-mole. Combining Equations 3 and 4 results in Equation 5.

$$N_A = \frac{p_A/H_A - c_A}{1/(H_A k_G) + 1/k_L} \quad (5)$$

This equation expresses the "two-film concept" of Whitman (40), the numerator being a concentration driving force and the denominator being the sum of two mass transfer resistances in series. Analogous expressions may be written for two liquid film resistances in series. Figure 1 illustrates qualitatively the concentration profiles through two liquid films.

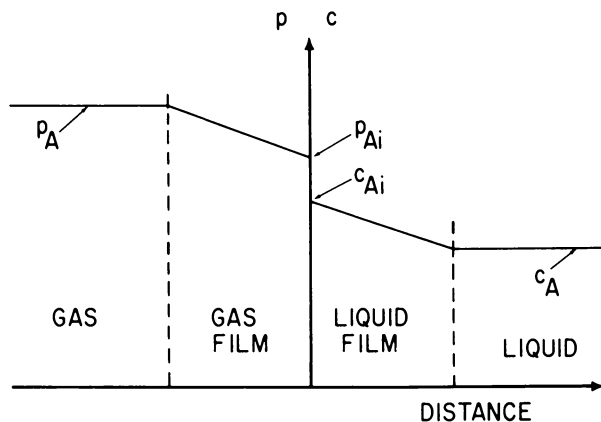


Figure 1. Concentration profile across a gas-liquid interface. Component A diffuses from the gas into the liquid.

$$N_A = k_G(p_A - p_{Ai}) = k_L(c_{Ai} - c_A).$$

The coefficients k_G and k_L have been experimentally determined for many mass transfer systems and correlated with gas and liquid flow rates, liquid density and viscosity, the diffusivity of A in the gas and the liquid, and the physical dimensions of the systems. Dimensional analysis suggests that dimensionless quantities of the form

$$\frac{kl}{D} = Sh = \text{Sherwood number}, \quad (6)$$

$$\rho ul/\mu = Re = \text{Reynolds number}, \quad (7)$$

$$\mu/(\rho D) = Sc = \text{Schmidt number} \quad (8)$$

should provide widely applicable correlations. The variables l and u are characteristic lengths and velocities of the system. Where gravitational effects are important, the dimensionless variable

$$\mu^2/(gl) = Fr = \text{Froude number} \quad (9)$$

must also be included.

When the interfacial area is not known, mass transfer rates may be based on a unit volume rather than a unit of interfacial area. The resulting coefficients are the products of k_G and k_L , as previously defined, and a , the interfacial area per unit volume. When concentration driving forces are used in defining k_G and k_L , the products $k_G a$ and $k_L a$ have the dimension sec^{-1} . Some typical mass transfer data are shown in Table III.

Table III. Mass Transfer Data for Some Typical Reactor Systems^a

<i>System</i>	<i>Mass Transfer Coefficient</i>	<i>Reference</i>
Gas bubbles rising through liquid	$k_L Sc_L^{2/3} = 0.31 (\mu_L g / \rho_L)^{1/3}$ for small, rigid bubbles;	8
	$k_L Sc_L^{2/3} = 0.42 (\mu_L g / \rho_L)^{1/2}$ for large, circulating bubbles	8
Solids suspended in liquids	$k_L Sc_L^{2/3} = 0.31 (\Delta \rho \mu_L g / \rho_L^2)^{1/3}$	8
Solids settling in liquids	$k_L d_p / D = 2.0 + 0.552 (\rho_L u d_p / \mu_L) Sc_L^{1/3}$	14, 30
Liquid drops in gas	$k_G d_p / D = 2.0 + 0.552 (\rho_G u d_p / \mu_G) Sc_G^{1/3}$	14, 30
Sieve tray, air humidification	$k_G a = 2-20 \text{ sec}^{-1}$	15, 39
Sieve tray, O ₂ —H ₂ O, CO ₂ —H ₂ O	$k_L a = 0.08-0.3 \text{ sec}^{-1}$	15, 39
O ₂ —H ₂ O	$k_L = 0.01-0.02 \text{ cm./sec.}$	10
Sparged column, O ₂ —H ₂ O	$k_L a / v_G = 0.3-0.55 \text{ sec}^{-1}$	44
Sparged stirred tank, O ₂ —H ₂ O	$k_L a = 0.002-0.10 \text{ sec}^{-1}$	41
Packed column—1" rings, air humidification	$k_G a = 0.55-4.5 \text{ sec}^{-1}$	30
	O ₂ —H ₂ O	$k_L a = 0.004-0.05 \text{ sec}^{-1}$
Spray column, air humidification	$k_G a = 0.14-0.6 \text{ sec}^{-1}$	30
	O ₂ —H ₂ O	$k_L a = 0.001-0.002 \text{ sec}^{-1}$

^a A more complete list of mass transfer correlations may be found in Ref. 32.

Mass Transfer with Chemical Reaction

Suppose a chemical component A enters the reactive liquid phase from another phase—gas, liquid or solid—and irreversibly reacts in the reactive liquid phase with n moles of component B per mole of A, B

originally being dissolved in the reactive liquid phase. Depending on the homogeneous reaction kinetics and the physical mass transfer rates, four distinct situations may arise. The rate of transfer of reactant A across the phase boundary per unit interfacial area will be designated by N_A and related to the concentration of A at the phase boundary, c_{Ai} , and a mass transfer coefficient k_L , by the definition

$$N_A \text{ (gram moles/sec./sq. cm.)} = k_L c_{Ai} \quad (10)$$

It is convenient for comparison to define the mass transfer rate in the absence of chemical reaction under otherwise identical conditions by

$$N_A^o = k_L^o c_{Ai}, \quad (11)$$

where the superscript *o* denotes "no chemical reaction," and the rate of reaction per unit volume by

$$R = N_A a. \quad (12)$$

Four distinct types of behavior have been observed. These will be identified as Regimes I, II, III, and IV.

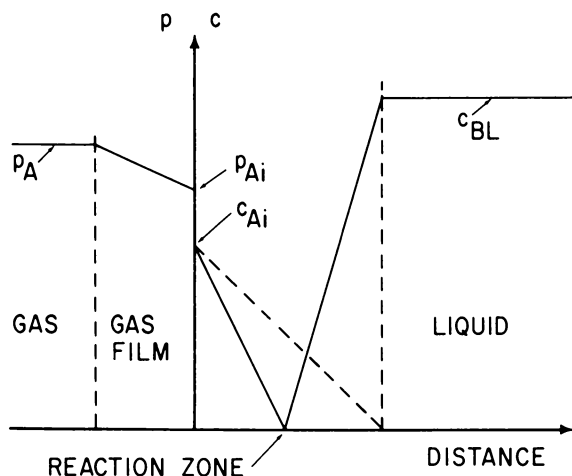


Figure 2. Concentration profile across a gas-liquid interface with very rapid reaction (Regime I). Reactants A and B diffuse into a narrow reaction zone in the liquid film. $N_A = k_L^o c_{Ai} [1 + D_{BCBL}/(nD_A c_{Ai})]$.

Regime I—Very Fast Reactions

If A and B react very rapidly, the liquid film at the phase boundary is depleted rapidly of reactants A and B, and the reaction can proceed only as fast as the reactants can diffuse into the surface film from both

sides—A from the phase boundary and B from the bulk of the liquid. A semiquantitative plot of the concentration profiles in and around the fluid film is shown in Figure 2. The dashed line indicates the approximate concentration gradient across the fluid film in the absence of chemical reaction. It will be noted that with chemical reaction, the concentration gradient of A is steeper. Thus, N_A should be greater than N_A° and

$$N_A/N_A^\circ = k_L/k_L^\circ > 1 \quad (13)$$

Hatta (19) first derived an expression for k_L/k_L° based on the assumption of a completely stagnant fluid film and found

$$k_L/k_L^\circ = 1 + \frac{D_B c_{BL}}{n D_A c_{A1}} \quad (14)$$

Of course, the assumption of a stagnant fluid film with an abrupt transition to the bulk of the liquid is not very plausible, but Equation 14 fits many experimental data well.

Two other theories for predicting k_L/k_L° for very fast reactions lead to similar results. Higbie's "penetration theory" (19), which is based on unsteady state diffusion into a laminar fluid stream, leads to the expression (11):

$$k_L/k_L^\circ = \left(1 + \frac{D_B c_{BL}}{n D_A c_{A1}} \right) \left(\frac{D_A}{D_B} \right)^{1/2} \quad (15)$$

This differs from Equation 14 only by the factor $\sqrt{D_A/D_B}$, which is often near unity. A derivation based on mass transfer in a turbulent boundary layer results in the expression (13, 24, 27, 31):

$$k_L/k_L^\circ = \left(1 + \frac{D_B c_{BL}}{n D_A c_{A1}} \right) \left(\frac{D_A}{D_B} \right)^{1/3} \quad (16)$$

Again, the difference between this expression and Equation 14 is unimportant.

We may now define the reaction rate in Regime I as the rate of consumption of A per unit volume

$$N_A a = k_L^\circ a c_{A1} \left(1 + \frac{D_B c_{BL}}{n D_A c_{A1}} \right) \equiv R_I \quad (17)$$

The chemical reaction rate constant does not appear in this expression. Increasing the rate constant by adding catalysts thus has no accelerating effect. Examples of reactions in Regime I are given in Table IV.

Regime II—Moderately Fast Reactions

A totally different situation arises with moderately fast chemical reactions in which the surface film is not appreciably depleted of reactant

Table IV. Reaction Systems in Regime I

Component A	Component B	Apparatus	Reference
CO ₂	OH ⁻ (NaOH)	packed column	1, 2, 36
Cl ₂	FeCl ₂	disc column	30
CO ₂	NH ₄ OH	packed tower	36
		valve tray	16
Benzoic acid	OH ⁻ (NaOH)	solid slab in stirred tank	24
		solid pieces on rotating cylinder	31
CO ₂	OH ⁻ (NaOH)	falling film	25
CO ₂	MEA	falling film	12

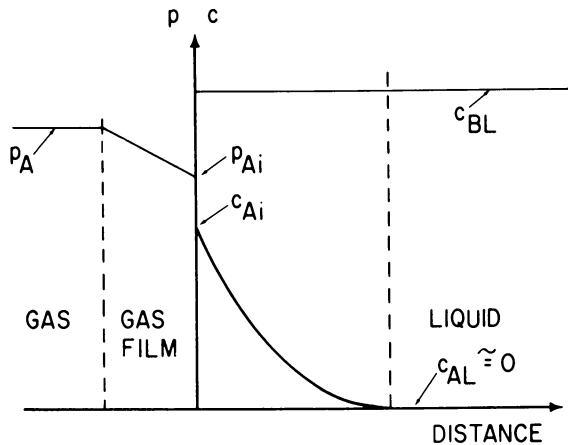


Figure 3. Concentration profile across a gas-liquid interface with moderately fast reaction (Regime II). Reactant A is partly consumed by chemical reaction in the liquid film

$$N_A = [2KD_A c_{BL}^\beta / (\alpha + 1)]^{1/2} c_{Ai}^{(\alpha+1)/2}$$

B. Reactant A diffuses across the surface film but at the same time partially disappears because of reaction with B. The concentration of reactant B is substantially constant throughout the surface film. Assuming the surface film to be stagnant, one can show that for a chemical reaction rate expression:

$$-dc_A/d\theta = Kc_A^\alpha c_B^\beta, \quad (18)$$

$$k_L \cong \left(\frac{2KD_A c_{BL}^\beta}{\alpha + 1} \right)^{1/2} c_{Ai}^{(\alpha-1)/2} \quad (19)$$

and the rate of consumption of A per unit volume is

$$N_A a = a \left(\frac{2KD_A c_{BL}^\beta}{\alpha + 1} \right)^{1/2} c_{Ai}^{(\alpha+1)/2} \equiv R_{II}. \quad (20)$$

For the frequently encountered case $\alpha = \beta = 1$, this reduces to

$$k_L = \sqrt{KD_{AC_{BL}}} \quad (21)$$

and

$$N_A a = ac_{Ai} \sqrt{KD_{AC_{BL}}} \equiv R_{II} \quad (22)$$

This expression is based on Hatta's film concept. Similar expressions result from "penetration theory." Figure 3 illustrates the concentration profiles for A and B in and around the fluid film for Regime II.

Examples of reaction systems which behave according to Equation 19 are given in Table V.

Table V. Reaction Systems in Regime II

<i>Reactant A</i>	<i>Reactant B</i>	<i>Apparatus</i>	<i>Reference</i>
CO ₂	OH ⁻ (Na ₂ CO ₃)	packed column	36, 42
		rotating drum	2
		laminar jet	29
		falling film	28
N ₂ O ₄	H ₂ O	laminar jet	23
CO ₂	methylisopropylamine	laminar jet	29
O ₂	Na ₂ SO ₃	flat liquid surface	26
CO ₂	OH ⁻ (NaOH)	packed column	42
		agitated sparged vessel	43
		sieve tray	18

It follows from Equations 19 and 20 that k_L may be increased by adding catalysts, which increase the chemical reaction rate constant K . A well-known example is the effect of arsenite ion on the rate of absorption of CO₂ into alkaline carbonate solutions (27).

Regime III—Slow Reactions

When the chemical reaction rate is so slow that the fraction of reactant A consumed in the surface film is negligibly small, but fast enough to maintain the concentration of A in the bulk of the liquid very low,

$$k_L = k_L^\circ \quad (23)$$

and

$$N_A a = k_L^\circ ac_{Ai} \equiv R_{III} \quad (24)$$

Here again, as in Regime I, catalytic effects on the chemical reaction rate constant have no effect on the rate. The concentration profile in Regime III is shown in Figure 4. Reactions showing this behavior are the oxidation of aqueous Na₂SO₃ with air or oxygen in presence of cata-

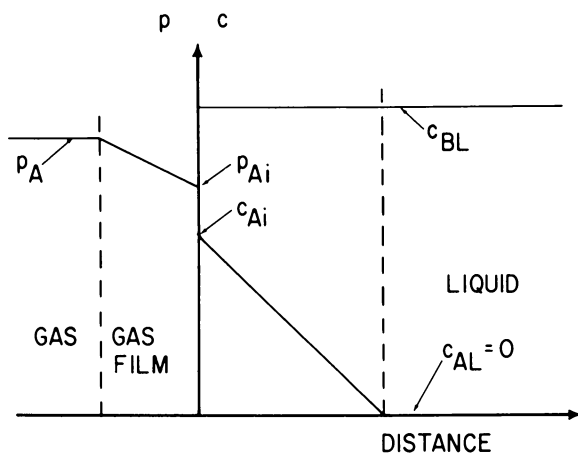


Figure 4. Concentration profile across a gas-liquid interface with slow chemical reaction (Regime III). Reactant A diffuses across the liquid film without appreciable chemical reaction. Virtually all chemical reaction takes place in bulk of liquid. $N_A = k_L c_{Ai}$

lytic amounts (10^{-5} to 10^{-3} molar) of CuSO_4 or CoSO_4 (4, 22, 26, 41, 44) and chlorine absorption into water with slow formation of HCl and HOCl (37).

Border Regions Between Regimes I, II, and III

For reactions which are first order in both A and B ($\alpha = \beta = 1$), a slightly more rigorous derivation than that resulting in Equation 22 yields

$$k_L = \sqrt{KD_{AC_{BL}}}/\tanh [\sqrt{KD_{AC_{BL}}}/k_L^\circ] \\ = (R_{II}/ac_{Ai})/\tanh (R_{II}/R_{III}) \quad (25)$$

which for $\sqrt{KD_{AC_{BL}}}/k_L^\circ > 2$ reduces to Equation 22, and for $\sqrt{KD_{AC_{BL}}}/k_L^\circ < 0.2$ to Equation 23. Equation 25 thus applies to both Regimes II and III, and the border region between these two regimes, which is roughly

$$0.2 < \sqrt{KD_{AC_{BL}}}/k_L^\circ < 2 \quad (26)$$

Equation 25 furthermore may be corrected for the partial depletion of reactant B in the surface film by substituting for c_{BL} , a concentration which takes into account the concentration gradient of B under which B diffuses into the surface film to replenish the B consumed by chemical

reaction with A. If the interface concentration of B,

$$c_{B1} = c_{BL} \left(1 - \left(\frac{k_L}{k_L^\circ} - 1 \right) \frac{nD_{AC_{A1}}}{D_{BC_{BL}}} \right) \quad (27)$$

is substituted in Equation 25,

$$k_L = \frac{\sqrt{KD_{AC_{BL}} \left[1 - \left(\frac{k_L}{k_L^\circ} - 1 \right) \frac{nD_{AC_{A1}}}{D_{BC_{BL}}} \right]}}{\tanh \left[\sqrt{KD_{AC_{BL}} \left[1 - \left(\frac{k_L}{k_L^\circ} - 1 \right) \frac{nD_{AC_{A1}}}{D_{BC_{BL}}} \right]} / k_L^\circ \right]} \quad (28)$$

This expression, which was first derived by Van Krevelen and Hoftijzer (35), cannot be solved explicitly for k_L . It is shown graphically in Figure 5.

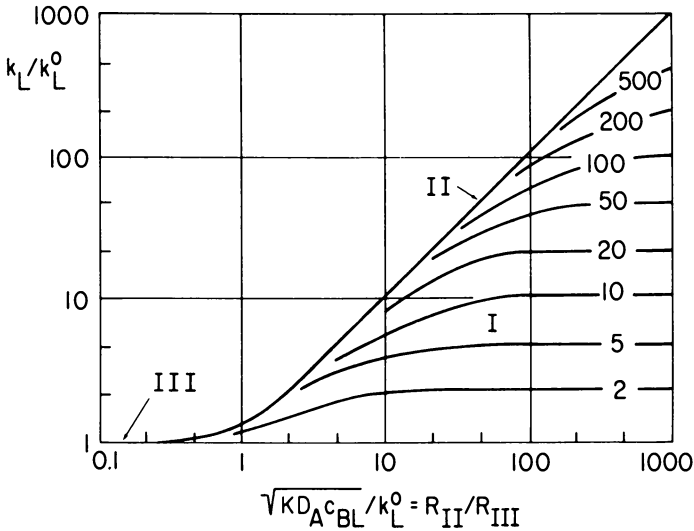


Figure 5. $k_L/k_L^\circ = R/R_{III}$ for Regimes I, II, and III vs. $\sqrt{KD_{AC_{BL}}}/k_L^\circ = R_{II}/R_{III}$. The parameter is $R_I/R_{III} = [1 + D_{BC_{BL}}/(nD_{AC_{A1}})]$. Roman numerals indicate the three regimes

The limits of Regimes I, II, and III may be defined roughly by Equations 29-31.

$$\left. \begin{aligned} \text{Regime I: } & \sqrt{KD_{AC_{BL}}}/k_L^\circ > 5 \left(1 + \frac{D_{BC_{BL}}}{nD_{AC_{A1}}} \right), \\ \text{or} & R_{II} > 5R_I; \end{aligned} \right\} \quad (29)$$

$$\text{Regime II: } \left. \begin{aligned} 0.5 \left(1 + \frac{D_B c_{BL}}{n D_A c_{A1}} \right) > \sqrt{K D_A c_{BL}} / k_L^\circ > 2.0 \\ \text{or} \quad 0.5 R_I > R_{II} > 2 R_{III} \end{aligned} \right\} \quad (30)$$

$$\text{Regime III: } \left. \begin{aligned} \sqrt{K D_A c_{BL}} / k_L^\circ < 0.2, \\ \text{or} \quad R_{II} < 0.2 R_{III} \end{aligned} \right\} \quad (31)$$

Regime IV—Very Slow Reactions

When the rate of consumption of reactant A by the chemical reaction is so low that the liquid phase is substantially saturated with A, $c_{AL} = c_{A1}$ and

$$N_A a = K c_{A1}^\alpha c_B^\beta v_L \equiv R_{IV} \quad (32)$$

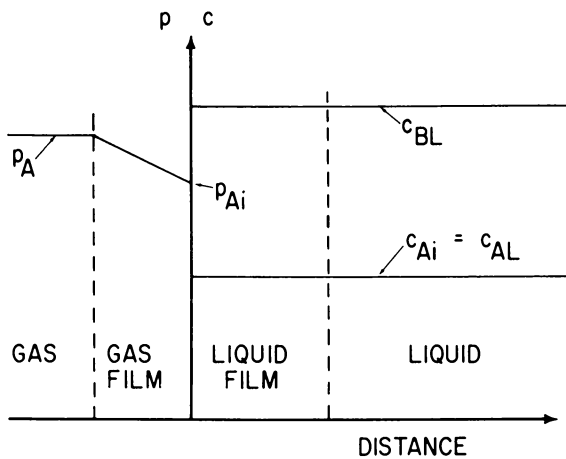


Figure 6. Concentration profile across a gas-liquid interface with very slow chemical reaction (Regime IV). $N_A a = R_{IV} = v_L K c_{A1}^\alpha c_B^\beta$.

The concentration profile for Regime IV is shown in Figure 6, where v_L is the volume fraction of reactive liquid phase. In the wide border region between Regimes III and IV,

$$N_A a = k_L^\circ a (c_{A1} - c_{AL}) = K c_{AL}^\alpha c_{BL}^\beta v_L \quad (33)$$

$$\text{or } N_A a = R = R_{III} \left(1 - \frac{c_{AL}}{c_{A1}} \right) = R_{IV} \left(\frac{c_{AL}}{c_{A1}} \right)^\alpha \quad (34)$$

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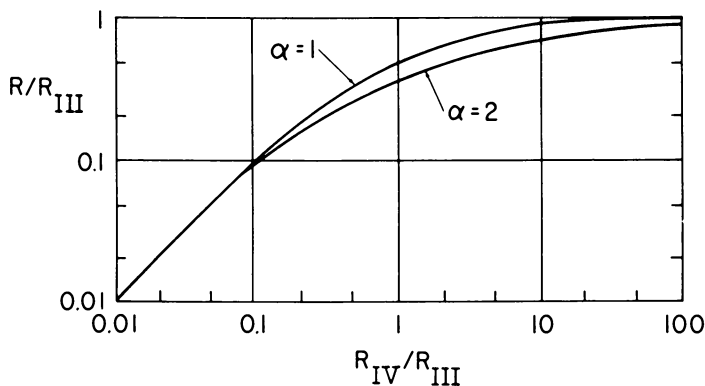


Figure 7. R/R_{III} vs. R_{IV}/R_{III} for Regimes III and IV and intermediate region for $\alpha = 1$ and $\alpha = 2$

Table VI. Summary of Rate

Regime	I
$N_A a = R$	$R_I = k_L^\circ a c_{A_i} \left(1 + \frac{D_B c_{BL}}{n D_A c_{A_i}} \right)$
Reaction order with respect to:	
c_{A_i}	~ 0 ($c_{BL} \gg c_{A_i}$)
c_{BL}	~ 1
K	0
D_A	~ -1 ($c_{BL} \gg c_{A_i}$)
D_B	$\sim +1$ ($c_{BL} \gg c_{A_i}$)
k_L°	1
a	1
v_L	0

The transition between Regimes III and IV is shown in Figure 7 for $\alpha = 1$ and $\alpha = 2$. When $R_{IV} > 100 R_{III}$, $R \cong R_{III}$, and when $R_{IV} < 0.1 R_{III}$, $R \cong R_{IV}$. Examples of very slow reactions in Regime IV and in the transition from III to IV are certain aerobic fermentations (3, 21).

Summary of Reaction Rate Expressions

It is interesting to examine the effect of various process variables on the rate R . A convenient way of doing this is in terms of the "reaction order" with respect to each independent variable,

$$\text{Reaction order} = \frac{\delta \log R}{\delta \log (\text{independent variable})} \quad (35)$$

Table VI summarizes the rate expressions and the reaction orders with respect to the independent variables, c_{A_i} , c_{B_i} , K , D_A , D_B , k_L° , a and v_L (k_L° and D_A are interdependent).

The actual rate, R , assumes a value approximately equal to one of the rates R_I , R_{II} , R_{III} , and R_{IV} , depending on which regime the reaction system is in. This in turn is determined by the relative magnitudes of these four rates. If these relative magnitudes are represented as follows:

$$R_I > R_{II} > R_{III} > R_{IV} \equiv 1234$$

$$R_{II} > R_I > R_{III} > R_{IV} \equiv 2134, \text{ etc.},$$

then the applicable rate expression for every permissible permutation is given in Table VII.

Expressions and Reaction Orders

	II	III		IV
$R_{II} = \sqrt{\frac{2KD_A}{\alpha + 1}} c_{A_i}^{\frac{\alpha + 1}{2}} c_{B_i}^{\beta/2} a$	$R_{III} = k_L^\circ a c_{A_i}$	$R_{IV} = K c_A^\alpha c_B^\beta v_L$		
$\frac{\alpha + 1}{2}$	1	α		
$\beta/2$	0	β		
$1/2$	0	1		
$1/2$	0	0		
0	0	0		
0	1	0		
1	1	0		
0	0	1		

Table VII. Relative Magnitudes of R_I , R_{II} , R_{III} , and R_{IV} and Applicable Rate Expression

1	2	3	4	IV	1	4	3	2	III
1	2	4	3	III	4	1	3	2	III
1	4	2	3	II	2	1	3	4	IV
4	1	2	3	II	2	1	4	3	IV
1	3	2	4	IV	2	4	1	3	I
1	3	4	2	IV	4	2	1	3	I

R_{III} cannot exceed R_I . Therefore, all permutations for which $R_{III} > R_I$ have been omitted. Figures 5 and 7 may be used to find the rate in the transition regions.

The type of reaction vessel best suited to a given reaction system depends in part on whether or not it is in Regime IV. To maximize the rate in Regime IV, the volume fraction of reactive liquid phase v_L should be maximized. Maximizing the interfacial area a has no effect. A stirred-tank reactor or sparged column with low gas holdup would be most suitable because v_L is near its maximum. To maximize the rate in Regimes I, II, and III, on the other hand, requires maximizing the interfacial area of the reactive liquid phase. This is best done in a sparged column with high gas holdup or a packed or tray column. Obviously, many other factors enter into the selection of the reactor type.

Nomenclature

Roman Letters

- a = interfacial area per unit volume, cm.^{-1}
 c = concentration, gram-mole/cc.
 c_{A1} = concentration of reactant A at phase boundary, gram-mole/cc.
 c_{BL} = concentration of reactant B in bulk of liquid phase, gram-mole/cc.
 D = diffusivity, sq. cm./sec.
 d_B = average bubble diameter, cm.
 d_p = average particle diameter, cm.
 g = gravitational acceleration, 981 cm./sq. sec.
 Fr = Froude number, $u^2/(gl)$
 H = Henry's law constant, p_i/c_i , atm.-cc./gram-mole
 K = chemical reaction rate constant, $(\text{gram-mole/cc.})^{(1-\alpha-\beta)}\text{sec.}^{-1}$
 k = mass transfer coefficient, cm./sec.
 k_G = mass transfer coefficient for gas film, cm./sec., or gram-mole/sec./sq. cm./atm.
 k_L = mass transfer coefficient for liquid film, cm./sec.
 k_L° = mass transfer coefficient of liquid film in absence of chemical reaction, cm./sec.
 l = a characteristic length dimension, cm.
 n = stoichiometric coefficient in chemical reaction $A + nB \rightarrow$ products
 p = pressure, atm.
 R = rate of consumption of reactant A per unit volume, gram-mole/cc./sec.
 $R_I, R_{II}, R_{III}, R_{IV}$ = rate expressions for the four regimes, gram-mole/cc./sec.
 Re = Reynolds number, $(\rho ul/\mu)$
 Sc = Schmidt number, $(\mu/\rho D)$
 Sh = Sherwood number, (kl/D)
 u = a characteristic velocity, cm./sec.
 u_B = bubble rise velocity, cm./sec.
 u_{SG} = superficial gas velocity, cm./sec.
 v_L, v_G = volume fraction of liquid and gas

Greek Letters

- α = exponent of c_A in rate expression
 β = exponent in c_B in rate expression
 θ = time, sec.
 μ = viscosity, gram/cm./sec.
 ρ = density, gram/cc.

Superscripts and Subscripts

- A = reactant A
 B = reactant B; bubble, in u_B
 G = gas
 i = interface
 L = liquid
 SG = superficial gas velocity, u_{SG}
 o = no chemical reaction
 I, II, III, IV = numerals referring to the four reaction regimes

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Recent Homogeneously Catalyzed Commercial Processes

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Oxidation of ethylene with oxygen or air, in an aqueous solution containing as catalyst a redox system—e.g., PdCl₂-CuCl₂—gives acetaldehyde and metallic Pd. The latter is reoxidized with the above oxidants. Technically, this procedure is performed as a one-stage or two-stage process, depending on whether ethylene oxidation and catalyst regeneration are carried out in the same or separate reactors. Vinyl acetate is obtained along with minor amounts of acetaldehyde when acetic acid is used instead of water. Phenol is prepared from toluene by oxidizing the latter first in the liquid phase with air to benzoic acid, oxidizing the acid in the molten state in the presence of cupric benzoate to phenyl benzoate, which is hydrolyzed to phenol and benzoic acid, which is recycled. Some technological and economical comparisons between these and other currently practiced commercial processes are presented.

Acetaldehyde had been manufactured until recently by the four major processes shown in Table I. Those starting from ethanol and C₂ to C₆ saturated hydrocarbons are used extensively in the United States, whereas the acetylene process was used almost exclusively in Europe until recently. These processes were extended by the late 1950's and early 1960's by a new approach called the Wacker process or the Wacker-Hoechst process, consisting of the liquid phase catalytic oxidation of ethylene to acetaldehyde, as outlined in Table II.

Acetaldehyde Manufacture

It is interesting to speculate on the factors which might have led to the development of the Wacker process. As Table I shows, the raw

Table I. Major Acetaldehyde

<i>Starting Materials</i>	<i>Process</i>	<i>System</i>	<i>Reaction Conditions</i>
C_2H_5OH	Vapor phase catalytic oxidation	Heterogeneous	Ethanol and preheated air are passed over Ag gauze at $\sim 300^\circ$ – $575^\circ C.$ and atmospheric pressure
C_2H_5OH	Vapor phase catalytic dehydrogenation	Heterogeneous	Ethanol is passed over Cr-activated Cu catalyst at $\sim 260^\circ$ – $290^\circ C.$ and atmospheric pressure
C_2 to C_6 saturated hydrocarbons (LPG)	Vapor phase noncatalytic oxidation	Heterogeneous	Butane, propane, or gas mixtures containing them are oxidized with air or O_2 , at $\sim 100^\circ$ – $450^\circ C.$
$CH\equiv CH$	Liquid phase catalytic hydration	Homogeneous	Acetylene is passed into 18–25% aqueous H_2SO_4 , containing $HgSO_4 + Fe_2(SO_4)_3$, at ~ 15 p.s.i.g. and $\sim 70^\circ$ – $100^\circ C.$

^a Literature:

Ascher, A., "Ullmanns Encyklopädie der Technischen Chemie," 3rd ed., pp. 2-13, Urban & Scharzenberg, München-Berlin, 1953. Sittig, M., "Organic Chemical Processes," pp. 1-4, The Noyes Press, Inc., New York, 1962. Hayes, E. R., "Encyclopedia

Table II. Acetaldehyde Manufacture

<i>Starting Materials</i>	<i>Process</i>	<i>System</i>	<i>Reaction Conditions</i>
$CH_2=CH_2$	Liquid phase catalytic oxidation	Homogeneous	Ethylene is oxidized in aqueous solution, in the presence of a salt of Pt group— <i>e.g.</i> , $PdCl_2$, in combination with a redox system— <i>e.g.</i> $CuCl_2$ at elevated or atmospheric pressure

^a Literature:

Petroleum Refiner **40** (11), 206 (1961).
 Bozeman, H. C., *Oil Gas J.* **60** (42), 216-21 (1962).
 Sittig, M., "Organic Chemical Processes," p. 1, The Noyes Press, New York, 1962.
 Berger, G., Mittag, R., *Erdöl Kohle* **15**, 699-702 (1962).
 Hayes, E. R., "Encyclopedia of Chemical Technology," 2nd ed., pp. 86-88, Wiley, New York, 1963.

materials used to produce acetaldehyde by the four processes presented there are ethanol, LPG (liquid petroleum gas), and acetylene. Ethyl alcohol, although cheap, can in turn be made by the catalytic hydration

Manufacturing Processes^a

<i>Yield, %</i>	<i>Conversion per pass, %</i>	<i>Basic Reactions</i>
~85-95	~25-35	$\text{CH}_3\text{CH}_2\text{OH} + 1/2\text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}$
~85-90	~50	$\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2$
~30-40	~25	$\text{C}_4\text{H}_{10}\text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{by-products}$
~95	~50-60	$\text{CH}\equiv\text{CH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CHO}$

of Chemical Technology," 2nd ed., pp. 77-95, Wiley, New York, 1963. Faith, W. L., Keyes, D. B., Clark, R. L., "Industrial Chemicals," 3rd ed., pp. 1-8, Wiley, New York, 1965. Sittig, M., "Organic Chemical Process Encyclopedia," pp. 1-4, The Noyes Development Corp., New York, 1967.

by the Wacker Process^a

<i>Yield</i>	<i>Conversion per pass, %</i>	<i>Basic Reactions</i>
~95	~95-99	$\text{CH}_2=\text{CH}_2 + 1/2\text{O}_2 \rightarrow \text{CH}_3\text{CHO}$

Guccione, E., *Chem. Eng.* **70** (25), 150-152 (1963).

Schmidt, J., *Chem.-Ing. Technik* **36**, 303-304 (1964).

Faith, W. L., Keyes, D. B., Clark, R. L., "Industrial Chemicals," 3rd ed., pp. 5-6, Wiley, New York, 1965.

Jira, R., *European Chem. News., Large Plant Suppl.* **60**, **62**, **64** (Sept. 1965).

Sittig, M., "Organic Chemical Process Encyclopedia," p. 2, The Noyes Development Corp., New York, 1967.

of ethylene. Obviously a process going directly from ethylene to acetaldehyde would be more economical than one *via* ethanol. In the process using LPG as starting material many by-products are formed from which

acetaldehyde must be separated. Finally, hydration of acetylene, an old standby, suffers from the economic disadvantage that acetylene is now more expensive than ethylene.

Table III. Catalytic Oxidation of Ethylene

Pertinent Literature Data to 1956^a

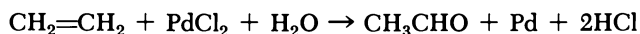
<i>Reference</i>	<i>Abstract</i>
Walter, J., German patent 168,291 (Oct. 28, 1904)	Mixture of C ₂ H ₄ , air, and H ₂ O vapors were passed at 400°C. over many catalysts, including Pt, Pd, and Ir, to give formaldehyde.
Karo, W., German patent 356,175 (March 16, 1919)	Mixtures of C ₂ H ₄ , H ₂ , O ₂ , and an inert gas were passed over a Pd-Ni catalyst at 100°C. to give predominantly ethanol.
Blair, E. W., Wheeler, T. S., <i>J. Chem. Soc. Ind.</i> 41, 303T-310T (1922)	Mixtures of C ₂ H ₄ and H ₂ O vapors were passed at 405°-540°C. through an oven, in the absence of catalysts, to give formaldehyde. The authors assume that acetaldehyde is the intermediate in the formaldehyde formation.
van Hoeck, H., French patent, 891,209 (March 1, 1944)	Mixtures of C ₂ H ₄ and air combined with a large excess of CO ₂ were passed over Ag, Au or Pt, to give acetaldehyde.
Imperial Chemical Industries, French patent 1,116,348 (May 7, 1956)	Mixtures of C ₂ H ₄ and H ₂ O vapors reacted at 200°-400°C. and pressures up to 1000 atm., in the presence of catalysts, having a hydrating component (<i>e.g.</i> , Al ₂ O ₃ , WO ₃ , etc.) and a dehydrogenation component (<i>e.g.</i> , Pt, Pd, Ni, Cu, etc.). The ethylene was hydrated to ethyl alcohol, and the latter dehydrogenated to acetaldehyde in one step.

^a Smidt, J. *et al.*, *Angew. Chem.* 71 (5), 176-182 (1959).

Research to convert ethylene directly to acetaldehyde was begun in 1956 at the Consortium für Elektrochemische Industrie G.m.b.H., a subsidiary of Wacker Chemie G.m.b.H., under the direction of J. Smidt. The results of this research were summarized (34, 35) in two fundamental publications and in numerous patents. Smidt and co-workers first surveyed the open literature to determine what approaches had been used to oxidize ethylene and what the resulting oxidation products were. Table III summarizes the pertinent literature findings up to 1956. None of the processes published offered much promise for converting ethylene to acetaldehyde directly. In their initial experiments, Smidt *et al.* (34) passed mixtures of ethylene, oxygen, and hydrogen over a catalyst of palladium deposited on activated carbon, obtaining traces of acetaldehyde. They also found that the acetaldehyde yield was increased when

the catalyst used contained traces of hydrochloric acid. At this point, a question was raised: what was the reaction responsible for acetaldehyde formation—*i.e.*, what kind of noble metal-ethylene interaction might give rise to acetaldehyde formation? Another literature search by the same authors unearthed the fact that interaction of ethylene with noble metal salts can lead to the formation of ethylene-noble metal salt complexes and that the decomposition of such complexes can give acetaldehyde. This literature search, as given by Smidt *et al.* (34) and reviewed recently by others, is given in Table IV. The recognition that acetaldehyde formation occurs *via* a palladium salt-ethylene complex—in particular a palladium chloride-ethylene complex—was fundamental for the further development of the industrial production of acetaldehyde. Decomposition of this complex with water gave acetaldehyde. It was assumed that in an aqueous system, a similar complex is formed, which is rapidly decomposed to acetaldehyde and metallic palladium.

The fact that acetaldehyde could be formed in an aqueous solution containing palladium chloride *a priori* didn't offer much hope for an industrial process since stoichiometric amounts of PdCl₂ are needed (34).



For each mole of acetaldehyde formed, one mole of palladium chloride was reduced to metallic palladium. To make this process industrially attractive, it must be conducted so that palladium chloride acts as a catalyst rather than as an oxidant—*i.e.*, so that the metallic palladium formed is reoxidized to palladium chloride and can be reused for the principal reaction. This was the second fundamental recognition, which helped make this process commercial. The search for proper oxidants for metallic palladium was facilitated by the observation of Smidt *et al.* (34) that if cupric or ferric chloride were added to palladium chloride in the vapor-phase oxidation of ethylene to acetaldehyde, the acetaldehyde yield was increased. Therefore, these compounds were also used in the liquid-phase oxidation. In such a system, the following reactions will occur in the presence of oxygen and hydrochloric acid, the latter being formed by the reaction above (34).

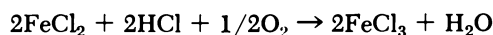
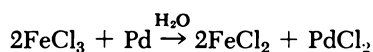
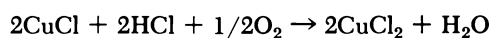
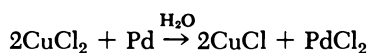
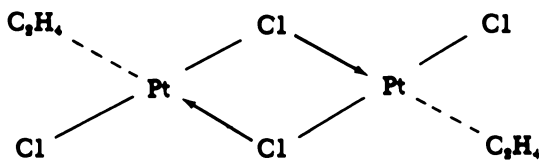


Table IV. Ethylene-Noble Metal Salts Interactions

Pertinent Literature Data to 1956^a

Date	Abstract	Reference
1831	Zeise found that ethylene forms a stable complex with K_2PtCl_4 , the "Zeise Salt," $K[Pt(C_2H_4)Cl_3] \cdot H_2O$.	Zeise, W. C., <i>Pogg. Ann. Chem.</i> 9, 632 (1827); <i>Ibid.</i> , 21, 497 (1831); Bond, G. C., <i>Platinum Metals Rev.</i> 8, 92 (1964).
1894	Introducing ethylene into an aqueous solution of $PdCl_2$ gave acetaldehyde with simultaneous formation of metallic Pd.	Phillips, F. C., <i>Am. Chem. J.</i> 16, 255 (1894).
1933	Analytical determination of palladium using the previous reaction— <i>i.e.</i> , separation from other noble metals.	Ogburn, S. C., Jr., Brastov, W. C., <i>J. Am. Chem. Soc.</i> 55, 1307 (1933).
1934 1936	Hydrolysis of "Zeise Salt," $K[Pt(C_2H_4)Cl_3] \cdot H_2O$ gave acetaldehyde $[PtCl_3 \cdot C_2H_4] + H_2O \rightarrow CH_3CHO + 2HCl + Pt + Cl^-$. In organic solvents a dimeric complex is formed from $PtCl_2$ and C_2H_4 , for which the following structure is proposed:	Anderson, J. S., <i>J. Chem. Soc.</i> 1934, 971; 1936, 1042.



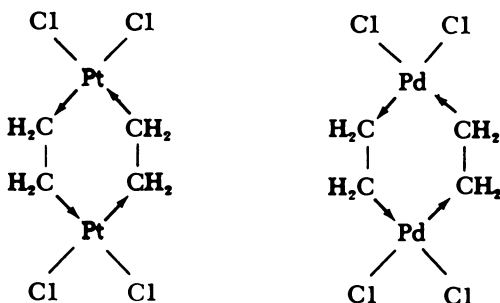
which is also decomposed by water to acetaldehyde.

1936 1938	Platinum complexes of ethylene, similar to those described by Anderson were prepared. No complexes could be obtained by direct interaction of $PdCl_2$ with C_2H_4 ; rather the latter was prepared as follows: $PdCl_2 + 2C_6H_5CN \rightarrow (C_6H_5CN)_2 \cdot PdCl_2$ $2(C_6H_5CN)_2 \cdot PdCl_2 + 2C_2H_4 \rightarrow (C_2H_4 \cdot PdCl_2)_2 + 4C_6H_5CN$	Kharasch, M. S., Ashford, T. A., <i>J. Am. Chem. Soc.</i> 58, 1733 (1936); Kharasch, M. S., Seyler, R. C., Mayo, F. R., <i>J. Am. Chem. Soc.</i> 60, 882 (1938).
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Table IV. Continued

<i>Date</i>	<i>Abstract</i>	<i>Reference</i>
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The following structures were proposed for the dimeric complexes:



When added to water, these dimers decompose into Pt° , Pd° , and acetaldehyde.

1953	For the Zeise salt, a π complex structure is proposed:	Chatt, J., Duncanson, L. A., <i>J. Chem. Soc.</i> 1953, 2939.
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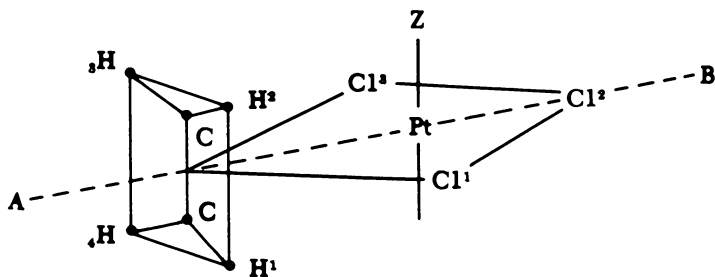
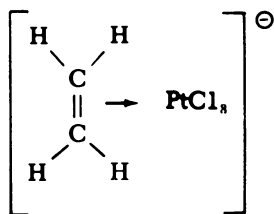
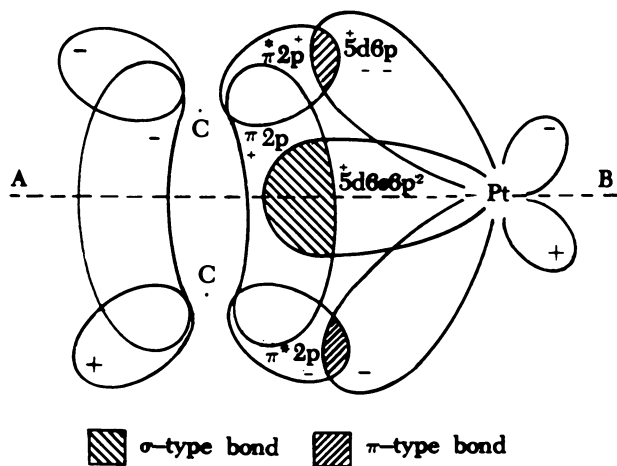


Table IV. Continued

Date	Abstract	Reference
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Hydrolysis here would give PdCl_2 and C_2H_4 ; the latter would be hydrated to $\text{C}_2\text{H}_5\text{OH}$ and oxidized in the presence of PdCl_2 to CH_3CHO .

1955 X-ray studies on the solid Pt-dimer complexes support the structure proposed by Anderson.

Dempsey, J. N., Baenziger, N. C., *J. Am. Chem. Soc.* **77**, 4984-87 (1955).

^a Literature:

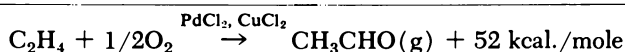
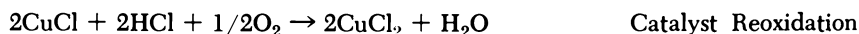
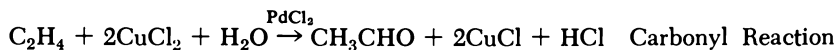
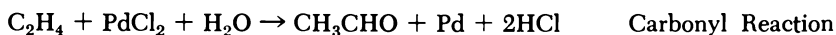
Smidt, J. *et al.*, *Angew Chem.* **71** (5), 176 (1959).

Suceveanu, A., Fordea, C., *Rev. Chim. (Bucharest)* **16**, 499 (1965).

Fischer, E. O., Werner, H., "Metal π -Complexes," Vol. 1, Elsevier, New York, 1966.

These reactions show that PdCl_2 in combination with CuCl_2 or FeCl_3 acts as oxidation-reduction system—*i.e.*, CuCl_2 or FeCl_3 will reoxidize the metallic palladium formed in the previous reaction, while being reduced themselves, and these in turn are reoxidized by air or oxygen to their original state. There is nothing unique about using cupric or ferric chloride. One can use any material whose redox potential is higher than that of palladium chloride. Cupric chloride was selected because of its ease of reoxidation from cuprous to cupric form and also because it is inexpensive. If ethylene is oxidized now with air or oxygen in the presence of palladium chloride and cupric chloride, one indeed has a catalytic rather than a stoichiometric process suitable for commercial application. Part of the cupric chloride in the system will also interact with ethylene

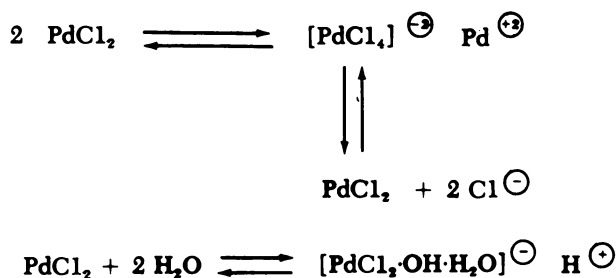
and will convert this to acetaldehyde. The formulas below are the basic equations of the Wacker process (17, 33, 34).



Several proposed mechanisms for the Wacker process are outlined briefly in Table V. Most of these are governed by two factors: the reversible equilibrium process leading to the formation of a palladium chloride-ethylene π -complex, and the irreversible decomposition of this complex. The most important parameters influencing the over-all process appear to be the total Cl^- and H^+ concentrations, as well as the ratios Cl^-/Cu and $\text{Cu}^{2+}/\text{Cu}_{\text{total}}$ (6, 17, 39). Newer investigations claim that the rate of formation of the π -complex depends mainly on the ratio $[\text{Cl}^-]/[\text{PdCl}_2]$, H^+ concentration, and reaction temperature, and that the decomposition rate of the complex is related to a certain critical concentration of the complex proper (3). Influence of mass transfer on the reaction rate owing to ethylene absorption was also investigated (40, 41, 42).

Table V. Some Proposed Reaction Mechanisms for Converting Ethylene to Acetaldehyde

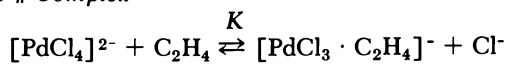
Reactive Species from PdCl₂



Droll, H. A., Block, B. P., Fernelius, W. C., *J. Phys. Chem.* **6**, 1000 (1957).

Zoellner, G., Ruzinko, L., *Magy. Tud. Akad. Kem. Tud. Oszt. Kozlemen.* **25**, 49 (1966).

Table V. Continued

Formation of the π -ComplexEquilibrium Constant, K

Temperature, °C.

18.7 \pm 1.4

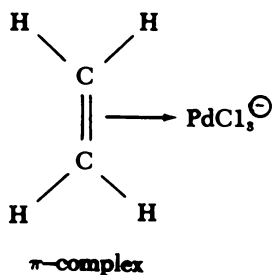
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17.4 \pm 0.4

25

9.7 \pm 1.5

35

Henry, P. M., *J. Am. Chem. Soc.* **86**, 3246 (1964).Henry, P. M., *ADVAN. CHEM. SER.* **70**, 126 (1968).

Acetaldehyde Formation

I.

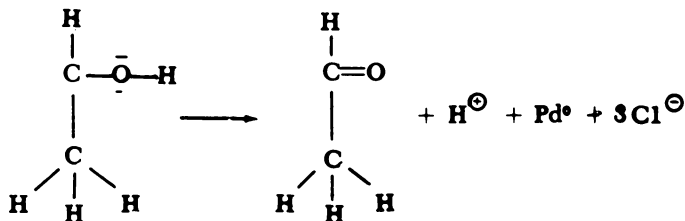
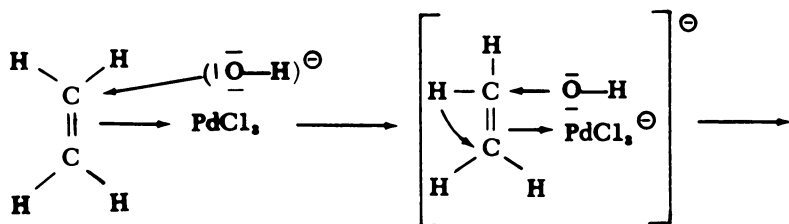
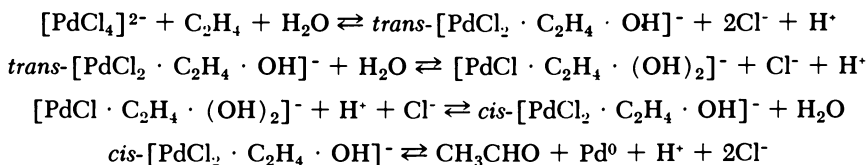
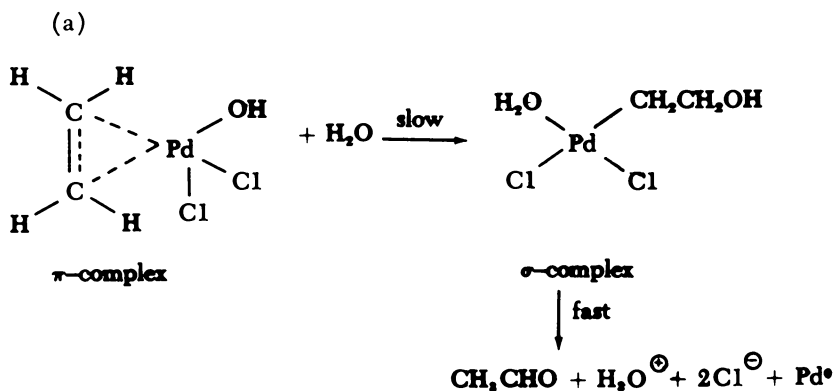
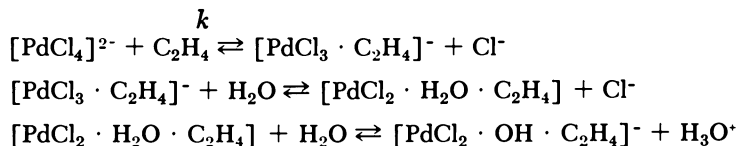
Smidt, J. *et al.*, *Angew. Chem.* **71** (5), 176 (1959); **74** (3), 92 (1962).

Table V. Continued

II.

Jira, R., Sedlmeier, J., Smidt, J., *Ann.* **693**, 99 (1966).

III.



$$\text{Over-all rate expression: } - \frac{d[\text{C}_2\text{H}_4]}{dt} = k'K \frac{[\text{PdCl}_4]^{2-}[\text{C}_2\text{H}_4]}{[\text{Cl}^-][\text{H}^+]}$$

k', sq. moles/sec. $\times 10^4$ 0.53 \pm 0.082.03 \pm 0.25.80 \pm 0.6Temp., $^{\circ}\text{C}$.

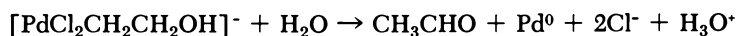
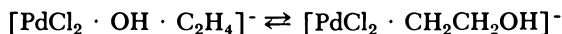
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35

$$\Delta H^{\circ} = 19.8 \text{ kcal./mole; } \Delta S^{\circ} = -8.7 \text{ e.u.}$$

(b)



$$k = 15.2 \pm 0.3 \times 10^2 \text{ liters/mole/sec. at } 25^{\circ}\text{C.; } \Delta H^{\circ} = 16.8 \text{ kcal./mole; } \Delta S^{\circ} = -6.4 \text{ e.u.}$$

(a)

Henry, P. M., *J. Am. Chem. Soc.* **86**, 3246 (1964).Henry, P. M., *ADVAN. CHEM. SER.* **70**, 126 (1968).

Table V. Continued

(b)

Vargaftik, M. N., Moiseev, I. I., Syrkin, Y. K., *Dokl. Akad. Nauk SSSR* **147**, 399 (1962).

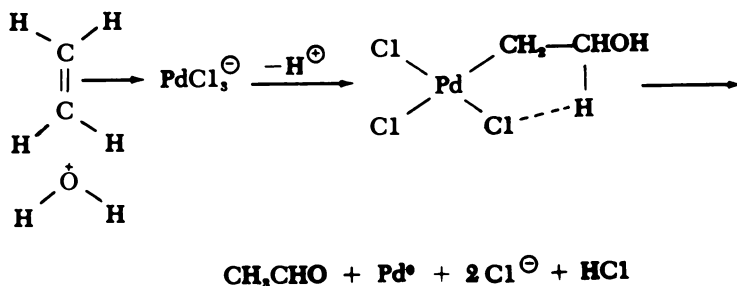
Moiseev, I. I., Vargaftik, M. N., Syrkin, Y. K., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1963**, 1144.

Ibid., *Dokl. Akad. Nauk SSSR* **152**, 147 (1963).

Ibid., **153**, 140 (1963).

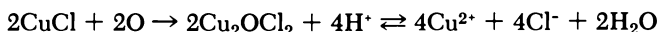
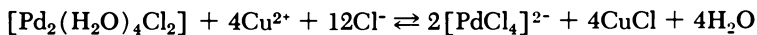
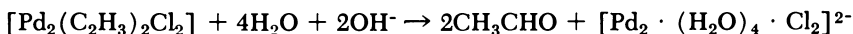
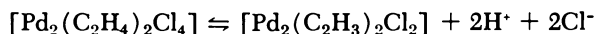
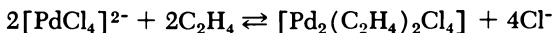
The mechanisms proposed by the authors in (a) and (b) are parallel up to a certain point and differ thereafter.

IV.



Moiseev, I. I., Vargaftik, M. N., Syrkin, Y. U., *Dokl. Akad. Nauk SSSR* **130**, 801-4, 821 (1960).

V.



Matveev, K. I., Osipov, A. M., Odyakov, V. F., Suzdalniskaya, Y. V., Bukhtoyarov, I. F., Emelyanova, O. A., *Kinetika i Kataliz* **3**, 661 (1962); *Kataliticheskie Reaktsii v Zhidkoi Faze, Akad. Nauk. Kaz. SSR, Kazakhsk. Gas Univ., Kazakhsk, Resp. Pravlenie Mendeleevskogo Obshchestva, Tr. Vses. Conf., Alma-Ata* **1962**, 371.

Matveev, K. I., Bukhtoyarov, I. F., Shutts, N. N., Emelyanova, O. A., *Kinetika i Kataliz* **5**, 649 (1964).

According to some authors (4), the rate can be expressed by:

$$-\frac{d\text{C}_2\text{H}_4}{dt} = 1.8 \times 10^6 \exp(-7.4 \times 10^3/RT) [\text{Pd}^{2+}]^{1.0} [\text{Cl}^-]^{-2} p^{1.0}_{\text{C}_2\text{H}_4}$$

whereas according to others (41, 42), the C_2H_4 absorption in the range 0° – 100°C . has the value 0.5 to 1.0×10^4 mole sec^{-1} liters $^{-1}$. An excellent review of the theoretical aspects of this process was given recently (39).

To oxidize ethylene to acetaldehyde technically, two major approaches seem feasible: (a) vapor-phase heterogeneous catalysis, and (b) liquid-phase homogeneous catalysis. The most pertinent references on the vapor-phase process are summarized in Table VI. However, neither this approach nor the electrolytic oxidation of ethylene (14) appears to have gained any commercial importance. Liquid-phase homogeneous catalysis is the approach practiced commercially, and this is understood when one talks about the Wacker process. The latter has been carried out in two principal ways:

(a) The one-stage process, in which ethylene oxidation and catalyst regeneration are carried out in the same reactor.

(b) The two-stage process, in which ethylene oxidation and catalyst regeneration are carried out in separate vessels.

The technical execution of these two approaches is described in Table VII, where some schematic flowsheets are also given.

Table VI. Oxidation of Ethylene to Acetaldehyde

Vapor-Phase Processes

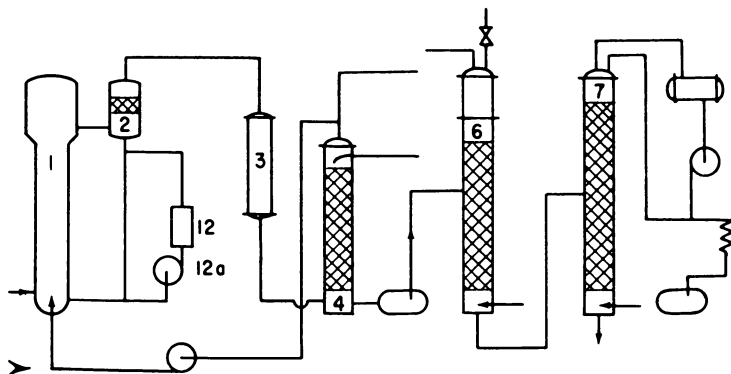
Consortium für Elektrochemische Industrie G.m.b.H.	German patent 1,049,845 (Feb. 5, 1959) 1,118,183 (Nov. 30, 1961)
Farbwerke Hoechst A.G.	German patent 1,123,310 (Feb. 8, 1962) 1,135,880 (Sept. 6, 1962) Netherlands Appl. 6,503,492 (Sept. 27, 1965) C.A. 64, 6497f (1966) Netherlands Appl. 6,504,768 (Oct. 18, 1965) C.A. 64, 11087g (1966) Belgian patent 662,624 (Oct. 18, 1965)
A. Mitsutani, K. Tanaka, and M. Yano	<i>Kogyo Kagaku Zasshi</i> 68 (7), 1219 (1965) C.A. 65, 3732e (1966)
Ruhrchemie A.G.	French patent 1,395,378 (April 9, 1965)
Shell Internationale Research Maatschappij N. V.	Belgian patent 632,884 (Nov. 27, 1963)
Societa Edison S.p.a.	Italian patent 631,868 (Jan. 17, 1962) 640,456 (May 29, 1962) British patent 990,639 (April 28, 1965)

No comparative economic evaluation of all the known commercial acetaldehyde processes has been described in the literature. Recently, the Wacker process was compared with the acetylene process, using European economic data (29). An economic comparison of the one-stage vs. two-stage Wacker processes, using German wage and material price levels of 1961, is given in Table VIII.

Table VII. Technical Execution of Acetaldehyde Manufacture from Ethylene^a

Liquid-Phase Processes

ONE-STAGE PROCESS



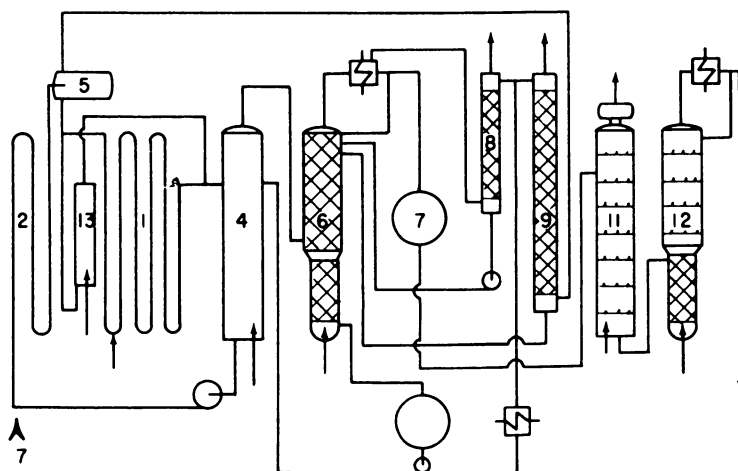
Essential features:

- (1) Synthesis
- (2) Production of pure aldehyde
- (3) Usage of off-gases
- (4) Catalyst regeneration

Into a pressure reactor (1), widened on its upper end, containing an aqueous solution of $\text{CuCl}_2\text{-CuCl-PdCl}_2\text{-HCl}$, 99.7% C_2H_4 and 99% O_2 is fed. At temperatures of $120^\circ\text{-}130^\circ\text{C.}$ and 3 atm., C_2H_4 interacts with O_2 to form CH_3CHO . Owing to the exothermic nature of the reaction, part of the H_2O vaporizes and absorbs the heat developed. Catalyst solution and gases pass into a separator and defoamer (2), where phase separation occurs. The solution is returned to the lower part of the reactor. A side-stream is passed *via* a pump (12a) to the regenerator (12) where thermal regeneration occurs. This serves to decompose the Cu oxalate formed (*see below*). Acetaldehyde, unreacted C_2H_4 , steam, and other residual gases are cooled in a condenser (3) and scrubbed in a scrubber (4) to remove all acetaldehyde. The waters thus obtained, "raw aldehyde"—*i.e.*, 10% CH_3CHO —are collected and submitted to distillation. The off-gases are recycled together with fresh C_2H_4 . Since part of the off-gases contain inert gases (*e.g.*, CH_4 , C_2H_6 , CO_2 , etc.), part of this stream is vented. The aqueous raw aldehyde is first submitted to extractive distillation (6), at which all lower boiling by-products—mainly CH_3Cl and $\text{C}_2\text{H}_5\text{Cl}$ —are removed. The bottoms are passed into a second column (7), which gives CH_3CHO as distillate, whereas the higher boiling impurities (*e.g.*, chlorinated acetaldehyde, acetic acid, crotonaldehyde, chloroform, methylene dichloride, ethylene dichloride, ethylene chlorohydrine, oxalic acid, and water) remain as residues. Acetaldehyde is obtained in 94.5% yield, based on ethylene which is also converted to 0.5% CO_2 , 2% acetic acid and 0.5% chlorinated compound.

Table VII. Continued

TWO-STAGE PROCESS



Essential features:

- (1) Synthesis
- (2) Production of pure aldehyde
- (3) Catalyst regeneration

Ethylene (99%) and air (or O_2) are fed into a reactor (1), where at 100° – $110^{\circ}C$. and 10–11 atm., ethylene oxidation and regeneration of metallic Pd by $CuCl_2$ takes place, whereas regeneration of the reduced $CuCl$ is carried out in a separate oxidation reactor (2), at same temperatures and pressure as above. The catalyst liquor is pumped back from a flash tower (4), where the pressure is reduced to normal. The air is used completely to reoxidize catalyst solution, so that after passing a separator (5) and scrubbers (8 and 9), it is vented. The raw aldehyde is distilled in a column (6) to give a 60–90% aldehyde, which is stored (7), then degassed (11) to remove lower boiling impurities, particularly CH_3Cl and C_2H_5Cl at the top. The bottoms are passed into the second column (12), which gives the pure aldehyde and the higher boiling impurities, as in the one-stage process. The Cu oxalate formed is decomposed in a separate regenerator (13). Acetaldehyde yield, based on ethylene is 95%, besides which 1.0–1.5% acetic acid, 1.0–1.5% CO_2 and 1.3% chlorinated compounds are obtained.

° Literature:

- Berger, G., Mittag, R., *Erdöl Kohle* **15**, 699 (1962).
 Bozeman, H. C., *Oil Gas J.* **60** (42), 216 (1962).
Chem. Eng. **68** (10), 66 (1961).
 Guccione, E., *Chem. Eng.* **70** (25), 150 (1963).
 Jira, R., *European Chem. News, Large Plant Suppl.* **60**, 62, 64 (Sept. 10, 1965).
 Smidt, J. et al., *Angew. Chem.* **71** (5), 176 (1959).
 Smidt, J., *Chem. Ing. Tech.* **36**, 303 (1964).

Table VIII. Economic Evaluation of the One-Stage and Two-Stage Oxidation of Ethylene to Acetaldehyde^a

Costs are based on:

- (1) Ethylene is available at 100-190 p.s.i.g. (min. purity 99%).
- (2) Oxygen comes from existing oxygen plant.
- (3) Investment costs are based on actual capital requirements of plants already in operation, and on German wage and material price levels, as for 1961.

Estimated Investment Including Engineering

<i>Capacity, (tons/yr.)</i>	<i>Single-Stage</i>	<i>Two-Stage</i>
16,530	\$1,375,000	\$1,675,000
33,060	2,025,000	2,400,000
66,120	2,925,000	3,700,000

Raw-Material, Utilities, Personnel Requirements

	<i>Per Ton of Acetaldehyde</i>	
<i>Raw material</i>	<i>Single-Stage</i>	<i>Two-Stage</i>
Ethylene (100-190 p.s.i.g., 99.7% pure)	1,342 lb.	1,342 lb.
Oxygen (100 p.s.i.g., 99% pure)	9,288 std. cu. ft.	—
Hydrochloric acid and catalyst	\$1.36	\$2.72
<i>Utilities</i>		
Cooling water	9,605 cu. ft.	6,403 cu. ft.
Well water	—	48 cu. ft.
Deionized water	96.1 cu. ft.	6.44 cu. ft.
Steam (200 p.s.i.g.)	1.3 ton	0.3 ton
Steam (66 p.s.i.g.)	0.3 ton	0.9 ton
Electric power	190 kwh.	336 kwh.
<i>Personnel (1 supervisor, 1 foreman)</i>		
<i>Man-Hours:</i>		
For 16,530 ton/yr.	1.741	1.741
For 33,060 ton/yr.	0.870	0.870
For 66,120 ton/yr.	0.435	0.435

Total Hourly Requirements (8000 Operating Hours Annually)

<i>Single-Stage with Oxygen</i>	<i>Capacity in tons per year</i>		
	<i>16,530</i>	<i>33,060</i>	<i>66,120</i>
Ethylene (100 p.s.i.g., 99.7% pure)	35,500 std. cu. ft.	71,000 std. cu. ft.	142,000 std. cu. ft.
Oxygen (100 p.s.i.g., 99% pure)	19,200 std. cu. ft.	38,400 std. cu. ft.	76,800 std. cu. ft.
Cooling water	20,300 cu. ft.	40,600 cu. ft.	81,200 cu. ft.

Table VIII. Continued

Deionized water	212 cu. ft.	424 cu. ft.	812 cu. ft.
Steam (200 p.s.i.g.)	2.75 ton	5.4 ton	10.8 ton
Steam (66 p.s.i.g.)	0.66 ton	1.2 ton	2.5 ton
Electric power	400 kwh.	800 kwh.	1,600 kwh.

Two-Stage with Air

Ethylene (190 p.s.i.g., 99.7% pure)	35,500 std. cu. ft.	71,000 std. cu. ft.	142,000 std. cu. ft.
Cooling water	13,240 cu. ft.	26,480 cu. ft.	52,960 cu. ft.
Well water	990 cu. ft.	1,940 cu. ft.	3,880 cu. ft.
Steam (200 p.s.i.g.)	0.66 ton	1.2 ton	2.5 ton
Steam (66 p.s.i.g.)	1.87 ton	3.75 ton	7.5 ton
Electric power	700 kwh.	1,400 kwh.	2,800 kwh.

^a *Literature:*

Chem. Eng. **68** (10), 66 (1961).

Jira, R., *European Chem. News, Large Plant Suppl.* 60, 62, 64 (Sept. 10, 1965).

The liquid-phase oxidation of ethylene to acetaldehyde was pioneered by the Consortium für Elektrochemische Industrie G.m.b.H. Industrially, the single-stage process was developed mainly by Farbwerke Hoechst A. G. and the two-stage process by Wacker Chemie G.m.b.H. itself. Both processes are licensed by Aldehyd G.m.b.H., jointly owned by Wacker Chemie G.m.b.H. and Farbwerke Hoechst G.m.b.H. The basic patents of these two companies on the Wacker process are listed in Table IV. In addition to these patents, which have given Wacker Chemie G.m.b.H. and Farbwerke Hoechst a dominant role in this field, other companies hold some patents in this area (Table X). How many of the patents listed in Tables IX and X are commercially important cannot be judged, based on the open literature alone.

In addition to plants already existing at Farbwerke Hoechst A. G. and Wacker Chemie G.m.b.H. in Germany, other plants have been or are being built by Rhône-Poulenc, France; Societa Edison, Italy; Pemex, Mexico; Celanese Corp. at Bay City, Tex.; and Shawinigan Chemicals Ltd., Canada. Plants are also being installed in Japan. Some use the one-stage, others the two-stage process for acetaldehyde manufacture, licensed by the Aldehyd G.m.b.H.

Apart from the commercial acetaldehyde processes thus far discussed, one noncommercial process currently being developed deserves some attention. It consists of isomerizing ethylene oxide to acetaldehyde, and its literature is summarized in Table XI. Since ethylene oxide is made by oxidizing ethylene, this method may be regarded as a variation of the Wacker process.

Table IX. Principal Patents of the Wacker Process Issued to Consortium für Elektrochemische Industrie G.m.b.H. and to Farbwerke Hoechst A.G.

<i>Consortium für Elektrochemische Industrie G.m.b.H.</i>	<i>Farbwerke Hoechst A.G.</i>
German Patents	German Patents
1,061,767 (July 23, 1959)	1,123,312 (Feb. 8, 1962)
1,080,994 (May 4, 1960)	1,129,469 (May 17, 1962)
1,118,183 (Nov. 30, 1961)	1,130,427-8 (May 30, 1962)
1,127,883 (April 19, 1962)	1,132,111 (June 28, 1962)
1,129,470 (May 17, 1962)	1,132,553 (July 5, 1962)
1,132,909 (July 12, 1962)	1,132,910 (July 12, 1962)
1,137,426 (Oct. 4, 1962)	1,134,364 (Aug. 9, 1962)
1,142,351 (Jan. 17, 1963)	1,145,602 (March 21, 1963)
1,152,496 (July 18, 1963)	1,147,569 (April 25, 1963)
1,163,308 (Feb. 20, 1964)	1,148,536 (May 16, 1963)
1,215,677 (May 5, 1966)	1,150,376 (June 20, 1963)
British Patents	1,150,668 (June 27, 1963)
878,777 (Oct. 4, 1961)	1,154,450 (Sept. 19, 1963)
884,962-3 (Dec. 20, 1961)	1,156,396 (Oct. 31, 1963)
893,157-8 (March 21, 1962)	1,183,488 (Dec. 17, 1964)
U.S. Patent	1,190,451 (April 8, 1965)
3,080,425 (March 5, 1963)	British Patents
	898,790 (June 14, 1962)
	900,829 (July 11, 1962)
	938,836 (Oct. 9, 1963)
	U.S. Patents
	3,076,032 (Jan. 29, 1963)
	3,121,673 (Feb. 18, 1964)
	Belgian Patents
	617,325 (Nov. 7, 1962)
	635,230 (Jan. 22, 1964)
	Netherlands Patent
	Appl. 6,507,077 (Dec. 6, 1965);
	C.A. 64, 15747c (1966)

Vinyl Acetate Manufacture

In contrast to acetaldehyde, where a choice exists between several well-established manufacturing processes, vinyl acetate has been produced until recently by two principal methods—*i.e.*, by the catalytic vapor-phase acylation of acetylene and by the acetalization of acetaldehyde. The new procedure for vinyl acetate manufacture consists of oxidizing ethylene in acetic acid—a process closely related to the Wacker acetaldehyde process. All three manufacturing approaches are outlined in Table XII.

The formation of vinyl acetate from ethylene was first reported by Moiseev *et al.* (31). The compound was obtained by reaction of ethylene with PdCl_2 in an acetic acid solution containing sodium acetate. Whether in this medium vinyl acetate formation occurs *via* the monomeric $[\text{PdCl}_3 \cdot \text{C}_2\text{H}_4]^- \pi$ -complex, postulated as intermediate in the Wacker acetaldehyde process, or *via* the dimer $(\text{C}_2\text{H}_4 \cdot \text{PdCl}_2)_2$, previously described by

Table X. Oxidation of Ethylene to Acetaldehyde by Liquid Phase Processes^a

Esso Research and Engineering Co.	British patent 902,368 (Aug. 1, 1962)
Japan Synthetic Chemical Ind. Co., Ltd.	Belgian patent 628,848 (June 16, 1963)
Union Carbide Corp.	Belgian patent 646,482 (July 3, 1964) French patent 1,395,129 (April 9, 1965)
A. V. Arbatskii <i>et al.</i>	Russian patent 163,602 (July 22, 1964) C.A. 62, 446f (1965)
M. Y. Klimenko <i>et al.</i>	Russian patent 145,231 (Feb. 5, 1965) C.A. 62, 14209a (1965)
D. V. Sokolskii <i>et al.</i>	Russian patent 171,860 (June 22, 1965) C.A. 63, 16217f (1965)
Eastman Kodak Co.	Belgian patent 662,066 (Aug. 2, 1965)
Dow Chemical Co.	British patent 914,561 (Jan. 2, 1965) U.S. patent 3,202,715 (Aug. 24, 1965)
Lummus Co.	French patent 1,412,247 (Sept. 24, 1965)
Inst. of Catalysis, Siberian Dept. of the Academy of Sciences, U.S.S.R. and Scientific-Research Inst. for Synthetic Alcohol and Organic Products	Russian patent 176,258 (Nov. 2, 1965) C.A. 64, 1066h (1966)
Halcon International	Netherlands Appl. 6,505,941 (Nov. 22, 1965); C.A. 64, 12551f (1966)

^a Companies other than those belonging to the Wacker concern.

Table XI. Acetaldehyde from Ethylene Oxide

Farbwerke Hoechst A.G.	German patent 1,035,635 (Aug. 7, 1958) U.S. patent 3,067,256 (Dec. 4, 1962) German patent 1,150,668 (June 27, 1963)
Sicedison Societa per Azioni	French patent 1,316,720 (Feb. 1, 1963)
British Petroleum Co. Ltd.	French patent 1,367,963 (July 24, 1964)

Table XII. Vinyl

Starting Materials	Process	System	Reaction Conditions
CH \equiv CH	Vapor phase catalytic acylation	Heterogeneous	Purified acetylene and acetic acid vapors are passed over Zn(OOCCH $_3$) $_2$ on carbon.
CH $_3$ CHO	Liquid phase catalytic acetalization	Homogeneous	Acetaldehyde and acetic anhydride react in liquid phase in the presence of a catalyst to give ethylidene diacetate, which decomposes to acetic acid and vinyl acetate.
CH $_2$ =CH $_2$	Liquid phase catalytic oxidative acylation	Homogeneous	Ethylene is oxidized in acetic acid solution containing a metal acetate (<i>e.g.</i> , NaOOCCH $_3$) in the presence of a Pt metal salt, (<i>e.g.</i> , PdCl $_2$), and a redox system (<i>e.g.</i> , CuCl $_2$, MnO, etc.) at elevated pressure.

* Literature:

Sittig, M., "Organic Chemical Processes," p. 103, Noyes Press, New York, 1962.

Anderson (2) and Kharasch (22, 23), was not established. [The complexes described by Anderson and Kharasch are believed today to be dimers of [PdCl $_3 \cdot C_2H_4$] $^-$ (7, 25, 28)]. Moiseev *et al.* left both possibilities open. Stern and Spector (37) favored the dimeric intermediate. They obtained vinyl acetate in 22 mole % yield, by reaction of ethylene with PdCl $_2$ in isooctane containing acetic acid and Na $_2$ HPO $_4$.

These publications gave impetus to the technological development of the vinyl acetate synthesis from ethylene. Since a close analogy exists between this process and the Wacker acetaldehyde process, the vinyl acetate process was developed along the same lines as the latter. Thus, PdCl $_2$ was combined with several redox systems to make the process technologically feasible, and although both vapor- and liquid-phase processes were developed, apparently only the liquid-phase procedure was adopted for commercial use. Both the one-stage and two-stage liquid phase processes are used. In contrast to the Wacker process, where the Consortium für Elektrochemische Industrie G.m.b.H. and Farbwerke Hoechst A.G. hold a dominant patent position, no such exclusiveness exists here, and many companies have been actively developing processes for producing vinyl acetate from ethylene. Table XIII gives the most pertinent patents of the liquid-phase process, arranged alphabetically by company rather than chronologically. Based on the published literature alone, it is difficult to judge which of the processes described is practiced

Acetate Manufacture^a

Yield, %	Conversion per pass, %	<i>Basic Equations</i>
~92-95	~60-70	$\text{CH}\equiv\text{CH} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COOCH}=\text{CH}_2$
—	—	$\text{CH}_3\text{CHO} + (\text{CH}_3\text{CO})_2\text{O} \rightarrow$ $\text{CH}_3\text{CH}(\text{OOCCH}_3)_2$ \downarrow $\text{CH}_2=\text{CHOOCCH}_3 + \text{CH}_3\text{COOH}$
~70-92	~30-50	$\text{CH}_2=\text{CH}_2 + 1/2\text{O}_2 + \text{CH}_3\text{COOH} \rightarrow$ $\text{CH}_2=\text{CHOOCCH}_3 + \text{H}_2\text{O}$

Arganbright, R. P., Evans, R. J., *Petroleum Refiner* **43** (11), 159 (1964).

Faith, W. L., Keyes, D. B., Clark, R. L., "Industrial Chemicals," 3rd ed., pp. 800-804, Wiley, New York, 1965.

Table XIII. Preparation of Vinyl Acetate from Ethylene*Liquid Phase Processes*

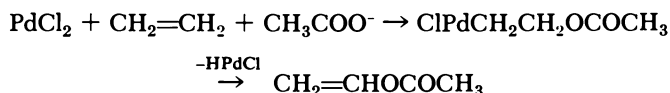
British Celanese Ltd.	Netherlands Appl. 6,506,734 (Nov. 29, 1965); C.A. 64 , 1574f (1966)
Celanese Corp. of America	Belgian patent 668,284 (Feb. 14, 1966)
Consortium für Elektrochemische Industrie G.m.b.H.	German patent 1,176,645 (Aug. 27, 1964) French patent 1,370,867 (Aug. 28, 1964) German patent 1,190,931 (April 15, 1965) 1,191,362 (April 22, 1965)
Courtaulds Ltd.	Netherlands Appl. 6,501,821 (Aug. 16, 1965); C.A. 64 , 8042e (1966)
Distillers Co.	British patent 928,739 (June 12, 1963) French patent 1,388,556 (Feb. 5, 1965) French patent 1,412,151 (Sept. 24, 1965) British patent 1,010,548 (Nov. 17, 1965) Netherlands Appl. 6,511,272 (March 7, 1966); C.A. 65 , 2129h (1966)
E. I. duPont deNemours & Co.	Netherlands Appl. 6,501,905 (Aug. 18, 1965); C.A. 64 , 4948d (1966); 6,509,-320 (Feb. 18, 1966); C.A. 65 , 2130b (1966)
Farbwerke Hoechst A.G.	Belgian patent 615,596 (Sept. 26, 1962)

Table XIII. Continued

Imperial Chemical Industries, Ltd.	Belgian patent 608,610-11 (Sept. 27, 1961) 634,595 (Jan. 6, 1964) 635,-425-6 (Jan. 27, 1964) 635,679 (Jan. 31, 1964) 638,268 (Apr. 6, 1964) British patent 964,001 (July 15, 1964) 969,162 (Sept. 9, 1964) 975,709 (Nov. 18, 1964) French patent 1,387,750 (Jan. 29, 1965) Netherlands Appl. 6,412,134 (May 10, 1965); C.A. 63, 13085f (1965); 6,413,-733 (May 31, 1965); C.A. 63, 17910c (1965)
Japan Synthetic Chemical Ind. Co., Ltd.	Belgian patent 618,071 (Sept. 17, 1962) Japan patent 28,090(65) (Dec. 13); C.A. 64, 11089c (1966); 28,089(65) (Dec. 13); C.A. 64, 12553f (1966)
I. I. Moiseev and M. N. Vargaftik	Russian patent 137,511 (Appl. April 19, 1960); C.A. 56, 1365a (1962)
M. N. Vargaftik and I. I. Moiseev	Russian patent 145,569 (March 21, 1962); C.A. 57, 16410g (1962)
National Distillers and Chemical Corp.	U.S. patent 3,227,747 (Jan. 4, 1966)
Rhône-Poulenc S.A.	French patent 1,339,614 (Oct. 11, 1963) Belgian patent 635,739 (Feb. 3, 1964) French Addn. 83,214 (July 3, 1964); Addn. to French 1,339,614 French patent 1,388,869 (Feb. 12, 1965) British patent 990,444 (April 28, 1965)
Shell Internationale Research Maatschappij N. V.	Belgian patent 614,970 (Sept. 12, 1962) Netherlands Appl. 6,406,180 (Dec. 3, 1965); C.A. 64, 11091d (1966) French patent 1,325,696 (March 25, 1963)
Societa Italiana Resine S.p.A.	Belgian patent 672,580 (March 16, 1966)
Union Carbide Corp.	Belgian patent 628,885 (March 21, 1963) 629,885 (July 15, 1963) 647,873 (Aug. 31, 1964) U.S. patent 3,221,945 (Nov. 30, 1965) 3,238,247 (March 1, 1966)
Union Oil Co. of California	British patent 1,032,325 (June 8, 1966) U.S. patent 3,260,739 (July 12, 1966) 3,277,158 (Oct. 4, 1966)

commercially and which is only in the development stage. For completeness, the most pertinent references of the vapor phase process are listed in Table XIV.

No detailed reaction mechanism for the formation of vinyl acetate from ethylene was found in the literature surveyed. Some aspects of this reaction were discussed recently by Henry (16), who formulates the reaction in the following way:



An interesting aspect of this reaction is that it does not postulate a complex intermediate.

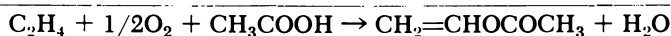
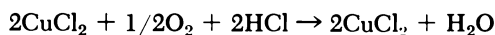
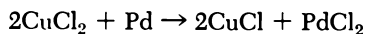
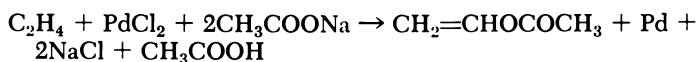
Table XIV. Preparation of Vinyl Acetate from Ethylene
Vapor Phase Processes

Asahi Chemical Industry	Belgian patent 638,489 (Oct. 10, 1963) French patent 1,371,111 (Aug. 28, 1964) British patent 1,003,499 (Sept. 12, 1965)
Distillers Co., Ltd.	German patent 1,160,846 (Dec. 8, 1965) British patent 928,739 (June 12, 1963) 1,003,347 (Sept. 2, 1965)
Farbenfabriken Bayer A.G.	German patent 1,185,694 (Feb. 3, 1962) French patent 1,346,219 (Dec. 13, 1963) British patent 981,987 (March 2, 1965) French patent 1,397,083 (April 23, 1965) Belgian patent 667,004 (Jan. 17, 1966)
Farbwerke Hoechst A.G.	Netherlands Appl. 6,503,432 (Sept. 27, 1965); C.A. 64, 4947b (1966) 6,504,302 (Oct. 18, 1965); C.A. 64, 12554a (1966) 6,507,073 (Dec. 6, 1965); C.A. 64, 17430e (1966)
National Distillers and Chemical Corp.	British patent 976,613 (Dec. 2, 1964) French patent 1,407,526 (July 30, 1965)
Pullman, Inc.	British patent 1,017,604 (Jan. 19, 1966)
M. Yano, A. Mitsutani, and K. Tanaka	<i>Kogyo Kagaku Zasshi</i> 68(8), 1620-1 (1965); C.A. 63, 17824h (1965)

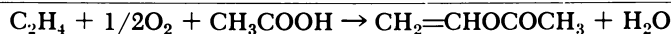
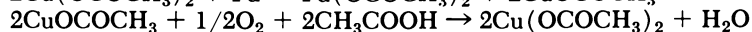
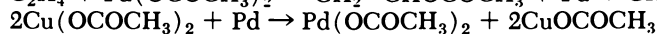
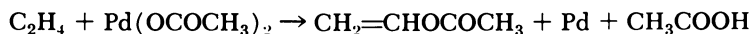
Some over-all reactions of the ethylene-to-vinyl acetate process with either $\text{PdCl}_2 + \text{CuCl}_2$ or with $\text{Pd}(\text{OCOCH}_3)_2 + \text{Cu}(\text{OCOCH}_3)_2$ as catalysts are formulated in Table XV. Simplified flowsheets of the one-stage and two-stage processes are shown in Figures 1 and 2.

Table XV. Basic Equations^a and Estimated Production Costs^b for Converting Ethylene to Vinyl Acetate^c

Catalyst System: PdCl₂ + CuCl₂



Catalyst System: Pd(OCOCH₃)₂ + Cu(OCOCH₃)₂



£ /ton of vinyl acetate

Raw materials

Ethylene 33,400 ton at £ 30/ton	20.0
Acetic acid 35,800 ton at £ 64/ton	45.8
Oxygen 19,200 ton at £ 5/ton	1.9
Catalyst and chemicals, say	2.0

69.7

Less acetaldehyde 25,600 ton at £ 48.2/ton

24.7

Net raw material cost

45.0

Steam, 200,000 ton at 15s./ton

3.0

Power, 8 × 10⁶ kwh at 1 day

0.7

Water, 10¹⁰ gal. at 3 days/10³ gal.

2.5

Sub Total

51.2

Labor and supervision (4 men/shift)

0.5

Work overhead, say

3.0

Sub Total

54.7

Depreciation at 10% of capital

9.0

Maintenance at 5% of capital

4.5

Insurance at 1.5% of capital

1.4

Production cost

69.6

^a Literature:

Arganbright, R. P., Evans, R. J., *Petrol. Refiner* **43** (11), 159 (1964).

Courtaulds, Ltd., Netherlands Appl. 6,501,821 (Aug. 16, 1965); C.A. **64**, 8042e (1966).

^b *Chem. Process Eng.* 71, 72, 78 (March 1967).

The estimated capital cost is based on the apparatus in Figure 1 using stainless steel for stills 1, 2, 4, 6, and 7; copper for stills 8 and 9, and mild steel for stills 3 and 5. The reactor is constructed from a mild steel pressure vessel with titanium lining.

The economics of this process, compared with the acetylene process, will depend on the ratio of acetylene to ethylene prices per unit weight. This ratio is 2:1 to 3:1, based on recent literature data (11, 29, 38). Although one cannot obtain exact data, prices of 10 cents per lb. for acetylene *vs.* 5 cents per lb. of ethylene have been quoted. A savings of \$28 per metric ton may be obtained using the Wacker process (11, 20).

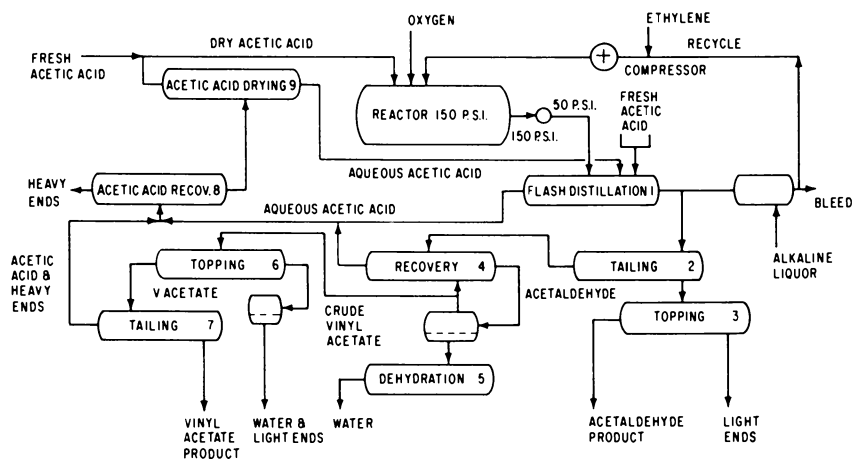


Figure 1. Schematic flowsheet for the liquid-phase conversion of ethylene to vinyl acetate in a one-stage process (Chem. Process Eng. 71, 72, 78 (March 1967))

Fresh ethylene and recycled gas are compressed to 150 p.s.i.g. and pumped into the reactor where the reaction is carried out at 120°–130°C. The latter contains a suspension of catalyst and promoters suspended in acetic acid. Recovered acetic acid and fresh acid and oxygen are pumped into the reactor. A supply of HCl (not shown) is also necessary. Excess ethylene, containing vinyl acetate, acetaldehyde, and a small amount of H₂O and acetic acid, is expanded to ca. 50 p.s.i.g. by flash distillation. At this point, acetaldehyde is separated from vinyl acetate. The bottoms from the acetaldehyde still will contain all the vinyl acetate together with H₂O and acetic acid. Vinyl acetate is separated from the H₂O by a decanter and distilled to remove H₂O and light ends. Subsequently, the bottom from this distillation is submitted to a final distillation to give pure vinyl acetate. Acetic acid is recovered by distillation.

A recent study indicates that if the Wacker process proves to be substantially cheaper than the acetylene route, no more vinyl acetate plants will be built in the United States, based on the latter process (38). Table XV gives estimated production costs for manufacturing vinyl acetate. Several companies are building or have already built plants to manufacture vinyl acetate from ethylene. These include Distillers Co., Ltd., British Celanese, Imperial Chemical Industries, and Celanese Corp., to name only a few.

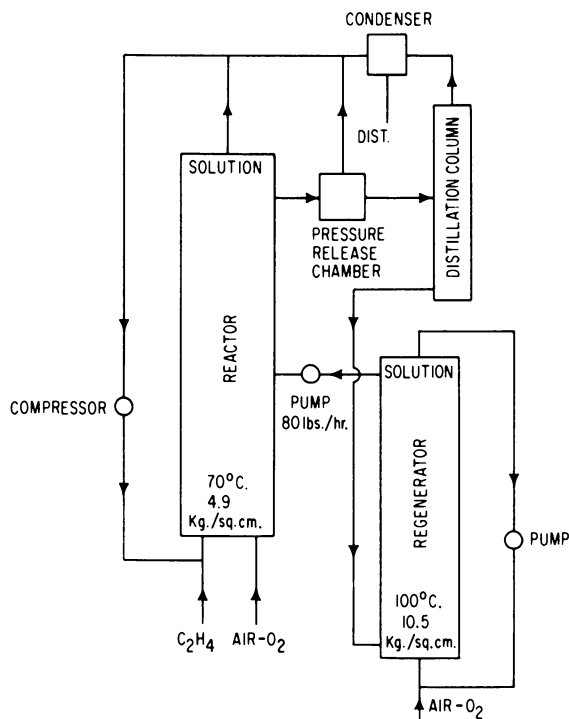


Figure 2. Schematic flowsheet for the liquid-phase conversion of ethylene to vinyl acetate in a two-stage process (Courtaulds, Ltd., Netherlands Appl. 6,501,821 (Aug. 16, 1965)); C.A. 64, 8042e (1966)

Solution	Parts by wt.	Distillate	(after 6 hrs. operation)
CH ₃ COOH	105	CH ₂ =CHOCOCH ₃	690.5 grams
KOCOCH ₃	10	CH ₃ CHO	13.5 grams
Pd(OCOCH ₃) ₂	0.18		
Cu(OCOCH ₃) ₂	2		

Both the regenerator and the reactor are charged with a solution of composition given above. The pump from the regenerator to the reactor is started. The reactor kept at 70°C. and 4.9 kg./sq. cm. and the regenerator at 100°C. and 10.5 kg./sq. cm. Mixture of C₂H₄ and air-O₂ is fed into the reactor in the proportion of 93:7 and at the rate of 7.7 cu. meters/hr.; that to the regenerator at the rate of 0.28 cu. meters/hr. The solution is passed to the pressure release chamber, unreacted gases recycled, vinyl acetate and acetaldehyde removed by distillation in the distillation column, the bottoms of which are passed into the regenerator for regeneration with air-O₂.

A recent article gave the following market figures for 1965 and estimates for 1970 for vinyl acetate production (12):

Production, 1965	503 million pounds
1970 ^a	1060
Production growth rate, last five years	15.81%
next five years ^a	14.68%
Capacity, 1965	575 million pounds
1970 ^a	1190
Capacity growth rate, last five years	14.74%
next five years ^a	13.75%
Price, 1965	0.11 cents per lb.
1970 ^a	0.09

^a These estimates were made using the exponential trend techniques and carrying out the computations on a time-shared computer.

Phenol Manufacture

The most important methods for producing phenol commercially and for obtaining phenol by methods other than direct synthesis (natural phenol) are briefly summarized in Table XVI. The essential features of

Table XVI. Principal Methods for Producing and Obtaining Phenol^a

From Benzene (major processes)	(a) Sulfonation, followed by alkaline fusion of sodium benzenesulfonate, and acidification to liberate the phenol produced (Benzene Sulfonate Process)
	(b) Chlorination, followed by alkaline fusion of chlorobenzene, and acidification (Chlorobenzene Caustic Process) (Dow Process)
	(c) Chlorination with HCl + O ₂ , followed by catalytic hydrolysis of chlorobenzene and recycle of the HCl produced (Regenerative Raschig Process) (Hooker Process)
	(d) Alkylation with propylene, followed by hydroperoxidation of the cumene formed, and acid cleavage of the hydroperoxide (Cumene Hydroperoxide Process)
From Benzene (minor processes, only partially commercial)	(a) Hydrogenation to cyclohexane, followed by oxidation to a mixture of cyclohexanol and cyclohexanone, and catalytic dehydrogenation of this mixture to phenol (Scientific Design Process)
	(b) Direct oxidation to phenol, using various oxidizing agents or irradiation, performing the process in liquid or vapor phase

Table XVI. Continued

From Various Sources (minor processes, only partially commercial)	(a) By dealkylation of alkyl phenols (b) By decomposition of certain diazo compounds
Natural Phenol (obtained as by-product from various sources; minor processes, only partially commercial)	(a) From coal tar by extraction (b) From gas liquor by steam distillation or extraction (c) From lignin by thermal decomposition or hydrogenation (d) From synthetic fuel oils, produced in coal hydrogenation, by extraction (e) From sour petroleum oils by extraction (f) From oil shale by distillation

* Literature:

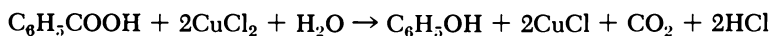
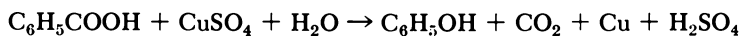
- Agnello, L. A., Williams, W. H., *Ind. Eng. Chem.* **52**, 894-897, 900 (1960).
 Agnello, L. A., Williams, W. H., "Modern Chemical Processes," Vol. VIII, pp. 55-61, Reinhold, New York, 1963.
 Banciu, A. S., *Rev. Chim. (Bucharest)* **16**, 211 (1965).
 Cubberley, A. H., "Encyclopedia of Chemical Technology," R. E. Kirk, D. F. Othmer, eds., 1st ed., Vol. 10, pp. 279-294, Wiley, New York, 1953.
 Faith, W. F., Keyes, D. B., Clark, R. L., "Industrial Chemicals," 3rd ed., pp. 583-594, Wiley, New York, 1965.
 Groggins, P. H., "Unit Processes in Organic Synthesis," 5th ed., pp. 795-803, McGraw-Hill, New York, 1958.
 Hay, J. M., Stirling, D. W., Weaver, C. W., *Oil Gas J.* 83-88 (Jan. 3, 1966).
 Kropf, H., *Chem. Ing. Tech.* **36**, 759 (1964).
 Lindner, O., *Chem. Ing. Tech.* **36**, 769 (1964).
 Lindner, O., "Ullmann's Encyklopaedie der Technischen Chemie," 3rd ed., Vol. 13, pp. 424-429, Urban & Scharzenberg, Munich-Berlin, 1962.
 Sittig, M., "Organic Chemical Processes," pp. 80-83, Noyes Press, New York, 1962.
 Sittig, M., "Organic Chemical Process Encyclopedia," pp. 428-433, The Noyes Development Corp., New York, 1967.

the major synthetic phenol manufacturing procedures are listed in Table XVII. All major procedures use benzene as starting material, and all are multistep processes. Although the one-step direct oxidation of benzene to phenol has been described in numerous publications, this approach is apparently not yet commercially feasible.

The incentive for a novel phenol synthesis was economical. Kaeding has noted that toluene is the cheapest and potentially the most abundant source for aromatic chemicals (19, 20, 21). In addition, market studies indicated that the potential yearly phenol volume in the 1960's will approach a billion pounds and two billion pounds in the 1970's (9, 12). With this background, phenol synthesis, based on toluene rather than benzene, was initiated. The essential features of this new process are given in Table XVIII. Using toluene as starting material, it was developed separately and independently by two research groups, one at the Dow Chemical Co. under the direction of Kaeding, the other at the

California Research Corp. under the direction of Toland. Since one-step oxidation of toluene to phenol did not seem feasible, a multistep synthesis was developed. Toluene can be oxidized under various conditions by known methods to benzoic acid. The easiest, most economical method is the catalytic, liquid-phase oxidation with air (27, 30).

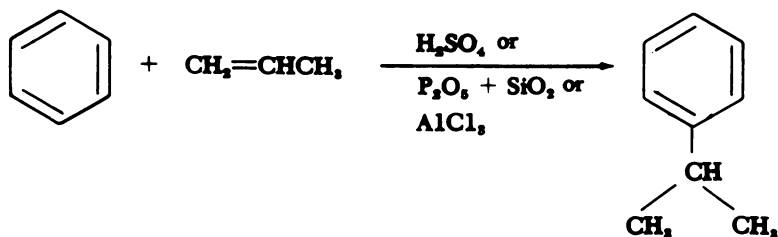
The crucial step of the new phenol synthesis is oxidizing the obtained benzoic acid to phenol. Early literature data indicated that heating copper benzoate or benzoic acid in the presence of copper salts gave various phenol precursors—*e.g.*, phenyl benzoate and salicylic acid, as well as phenol itself (3, 10, 13, 24, 26, 36). In one of the initial approaches, by Dow Chemical Co., mixtures of benzoic acid vapors, air, and steam were passed over a CuO catalyst promoted with metal salts, giving phenol and phenyl benzoate (5). However, much tar was produced, probably because of the high reaction temperature, which led to excessive decomposition. Because of this, the vapor-phase method was abandoned in favor of the liquid-phase process. Next, benzoic acid was oxidized in aqueous solution with inorganic copper salts, as shown below (18):



These reactions were carried out in an autoclave, giving relatively low phenol yields, probably because the phenol formed was further oxidized at the high reaction temperatures. Organic solvents were used next, and benzoic acid itself was an attractive solvent since its high boiling point permits the reaction to be carried out at atmospheric pressure. It is also a good solvent for the key catalyst, copper benzoate, and for the promoter, magnesium oxide or benzoate. It gives a high yield of the key intermediate—phenyl benzoate—whose hydrolysis leads to the desired phenol. The basic reactions for the process are given in Table XIX. The essential feature of this process, as with the Wacker acetaldehyde and the ethylene-to-vinyl acetate process, is the use of a redox system—in this case, cupric benzoate. The latter is reduced to the cupro form and reoxidized back to the cupric form with air. Steam is added to the mixture, after the reaction has been terminated, to hydrolyze the phenol precursors to phenol itself. Some tar formation occurs during manufacture, probably because of ring cleavage of both the precursors and of phenol itself, to olefinic products, which in turn are probably polymerized (1). In a recent publication several oxidation inhibitors have been proposed to reduce tar formation and increase phenol yield (1). Some proposed mechanisms for the decomposition of cupric benzoate to phenol are outlined briefly in Table XX.

Table XVII. Major Synthetic

<i>Process</i>	<i>Major Reaction Steps</i>
Benzene Sulfonate Process	(a) Sulfonation $C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O$
	(b) Neutralization $2C_6H_5SO_3H + Na_2SO_3 \rightarrow 2C_6H_5SO_3Na + H_2O + SO_2$ $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$
	(c) Separation of $C_6H_5SO_3Na$ from Na_2SO_4
	(d) Fusion $2C_6H_5SO_3Na + 4NaOH \rightarrow 2C_6H_5ONa + 2Na_2SO_3 + 2H_2O$
	(e) Acidification $2C_6H_5ONa + SO_2 + H_2O \rightarrow 2C_6H_5OH + Na_2SO_3$
	(f) Purification of C_6H_5OH by distillation
Chlorobenzene Caustic Process (Dow Process)	(a) Electrolysis $2NaCl + 2H_2O \xrightarrow{2F} 2NaOH + H_2 + Cl_2$
	(b) Chlorination $C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$
	(c) Alkaline hydrolysis $C_6H_5Cl + 2NaOH \rightarrow C_6H_5ONa + NaCl + H_2O$
	(d) Acidification $C_6H_5ONa + HCl \rightarrow C_6H_5OH + NaCl$
Regenerative Raschig Process (Hooker Process)	(a) Chlorination $C_6H_6 + HCl + 1/2O_2 \rightarrow C_6H_5Cl + H_2O$
	(b) Hydrolysis $C_6H_5Cl + H_2O \rightarrow C_6H_5OH + HCl$
Cumene Hydroperoxide Process	(a) Alkylation



Phenol Manufacturing Processes*

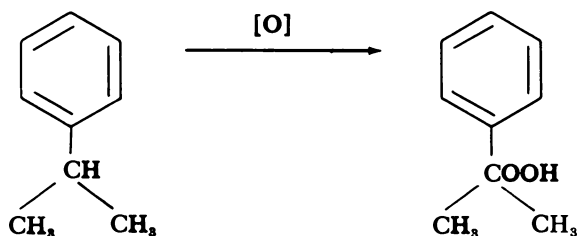
<i>Reaction Conditions</i>	<i>Over-all Yield, %</i>
Countercurrently, 100°–185°C.	~85–90
Agitated tank	
Centrifugation	
300°–380°C. 5–6 hrs.	
Dilution with H ₂ O	
Vacuum distillation	~80–95
Anhydrous condition	
Diphenyl ether is added: 4000–5000 p.s.i.g. 260°–370°C. turbulent flow	
Vapor phase 210°–290°C., CuCl ₂ -FeCl ₃ catalysts	~72–92
Vapor phase 420°–500°C., SiO ₂ or Ca ₃ (PO ₄) ₂ catalyst, conversion per pass 8–15%	
Liquid phase (or vapor phase)	~70–90

Table XVII. Continued

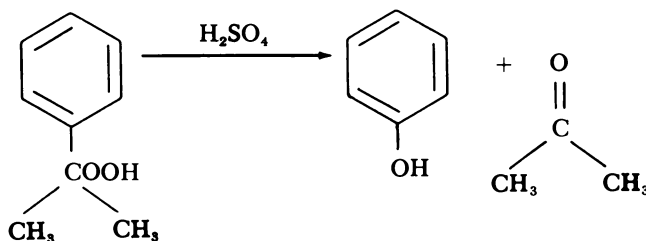
Cumene Hydroperoxide
Process (Continued)

Reaction Conditions

(b) Oxidation

80°–130°C., air
or O₂, 4–6 atm.

(c) Acid Cleavage

40°–70°C.,
10–60% H₂SO₄
in (CH₃)₂CO

* Literature: see Table XVI.

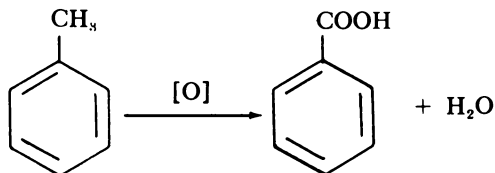
Table XVIII. Manufacture of Phenol from Toluene*

Process: Toluene-Benzoic Acid (Dow Toluene Process) (Kaeding Process)

Major Reaction Steps

Reaction Conditions

(a) Initial Oxidation

Liquid phase air, CO salts as
catalyst 130–140°C., 2–3 atm.
85–90% yield

(b) Second Oxidation

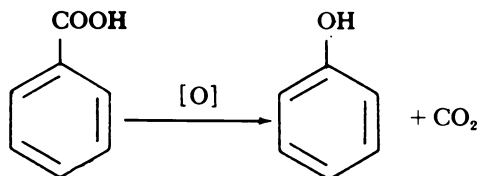
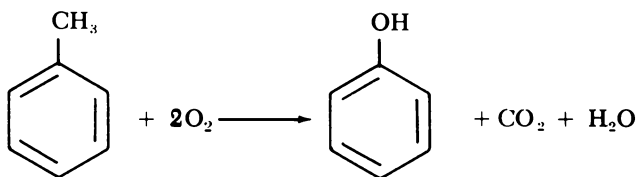
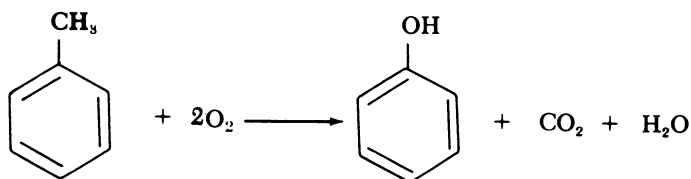
Liquid phase 190–250°C., atm.
pressure (molten benzoic
acid) 5–10% Cu(OCOC₆H₅)₂
catalyst + 4% MgO or
Mg(OCOC₆H₅)₂ promoter
80–85% yield

Table XVIII. Continued

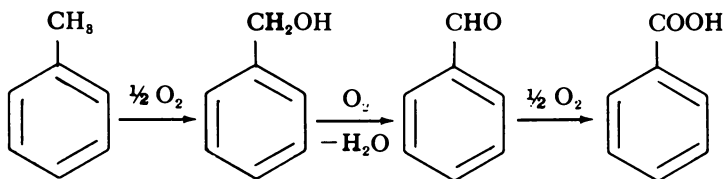
Over-all Process (70–85% Yield)

^a Literature:Banciu, A. S., *Rev. Chim. (Bucharest)* **16**, 211 (1965).Hay, J. M., Stirling, D. W., Weaver, C. W., *Oil Gas J.* **83** (Jan. 3, 1966).Kaeding, W. W., *Petrol. Refiner* **43** (11), 173 (1964).Kropf, H., *Chem. Ing. Tech.* **36**, 759 (1964).**Table XIX. Basic Equations for Oxidizing Toluene to Phenol^a**

OVER-ALL EQUATION



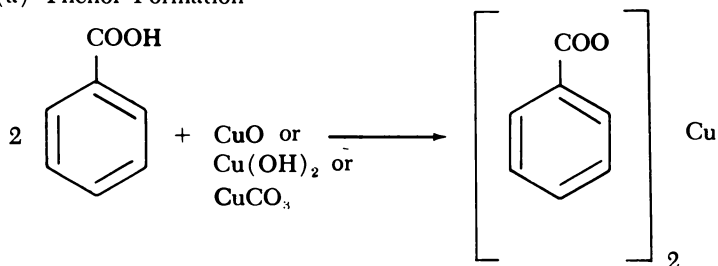
Oxidation of Toluene to Benzoic Acid



by-products: benzyl benzoate and various biphenyls

Oxidation of Benzoic Acid to Phenol

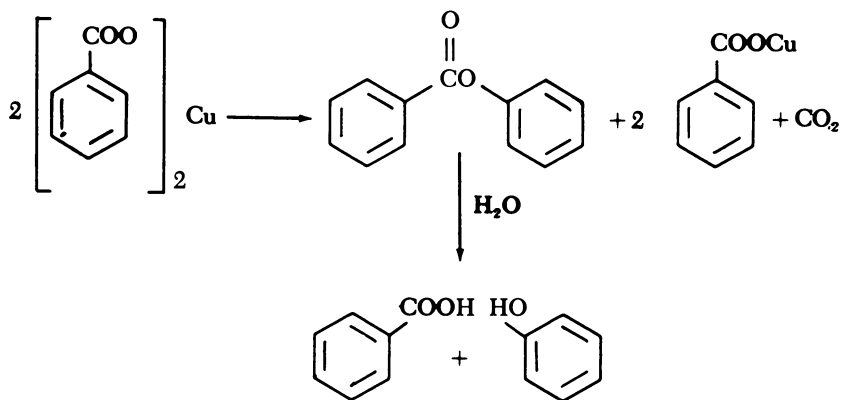
(a) Phenol Formation



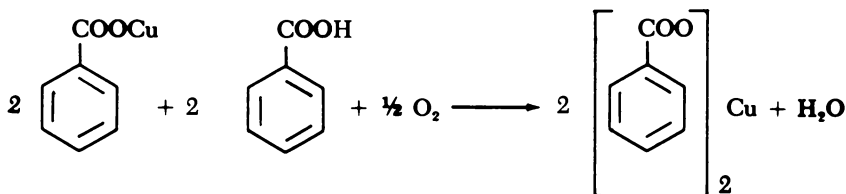
In Homogeneous Catalysis; Luberoff, B.;

Advances in Chemistry; American Chemical Society: Washington, DC, 1974.

Table XIX. Continued



(b) Catalyst Regeneration



by-product: tar

^a Literature:

- Kaeding, W. W., *J. Org. Chem.* **26**, 3144 (1961).
 Kaeding, W. W., *Petrol. Refiner* **43** (11), 173 (1964).
 Kaeding, W. W., *Proc. World Petrol. Congr., 6th*, Section II, Paper 30, 1963.
 Kaeding, W. W., Lindbloom, R. O., Temple, R. G., *Ind. Eng. Chem.* **53**, 805 (1961).
 Kaeding, W. W., Lindbloom, R. O., Temple, R. G., Mahon, H. I., *Ind. Eng. Chem., Process Design Develop.* **4**, 97 (1965).
 Kaeding, W. W., Collins, G. R., *J. Org. Chem.* **30**, 3750 (1965).
 Kaeding, W. W., Kerlinger, H. O., Collins, G. R., *J. Org. Chem.* **30**, 3754 (1965).
 Toland, W. G., *J. Am. Chem. Soc.* **83**, 2507 (1961).

Table XX. Some Proposed Mechanisms for the Decomposition of Cupric Benzoate

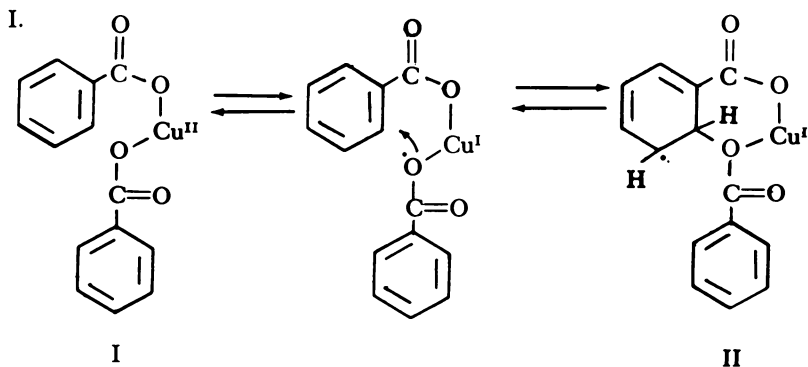


Table XX. Continued

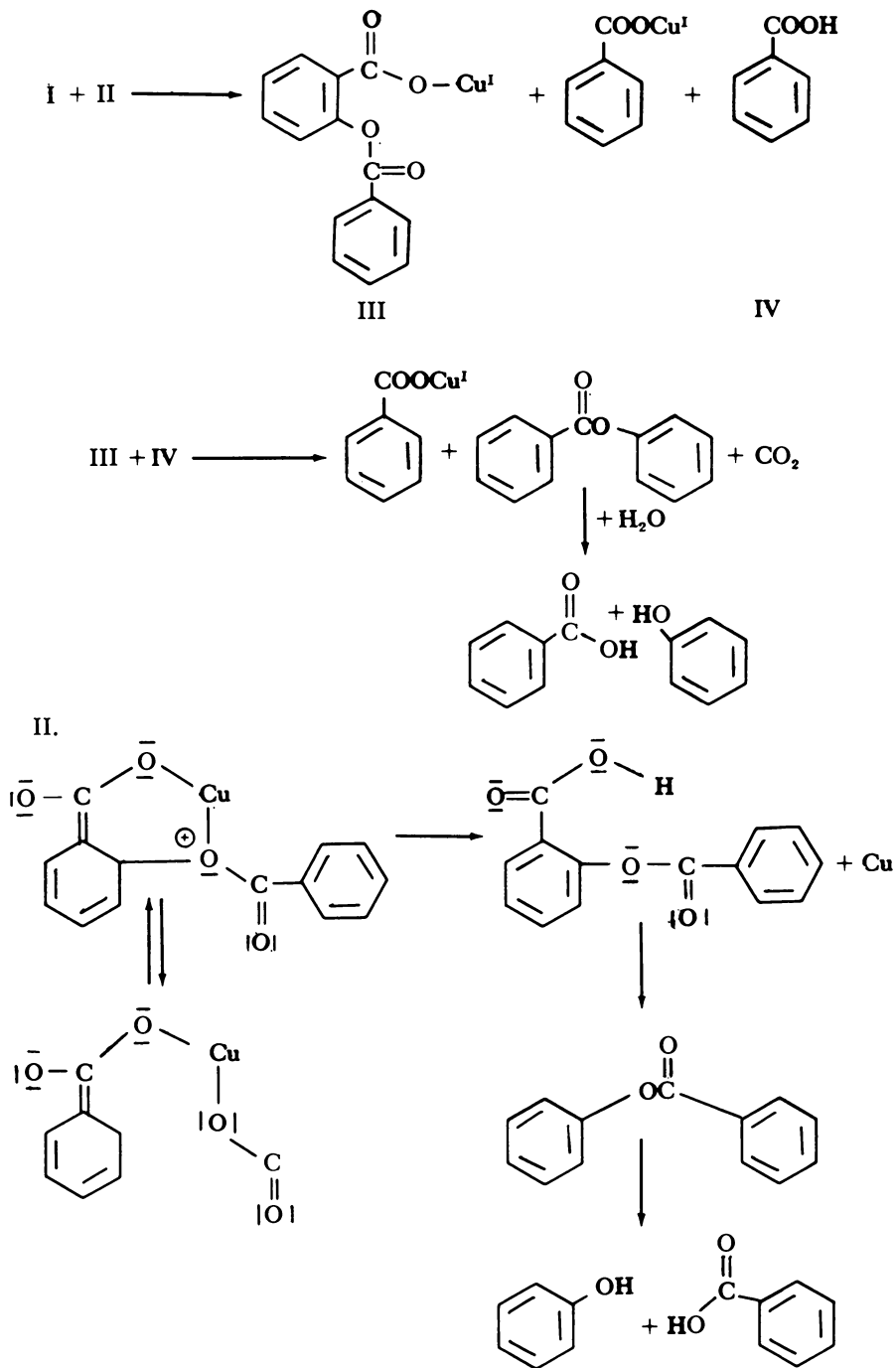
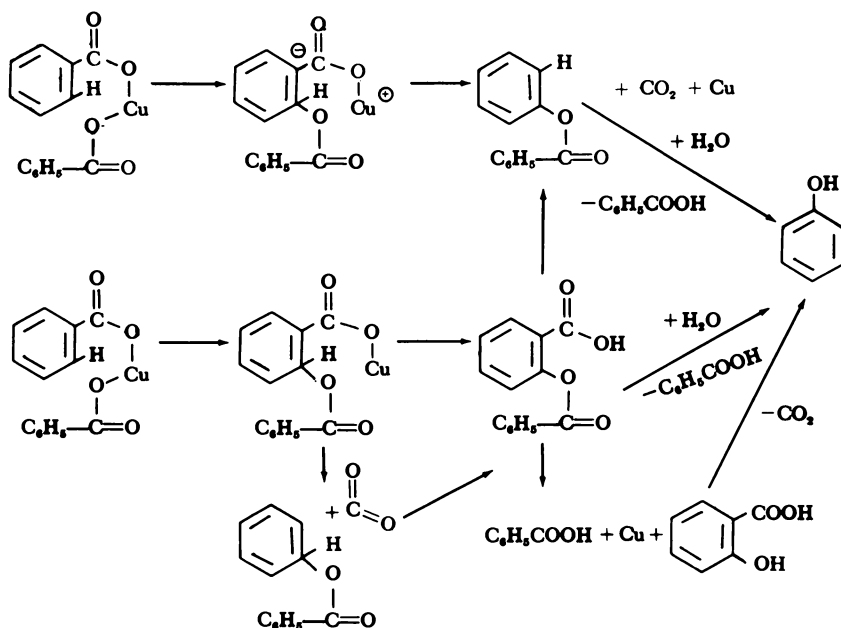


Table XX. Continued

III.

**Literature:**

I:

- Kaeding, W. W., *J. Org. Chem.* **26**, 3144 (1961).
 Kaeding, W. W., Shulgini, A. T., *J. Org. Chem.* **27**, 3551 (1962).
 Kaeding, W. W., Collins, G. R., *J. Org. Chem.* **30**, 3750 (1965).
 Kaeding, W. W., Kerlinger, H. O., Collins, G. R., *J. Org. Chem.* **30**, 3754 (1965).

II:

- Schoo, W., Veenland, J. U., Bigot, J. A., Sixma, F. L. J., *Rec. Trav. Chim.* **80**, 134 (1961).
 Schoo, W., Veenland, J. U., DeBoer, T. J., Sixma, F. L. J., *Rec. Trav. Chim.* **82**, 954; 172 (1963).
 Schoo, W., Veenland, J. U., Van Velzen, J. C., DeBoer, T. J., Sixma, F. L. J., *Rec. Trav. Chim.* **82**, 959 (1963).

III:

- Toland, W. G., *J. Am. Chem. Soc.* **83**, 2507 (1961).

Pertinent patents dealing with the toluene-to-phenol process are listed in Table XXI. It is difficult to judge, based on the published literature alone, which of the processes described in the patents are practiced. According to a recent article, Dow Chemical Co. apparently manufactures phenol by processes described in their own patents as well as by some California Research Corp. patents licensed to Dow (8). A schematic flowsheet illustrating the technical execution of the process is given in Figure 3.

An economical evaluation of phenol processes is complicated by the number and variety of competing processes. Table XXII compares some key features of various phenol processes, based on two excellent, recent reviews (4, 15). Hay *et al.* (15) point out that synthetic phenol processes currently account for 98% of the phenol produced in the United States and Canada. The various phenol processes currently used are listed in Table XXIII. An economic comparison between a number of phenol processes is given in Table XXIV. Based on this table, the Raschig, Cumene, and Dow toluene processes are equivalent with regard to return price. Therefore, selection must be made on the basis of other factors, such as value of intermediates and by-products, ease of operation, and initial investment.

Table XXI. Principal Patents for Producing Phenol from Benzoic Acid or Related Aromatic Carboxylic Acids

Badische Anilin- & Soda-Fabrik A.G.	Belgian patent 621,999 (Feb. 28, 1963)
California Research Co.	U.S. patent 2,762,838 (Sept. 11, 1956) 2,766,294 (Oct. 9, 1956)
Dow Chemical Co.	U.S. patent 2,727,924 (Dec. 20, 1955) 2,727,926 (Dec. 20, 1955) German patent 1,015,444 (Feb. 20, 1958) U.S. patent 2,839,541 (June 17, 1958) 2,852,567 (Sept. 16, 1958) 2,954,407 (Sept. 27, 1960) 3,061,651 (Oct. 30, 1962)
I. I. Ioffe, V. V. Suchkov, V. I. Sushchenya, and E. A. Migge	Russian patent 176,915 (Dec. 1, 1965); C.A. 64, 12601c (1966)
"Montecatini" Societa Generale per Industria Mineraria e Chimica	French patent 1,339,394 (Oct. 4, 1963) 1,383,531 (Dec. 24, 1964)
Shell Internationale Research Maatschappij N. V.	Belgian patent 637,598 (March 19, 1964) Netherlands Appl. 6,411,251 (March 31, 1965); C.A. 63, 8261d (1965)
Stamicarbon N. V.	Belgian patent 627,445 (July 23, 1963) Netherlands patent 106,100 (Sept. 16, 1963); C.A. 60, 14441f (1964) Belgian patent 633,115 (Dec. 2, 1963) French patent 1,385,243 (March 2, 1964)
Sun Oil Co.	U.S. patent 3,078,299 (Feb. 19, 1963) 3,171,854 (March 2, 1965)
U. S. Steel Corp.	U.S. patent 3,274,262 (Sept. 20, 1966)

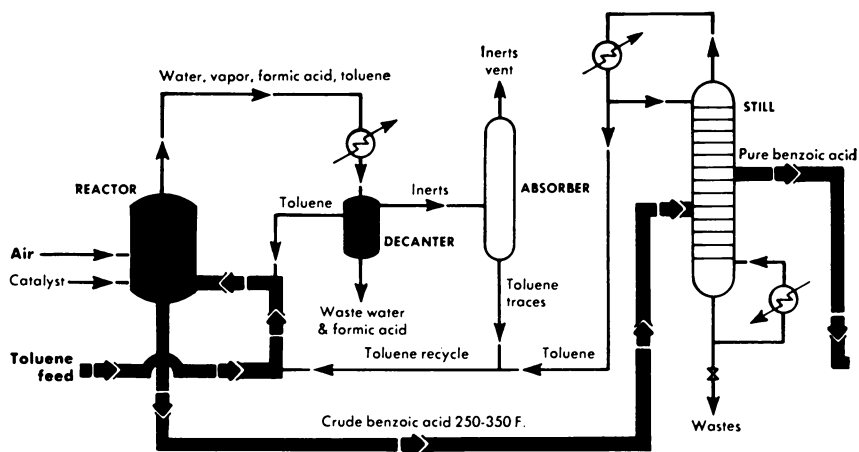
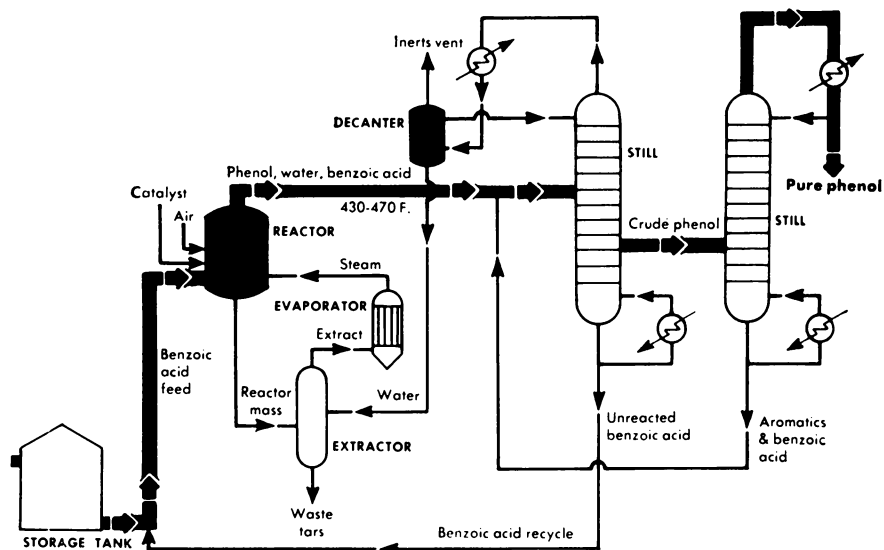


Figure 3. Schematic flowsheet for oxidizing toluene to phenol (reprinted with permission from *Chemical Engineering* (Sept. 28, 1964) Copyright © (1964), McGraw-Hill, Inc.

Toluene is fed to the reactor with air and a cobalt salt catalyst while the reactor is kept at 120°–180°C. and 30 p.s.i.g. Crude benzoic acid taken from the bottom of the reactor is fed to a distillation column while vapors from the top containing toluene,

Table XXII. Comparison of

Process	Major Raw Materials	Principal By-Products
Benzene Sulfonate	Benzene, oleum, and caustic	Na ₂ SO ₄
Chlorobenzene Caustic (Dow Process)	Benzene and electrical power	Diphenyloxide and dichlorobenzene
Regenerative Raschig (Hooker Process)	Benzene, air, and makeup HCl	Dichlorobenzene



formic acid, and water are worked up as shown above. The benzoic acid is stored in a tank and fed from there to a reactor with air, steam, and a catalyst mix consisting of copper and magnesium salts. The reaction is carried out at atmospheric pressure and 220°–250°C. Reactor vapors consisting of phenol, water, and benzoic acid are taken from the top to a distillation column where crude phenol is removed and sent to a second distillation column for purification. Unreacted benzoic acid is recycled.

Various Phenol Processes

<i>Advantages</i>	<i>Disadvantages</i>	<i>Remarks</i>
Old, but proved process. Can be run continuously or semicontinuously. Requires relatively little initial investment.	Requires large amounts of heat to concentrate solutions.	Process depends largely on the price of H_2SO_4 and NaOH and on the selling price of Na_2SO_4 , which is sold for wood pulping.
Useful by-products.	Requires electrolysis units to convert NaCl to Cl_2 + NaOH .	Process economics depends on the economics of Cl_2 , on the alkaline hydrolysis, and use or sale of the by-products.
Other than benzene, cheap, easily obtainable raw materials are required; the HCl produced is regenerated.	Corrosion of apparatus owing to HCl .	Profitability increases with increasing capacity. Dichlorobenzene can be converted to phenol.

Table XXII.

<i>Process</i>	<i>Major Raw Materials</i>	<i>Principal By-Products</i>
Cumene Hydroperoxide	Benzene, propylene, air, and H ₂ SO ₄	Acetone, Diisopropylbenzene and α -methylstyrene
Toluene Oxidation (Dow Toluene Process) (Kaeding Process)	Toluene	Tar
Cyclohexane-to-Phenol (Scientific Design Process)	Benzene or Cyclohexane	(No information)

* *Literature:*

Banciu, A. S., *Rev. Chim. (Bucharest)* **16**, 211 (1965).
 Hay, J. M., Stirling, D. W., Weaver, C. W., *Oil Gas J.* **83** (Jan. 3, 1966).

Table XXIII. Distribution of

	<i>In 1000 tons per yr.</i>
<i>Cumene Hydroperoxide Process</i>	
Petrochim, Antwerp, Belgium	10
Phenolchemie, Gladbeck, Germany	90
Progil Pont de Claix, France	20
Rhône-Poulence, Rousillon, France	30
British Hydrocarbon, England	20
Resine-Gulf, Porto Torres, Italy	90
Sicedison, Mantua, Italy	15
SIR, Milano, Italy	27.5
BA-Shawinigan, Montreal, Canada	18
Combine No. 1, Fagaras, Rumania	3
Refinery No. 10, Borzesti-Onesti, Rumania	18
Refinery Slovnaft, Bratislava, Czechoslovakia	5
Chemical Works—Chernorechensk, U.S.S.R.	15
Chemical Works—Novokuybyshevsk, U.S.S.R.	15
Combine—Grosny, U.S.S.R.	45
Allied Chemicals, Frankford, Pa.	45
California Chemicals, Richmond, Calif.	22.5
Clark Oil, Blue Island, Ill.	13.5
Hercules, Gibbstown, N. Y.	13.5
Monsanto, Chocolate Bayou, Texas	34
Shell Chemical, Houston, Texas	22.5
Skelly Oil, Eldorado, Kansas	22.5

Continued

<i>Advantages</i>	<i>Disadvantages</i>	<i>Remarks</i>
Organic raw materials are easily obtained from petrochemical sources. Relatively simple apparatus.	Necessitates the installation of an alkylation unit.	Phenol costs will depend mainly on the selling price of acetone since 640 kg. acetone is produced per ton phenol.
Toluene is cheaper than benzene. No corrosion problems. Only small amounts of by-product tar.	Extraction of catalyst from the tar by water before recycling.	Intermediate high purity benzoic acid is produced which can be sold for other uses.
Direct usage of petroleum fractions.	Insufficient industrial experience.	The intermediate cyclohexane is a nylon intermediate. Economics depends on raw materials and selling price of cyclohexanone.

Phenol Processes by Manufacturers*

	<i>In 1000 tons per yr.</i>
<i>Chlorobenzene Process</i>	
Farbenfabriken Bayer, Leverkusen, Germany	40
Dow, Midland, Mich.	106
<i>Raschig Process</i>	
Duranor, Rio Torcero, Argentina	9
Hocker, N. Tonawanda, N. Y.	30
Hooker, South Shore, Ky.	30
Union Carbide, Marietta, Ohio	50
<i>Sulfonation Process</i>	
Honshu Chemical Industry, Japan	15
Monsanto, Avon, Calif.	16
Monsanto, Monsanto, Ill.	55
Reichold, Tuscaloosa, Ala.	40
<i>Toluene Benzoic Acid Process</i>	
Dow, Lardner, B.C., Canada	11
Staatimijnen-Dow, Botlek, Holland	25
Dow, Kalama, Wash.	16.5

* *Literature:*Kropf, H., *Chem. Ing. Tech.* **36**, 759 (1964).

Table XXIV. Economic Comparison of a Number of Phenol Processes^a**Assumptions:**

A plant producing 36 million lb./year, assuming published yields for the various processes. Capital costs were also taken from the literature, and capital charges were calculated at 40% /year of capital cost of the plant, including maintenance (5%), depreciation (10%), profit (20%), and overhead (5%).

The following raw material and by-product prices were assumed:

Benzene, cents/U.S. gal.	27
Toluene, cents/U.S. gal.	19
Propylene, cents/lb.	2
H ₂ SO ₄ (Oleum), \$/ton	25
NaOH (50%), \$/ton	60
Chlorine, \$/ton	65
Acetone, cents/lb.	5.5
Salt cake (Na ₂ SO ₄), \$/ton	20
Sodium chloride, \$/ton	0.5

	<i>Chloro- benzene</i>	<i>Sulfona- tion</i>	<i>Scientific Design</i>	<i>Raschig</i>	<i>Cumene</i>	<i>Dow Toluene</i>
Plant cost, million dollars	7.0	4.5	4.2	4.5	6.1	4.5
Yield (molar)	0.83	0.83	0.80	0.89	0.80	0.74
Raw materials, cents/lb.	9.15	10.94	3.80	3.40	4.88	3.48
Direct operating, cents/lb.	0.63	1.06	1.95	1.93	1.91	1.85
Capital charges (incl. profit), cents/lb.	7.78	5.00	4.66	5.00	6.84	5.00
By-product credit, cents/lb.	-0.05	-2.30	—	—	-3.30	—
Return price, cents/lb.	17.51	14.70	10.41	10.33	10.33	10.33

^a *Literature:*

Hay, J. M., Stirling, D. W., Weaver, C. W., *Oil Gas J.* **83** (Jan. 3, 1966).

A recent article gave the following market figures for 1965 and estimates for 1970 for synthetic phenol (12).

Production, 1965	1174 million pounds
1970 ^a	1910
Production growth rate, last five years	10.92%
next five years ^a	10.36%
Capacity, 1965	1400 million pounds
1970 ^a	2430
Capacity growth rate, last five years	11.89%
next five years ^a	11.24%
Price, 1965	0.1125 cents per lb.
1970 ^a	0.097

^a These estimates were made using the exponential trend techniques and carrying out the computations on a time-shared computer.

Acknowledgment

Although this work was carried out with the knowledge of CIBA's management, it does not reflect CIBA's interests. The author carried out this work on his own and bears full responsibility for its contents.

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Chemistry of Palladium Complexes

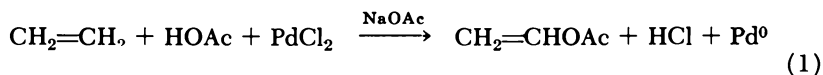
V. Vinylation of Acetic Acid by Higher Olefins

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The vinylation of acetic acid by higher olefins has been studied. Using the hexenes as model compounds, the structures of the products have been elucidated both for the vinylation products and for the higher boiling materials produced under certain conditions. The effect of several reaction parameters on the course of the reaction has been studied. Both the ratio of vinylation products to higher boiling products and the distribution of isomers within the vinyl esters depend on the relative amount of acetate ion present. High levels of specific vinyl esters could be produced by the correct choice of olefin and reaction parameters. With α -olefins, primary esters could be produced with greater than 75% specificity. As an alternate for the currently accepted vinylation mechanism, a new reaction pathway is proposed.

Since the first report of synthesizing vinyl acetate from ethylene (37), a number of other reports on this reaction (Reaction 1) have appeared (4, 5, 9, 10, 12, 13, 14, 16, 21, 22, 23, 24, 25, 26, 30, 31, 32, 33, 34, 40, 41, 42, 43, 49, 50, 51, 55, 57). Most are limited to the ethylene reaction,

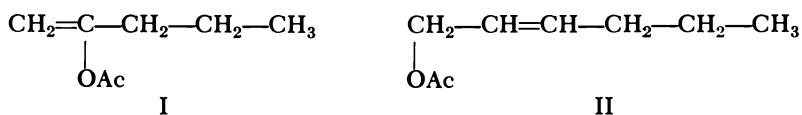


and few vinylation (oxidative esterification) reactions using higher olefins have been reported.

The term vinylation is used here in the sense of oxidative esterification and is not meant to imply either a particular reaction mechanism or a particular type of reaction product, such as a vinyl ester. Because of

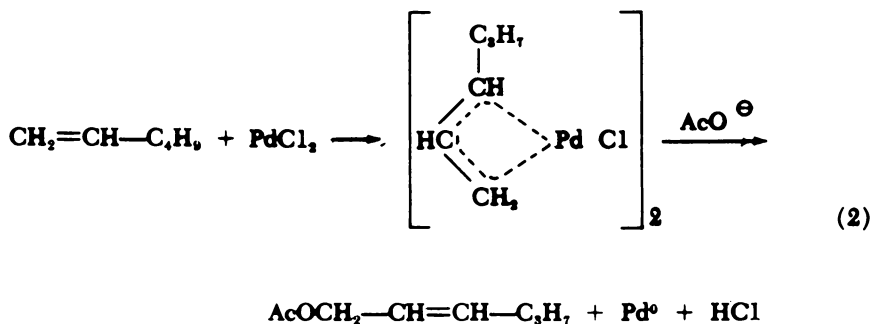
the possibilities of isomerization—both olefinic and oxygen positional—a general term is needed to describe the reaction products. For example, hexenyl acetate has been chosen here to designate all the products of oxidative esterification of the hexenes with acetic acid. The term “oxy-palladation” has been avoided since it also implies a specific reaction pathway.

For cases in which vinylation with higher olefins has been studied, conflicting results have been reported. In one case, it has been reported (29) that olefins give predominantly 2-substitution—*e.g.*, 1-penten-2-yl acetate (I) from pentene when a palladium acetate–acetic acid system is used. On the other hand, a buffered (sodium acetate) acetic acid solution of palladium chloride has been reported (58) to give 1-substitution—*e.g.*, 2-hexen-1-yl acetate (II) from hexene. Propylene has been



reported to afford exclusively isopropenyl acetate (58), a 64:36 mixture of isopropenyl:propenyl acetates (54), and high levels (50–90%) of allyl acetate (9, 10, 26, 30, 52). Additional conflicting results have been reported when the butenes are oxidized in similar systems (7, 9, 10, 29). Drastic product distribution changes have also been noted when mixed solvents were used (9, 10, 29). In studies of vinylation effected by palladium salts additional complications not found in many other oxymetal-lations—olefinic isomerization (6, 8, 11, 17, 53) and allylic isomerization of the ester group—are possible and must be considered in interpreting any results. Only one report (29) considers these possibilities.

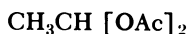
From previously reported studies then, several different products are possible. The initial attack by the oxygen moiety may apparently be vinylic (on either of the two carbons of the double bond) or allylic (on the carbon next to the doubly bonded carbons). Distinction must be made between allylic attack as described here and allylic products which can arise either by true allylic attack or by vinylic attack followed by olefinic isomerization. Thus it is not clear whether such products as 2-hexen-1-yl acetate (II) (58) have been formed by vinylic attack upon hexene followed by olefinic isomerization, by olefin isomerization of hexene to 2-hexene followed by allylic attack, or by some type of synchronous mechanism in which oxygen attack and olefin isomerization occur simultaneously. This last possibility could be visualized as involving some type of π -allylic complex (Reaction 2). This involvement of π -allylic complex can be ruled out only in the production of isopropenyl acetate from propylene since a mechanism such as this followed by olefin isomerization could not be used in that case. For the butenes and higher



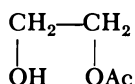
olefins vinylic products could be rationalized on the basis of olefinic isomerization of allylic products.

The location of the olefinic bond may therefore give, at best, somewhat ambiguous information as to the reaction pathway. If one were able to find conditions (*e.g.*, short reaction times) in which unreacted olefin was also unisomerized, one could argue better for the importance of olefin position in the product. However, even in these cases a situation in which the rate-determining step would be initial olefin-metal salt π -complex formation, followed by rapid vinylation and specific isomerization of the intermediate or vinylation product cannot be precluded.

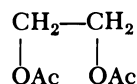
In some of the studies on the vinyl acetate synthesis from ethylene, high boiling products were reported (9, 10, 24, 25, 26). These included ethylidene diacetate (III), ethylene glycol monoacetate (IV) and ethylene glycol diacetate (V). Little attention has been given to the reactions by which these products are formed. No dioxygenated products have been reported previously when higher olefins have been used.



III



IV

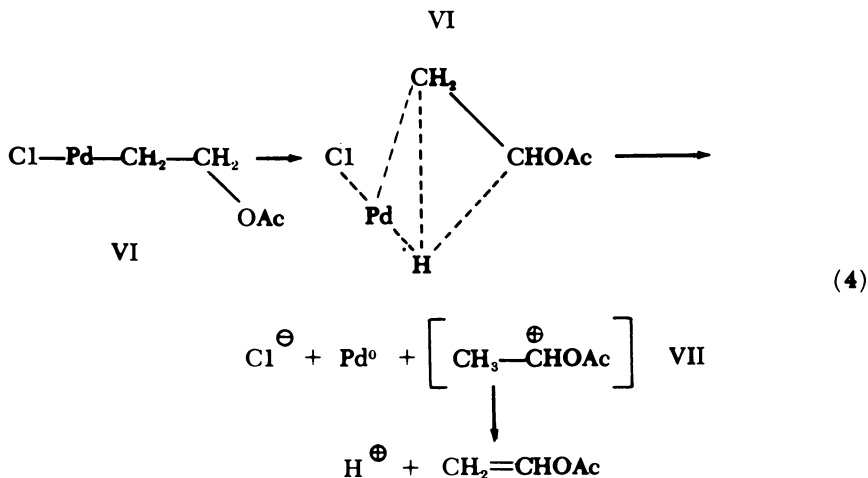
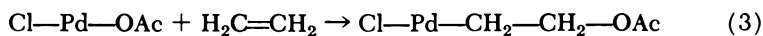


V

Preliminary mechanistic studies (36) on synthesizing vinyl acetate from ethylene have indicated that it probably proceeds in a manner similar to the synthesis of acetaldehyde from ethylene (19).

The most generally accepted mechanistic speculations center about a β -acetoxyalkylpalladium intermediate (VI) formed by an insertion reaction of ethylene into a palladium-oxygen bond (Reaction 3). It is proposed that this intermediate would then decompose *via* a palladium-assisted hydride transfer to vinyl acetate (Reaction 4) (36). While Reaction 4 would appear more awkward than a simple β -hydrogen

elimination, it has the advantage of explaining the results of several deuterium studies on this reaction.



Moiseev and Vargaftik (36) have reported that deuterium is not incorporated into either vinyl acetate or ethylidene diacetate (III) when the vinyl acetate synthesis reaction is carried out in deuterioacetic acid. They considered this observation as evidence for a process such as Reaction 4 in which the final carbonium ion (VII) is forming products either by losing a proton or by reacting with acetate to give ethylidene diacetate (III).

The existence of a free carbonium ion such as VII in a strongly solvating medium is highly improbable. Only if VII could exist in association with the palladium could decomposition to vinyl acetate be expected to occur with a reasonable degree of frequency, in competition with the reaction with acetate to form ethylidene diacetate. Similar results have been reported in the Wacker acetaldehyde synthesis when D_2O is used as the solvent (15). Stern (54) has reported results in which 2-deuteropropylene was used as substrate in the reaction. Based on assumed β -acetoxyalkylpalladium intermediates, on the absence of an appreciable isotope effect in the proton-loss step, and on the product distribution observed, excellent agreement between calculated (71%) and observed (75%) deuterium retention was obtained. Several problems inherent in this study (54) have been discussed in a recent review (1). Hence, considerable additional effort must be expended before a clear-cut decision can be made between a simple β -hydrogen elimination and a palladium-assisted hydride shift in this reaction.

As part of general study in our laboratories on the chemistry of palladium complexes (44, 45, 46) we investigated the vinylation of acetic acid by higher olefins. We hoped these studies could shed light on the reaction pathway and that the causes of changes in product distribution could be elucidated and controlled.

Experimental

Reactions at elevated temperature and pressure were carried out in an Autoclave Engineers 300 ml. Magnedrive autoclave, fabricated entirely from titanium to eliminate corrosion. NMR spectra were obtained using a Varian model A-60 instrument. Deuteriochloroform solutions and neat samples were used with an internal tetramethylsilane standard. Gas chromatograms were obtained using an F and M Model 810 instrument, equipped with a hydrogen flame detection system. Separation of the hexanol acetates was effected using a 200 ft. \times 0.02 in. capillary column coated with a six-ring phenyl ether. This same column was used to separate the hexenyl acetate isomers. Separation of these acetates from the high boiling products was effected using a 5 ft. \times 1/8 in. column packed with a 10% six-ring polyphenyl ether on Anakrom ABS support. The specific hexene isomers were Phillips Petroleum Co. pure (99 + mole %) grade. Palladium chloride was supplied by Engelhard Industries, palladium acetate by J. Bishop and Co.

Typical Vinylations in the Absence of Copper(II). At 25°C. A mixture of palladium(II) acetate (1.00 gram, 4.46 mmoles), sodium acetate (0.73 gram, 8.92 mmoles) (AcO/Cl/Pd ratio of 4/0/1), and glacial acetic acid (50 ml.) was stirred at 25°C. for 30 min. in a 250 ml. round-bottomed flask. Then 5 ml. of hexene (3.37 grams, 40 mmoles) were added, and the stirring was continued for 1 hour. (Within 15 min. of the addition, extensive palladium precipitation had occurred.) The mixture was then filtered to remove the palladium precipitate, and 100 ml. of water were added to the dark brown filtrate, giving a further palladium precipitate. The acetic acid-water mixture was extracted with three 50-ml. portions of benzene, and the combined benzene extracts were washed with water, dilute aqueous sodium bicarbonate, and water and were dried over sodium sulfate. Evaporation of the yellow-brown benzene solution to small volume caused additional palladium metal precipitation and a dark red solution. When this sample was hydrogenated (diluted to 7 ml. with heptane) using 150 mg. 5% platinum on carbon catalyst at 25°C. and atmospheric pressure, an uptake of hydrogen of 70 ml.—equivalent to a yield of 64.1% of vinylation products based on palladium(II) acetate—was found. The reduction products from the hexenyl acetates consisted of 38.2% hexanol-1-acetate, 60.6% hexanol-2-acetate, and 1.2% hexanol-3-acetate (by gas chromatography).

At 100°C. Palladium(II) chloride (0.79 gram, 4.46 mmole) and sodium acetate (2.92 grams, 35.68 mmole) (AcO/Cl/Pd ratio of 8/2/1) were added to 50 ml. glacial acetic acid, and the mixture was heated at 100°C. with stirring for 20 min. Hexene was then added through the reflux condenser. Palladium precipitated immediately. The mixture was cooled

rapidly to 25°C. (total reaction time at 100°C. was 1 min.), filtered, and 100 ml. of water were added to the yellow-orange filtrate. No palladium precipitation occurred. This mixture was extracted, washed, and dried as described above. Evaporation of the bright yellow benzene solution did not cause additional palladium metal precipitation. On hydrogenation, an uptake of 84 ml. of hydrogen—equivalent to a yield of 76.9% of vinylation products—was found. The reduction products from the hexenyl acetates consisted of 74.0% hexanol-1-acetate, 22.2% hexanol-2-acetate, and 3.8% hexanol-3-acetate.

Vinylations in the Presence of Copper(II). AUTOCLAVE STUDIES. A 300-ml. autoclave was charged with 0.364 gram (2.06 mmole) palladium chloride, 5.0 grams (37.4 mmoles) anhydrous cupric chloride, 14.5 grams (177 mmoles) anhydrous sodium acetate, and 100 ml. glacial acetic acid under nitrogen (AcO/Cl ratio, 2.25). The autoclave was heated to 115°C. with stirring (500 r.p.m.). Hexene (10 ml., 6.73 grams, 80 moles) was injected through a septum assembly attached to the reactor head. (In studies at higher temperatures a nitrogen-pressured vessel was used to charge the olefin into the reactor.) After 15 min. the heating was stopped, and the reactor was cooled rapidly to 25°C. by immersion in an ice bath. Those reactions studied at "zero" time were cooled to 25°C. immediately upon adding the olefin. The rate of vinylation was found to be negligible at 25°C. under these reaction conditions. The cooled reaction mixture was filtered, diluted with 300 ml. of water and extracted with three 50-ml. portions of benzene. Water dilution effectively stops any further vinylation. The combined benzene extracts were washed with water, dilute aqueous sodium bicarbonate, and with water and dried over sodium sulfate. Benzene was then removed by distillation at atmospheric pressure, and the residue (containing products and benzene) was examined by gas chromatography. The organic products were found to consist only of hexenyl acetates, no high boiling products being found. Hydrogenating a portion of this crude sample, using the procedure described above, showed 72.0% hexanol-1-acetate, 24.8% hexanol-2-acetate, and 3.2% hexanol-3-acetate in the product.

OPEN FLASK REACTION. To a 2-liter, four-neck flask equipped with thermometer, reflux condenser (1 meter in length), and stirrer was added 3.64 grams (0.0206 mole) palladium chloride, 50.0 grams (0.374 mole) anhydrous cupric chloride, 40.2 grams (0.489 mole) anhydrous sodium acetate, and 1 liter glacial acetic acid (CO/Cl ratio 0.62). The mixture was stirred and heated to reflux (118°C.). Then 100 ml. (67.3 grams, 0.801 mole) of hexene were added over a period of 5 min. through the reflux condenser. At the end of the addition, the solution reflux temperature was 90°C. Heating at this temperature was continued for 1 hour. A 12-in. column packed with metal saddles was then attached, and the unreacted hexenes were distilled out of the reaction mixture and recovered (51.0 grams). After cooling, the mixture was filtered, and the solid washed with acetic acid. The filtrate was poured into 3 liters of distilled water, and the acetic acid-water mixture was extracted four times with benzene. The combined benzene solutions were washed with water, dilute aqueous sodium bicarbonate, and water and were dried over sodium sulfate. Most of the benzene was then removed by distillation.

Distillation of the reaction product gave four fractions:

- (1) b.p. 25-55°C. at 11 mm. 0.40 grams
- (2) b.p. 58-64°C. at 11 mm. 6.21 grams hexenyl acetates
- (3) b.p. 30-50°C. at 0.5 mm. 0.74 grams
- (4) b.p. 57-62°C. at 0.5 mm. 8.72 grams high boilers

Pot residue 4.33 grams

The yield of products was 60.5% of theoretical based on copper. Total recovery of hexenes (as hexene, hexenyl acetates, and high boilers, but disregarding that which appeared in the pot residue) was 88.5%.

Attempted Synthesis of Specific Hexenyl Acetate Isomers. FROM HEXANAL. Hexanal (5 ml. of 40% technical material) and 25 ml. 2-propenyl acetate were mixed, and 750 mg. *p*-toluene sulfonic acid was added. This solution was heated at reflux for 12 hours. The solution was then poured into 100 ml. water and extracted with two 50-ml. portions of ether. The combined ether extracts were washed with water, dilute aqueous sodium bicarbonate, and water and dried over sodium sulfate. After evaporating the ether, a gas chromatogram showed two major components present in a 3:2 ratio (probably the *trans*- and *cis*-hex-1-en-1-ol acetates, respectively). These components had identical retention times in the gas chromatograms to two of the major components present in the hexene-1 vinylation reactions.

FROM 2-HEXANONE. The procedure above was repeated using 4.98 grams 2-hexanone, 20 ml. 2-propenyl acetate, and 750 mg. *p*-toluene sulfonic acid. A product was obtained which had three hexen-2-ol acetate components in a 3:1:1 ratio which again were identical in retention time to three of the major components present in the gas chromatograms of the hexene-1 vinylation reactions.

FROM 3-HEXANONE. The procedure above was again repeated using 3-hexanone (4.88 grams); 2-propenyl acetate (20 ml.), and *p*-toluene sulfonic acid (750 mg.). A product was obtained which had four hexen-3-ol-acetate components in a 6:7:3:4 ratio. None of these components corresponded to major peaks in the gas chromatograms of hexene vinylation reactions.

Studies on the Structure of the High Boiling Products. PRELIMINARY STUDIES. Vapor phase chromatographic studies indicated that a peak later identified as a diacetate was present in varying amounts in different vinylation runs. Not enough runs were made to allow us to determine the reason for this variation. NMR spectroscopy on a high boiler sample in which this diacetate component was present to only a small degree indicated that the major components (a peak with trailing shoulder in the gas chromatogram) were hydroxy acetates. Peaks in the

NMR were observed at -1.82δ $\left(\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{O} \end{array} \right)$, -2.98δ (broad singlet, —OH), and centered at -3.85δ (complex, overlapping multiplets, —CH—O—) with a relative intensity of 3:1:3.

ACETYLATION. A sample of high boiling product (1.11 grams) was added to a mixture of 11 ml. acetic anhydride and 12 ml. anhydrous pyridine, and the solution was held at 35°C. for 24 hours. The solution was poured into 200 ml. water, and the mixture was extracted with two 50-ml. portions of ether. The ether solution was washed with water,

dilute aqueous hydrochloric acid, water, dilute aqueous sodium bicarbonate, and water and dried over sodium sulfate. Evaporation of the ether left a residue (1.20 grams) which was characterized by NMR and gas chromatography. The NMR spectrum [neat liquid] showed peaks at -2.0δ $\left(\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}- \end{array}\right)$, (relative intensity, 6), -3.41δ $\left(\begin{array}{c} \text{H} \\ | \\ -\text{C}-\text{O}- \end{array}\right)$, (multiplet, relative intensity, 1), and -4.13δ (multiplet, $\text{O}-\text{CH}_2-$, relative intensity, 2), which were indicative of the proposed diacetate structure. Vapor phase chromatography showed that the original major peak (with shoulder) was transformed into a higher boiling material which had previously been a minor component of the reaction mixture.

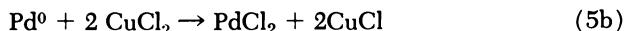
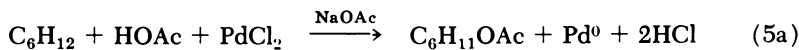
PYROLYSIS REACTIONS. A pyrolysis apparatus consisting of a 30 mm. o.d. borosilicate glass tube filled with 75 ml. of 3 mm. borosilicate glass beads was heated to 435°C . in a tubular furnace. The sample to be pyrolyzed was introduced at a rate of two drops every 5 sec. in a stream of nitrogen (16 ml./min.). The effluent from the reactor was condensed and collected from a dry-ice cooled trap.

Pyrolysis of 1.0 ml. of high boiling product afforded 0.8 ml. of condensate which from gas chromatography was shown to consist of hexanal, 28.6% (from hexan-1, 2-diol-2-acetate), hexanone-2, 16.0% (from hexan-1, 2-diol-1-acetate), and hexenyl acetates 55.4% (from hexan-1-2-diol diacetate). These hexenyl acetates upon reduction gave only hexanol-1-acetate.

Pyrolysis of 0.5 ml. of acetylated high boiling product afforded 0.3 ml. condensate which from gas chromatography was shown to consist exclusively of hexenyl acetates. Upon reduction, only hexanol-1-acetate was obtained.

Results and Discussion

The substrates chosen for study were the hexenes. The vinylation reaction was effected without or with added copper salts to effect regeneration of the palladium metal formed (Reactions 5a and b).

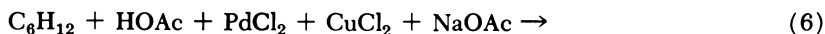


When reactant ratios were at certain specified levels, the ultimate fate of the palladium (II) was not reduction to palladium metal but formation of the π -allylpalladium chloride complex, $(\text{C}_6\text{H}_{11}\text{PdCl})_2$.

The structure of this complex was shown (by NMR) to be di- μ -chloro-di- π -[1-methyl-3-ethylallyl]dipalladium(II). In no case was the presence of 1-propyl allyl analog detected.

Similar results have been reported (35) for the reaction of propylene under these conditions. Dimerization of propylene was observed, and

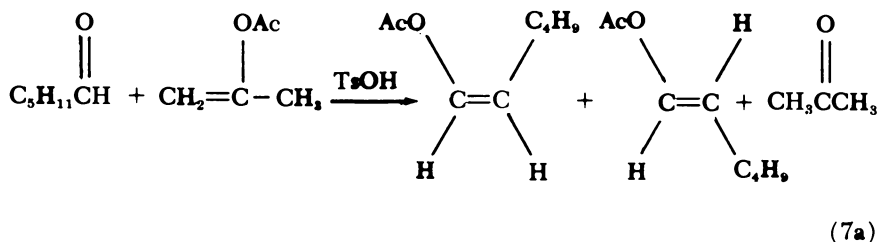
a major part of the input palladium was recovered as the 1-methyl-3-ethyl- π -allyl complex. This aspect of the reaction and the possibilities of its general utilization for synthesizing π -allylpalladium complexes is the subject of another paper. The over-all reaction system under study is given in Reaction 6.

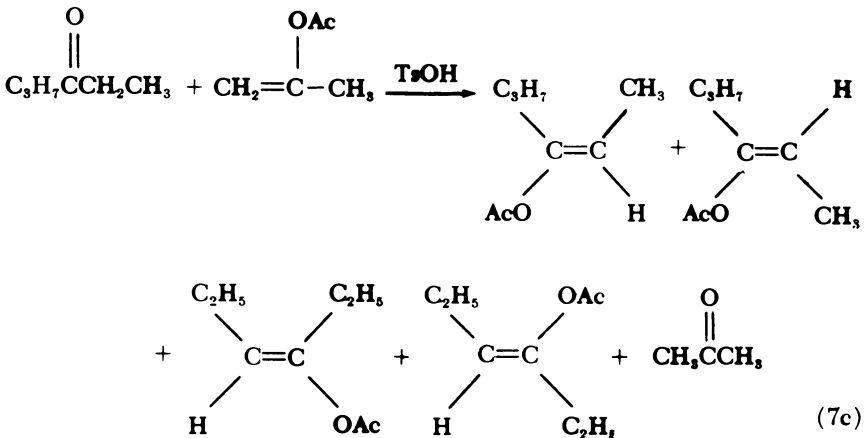
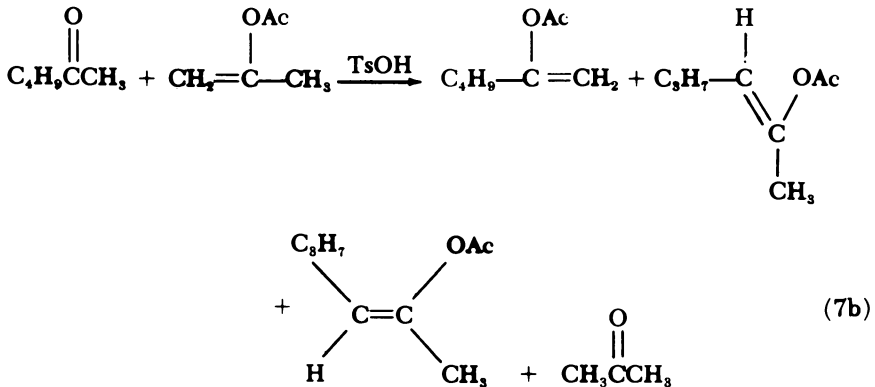


By suitable choice of reaction conditions using hexene it was possible to vary the pattern of substitution from 88% 2-acetate, 11% 1-acetate to 84% 1-acetate, 14% 2-acetate, and from 100% hexenyl acetates to 20% hexenyl acetates, 80% high boilers.

Problems in characterizing and rationalizing these products are immediately apparent. It is necessary to know whether they are primary reaction products or products of isomerization or other secondary reactions, and it is desirable to know as far as possible the specific structures of the products even though 25 hexenyl acetate isomers (ester and olefinic positional) are possible. In addition, the structures of the high boiling products must be elucidated, and a reasonable explanation for their formation presented.

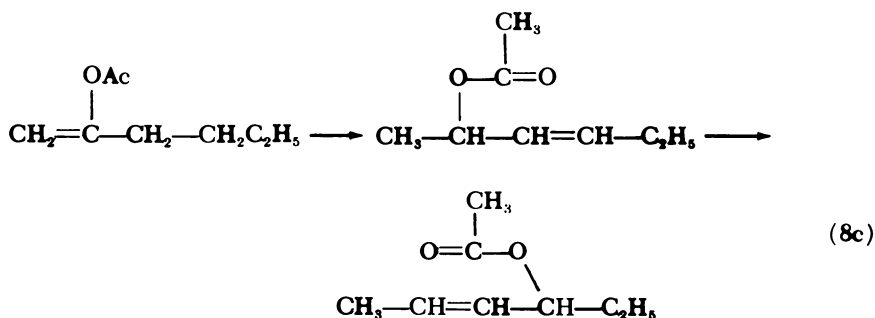
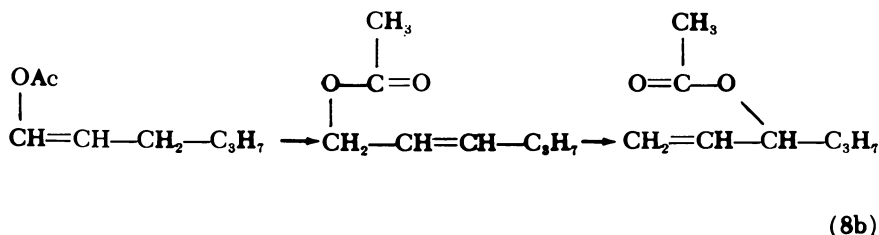
Several approaches were taken. Capillary-column gas chromatography on a vinylation reaction product showed 24 separate peaks present in the hexenyl acetate fraction; however, six of the peaks accounted for about 90% of the total sample. Hydrogenation of the reaction mixture (hydrogen over platinum on carbon) reduced the hexenyl acetates to a mixture of three hexyl acetates and thereby greatly simplified determining the position of oxygen substitution with, however, loss of information on olefin position. We tried to synthesize the specific hexenyl acetate isomers by the ester interchange reactions (Reactions 7a, 7b, and 7c). Mixtures of isomers were obtained, but they corresponded to the main components of the vinylation reaction mixture. For example, the main products isolated from the vinylation of hexene-1 corresponded to the products from Reactions 7a and 7b—*i.e.*, vinyl rather than allyl esters.





The choice of short reaction times was dictated by studies on the unreacted olefin during the reaction. While the vinylation reaction occurred rapidly and extensively in less than 5 minutes at 100°–115°C., little or no olefin isomerization was observed for more than 15 minutes. After this apparent induction period, isomerization to the equilibrium mixture of isomers was rapid and complete (47). The reason for the existence of an induction period is unknown. Further studies are now in progress. Even though the observation that the unreacted olefins are unisomerized does not preclude isomerization after the initial π -complex formation, and prior to the vinylation reaction it is certainly more probable that the olefin reacts in its original configuration. When these observations are coupled with attempts to synthesize the specific vinyl esters reported above, one may reasonably assume the major products isolated are primary products and not products of olefin isomerization either before or after vinylation.

The maximum allylic ester isomerization possible can be measured when hexene is used in the reaction. Both hexene-1-yl acetates and hexen-2-yl acetates will give hexen-3-yl acetates upon allylic ester isomerization (Reactions 8a, 8b, and 8c). Therefore, the hexanol-3-acetate found after hydrogenating the hexenyl acetate product will be representative of the sum of both allylic attack on hexene during vinylation and allylic ester isomerization after vinylation and olefinic isomerization. If hexanol-3-acetate is found in only low levels in the reaction product, then both allylic attack during vinylation and allylic ester isomerization can be discounted in considering the major reaction pathways.



Vinylation Studies in the Absence of Copper(II). Our results obtained with various systems in the absence of cupric salts—*i.e.*, a “one-pass” reaction of palladium(II), are given in Table I. No higher boiling products were obtained than hexenyl acetates. This agrees with Henry (20), who reports that in this system (Pd (II), HOAc, NaOAc) cupric ion is necessary for forming higher boiling products.

Also, the low levels of hexanol-3-acetate found in all these experiments indicate that neither attack on the allylic position of hexene nor allylic ester isomerization is important under these reaction conditions. When the procedure of Kitching *et al.* (29) was repeated, a high level

Table I. Vinylation Reactions of Hexene in the

	<i>Palladium Salt</i>	<i>Added Salts</i>	<i>Ratio AcO/Cl/Pd</i>	<i>Time, min.</i>
1a	Pd[OAc] ₂	None	2/0/1	60
b				1
2a	Pd[OAc] ₂	NaOAc	4/0/1	60
b				1
3a	Pd[OAc] ₂	NaOAc,NaCl	4/2/1	60
b				1
4a	PdCl ₂	NaOAc	4/2/1	60
b				1
5a	PdCl ₂	NaOAc	8/2/1	60
b				1
6a	PdCl ₂	NaOAc,NaCl	36/17/1	60
b				1

* All reactions run using 50 ml. glacial acetic acid 4.46 mmoles palladium(II) salt, and 5 ml. hexene except for runs 6a and b in which 100 ml. glacial acetic acid and

of 2-acetate was obtained, as previously reported (Table I, line 1a). Increasing the reaction temperature had no significant effect upon the reaction (line 1b). When sodium acetate was added (AcO/Pd ratio of 4/1), a significant change in product was found (Table I, lines 2a and b) although again little difference was noted when the reaction temperature was changed. Whether this effect is caused by buffering of the acetic acid by the added acetate or by formation of species such as $(\text{Pd}(\text{OAc})_4)^{2-}$ is not known. While studies on monomer-dimer equilibria of palladium(II) salts in acetic acid have not been reported, it would seem likely that in the presence of such high acetate and chloride ion concentrations relative to palladium, the monomeric species should be significantly favored. Other studies in similar systems have been reported which also seem to favor the monomeric palladium(II) species (48).

When chloride was added to the system either as sodium chloride (Table I, lines 3a and b) or as palladium chloride (lines 4-6) a drastic change in the reaction path occurred. The source of the halide is unimportant; apparently a rapid scrambling of anionic ligands occurs during the preparation of the solutions prior to olefin addition (*cf.*, Table I, lines 3a and 4a). However, in the presence of chloride, temperature effects become pronounced. In all cases, the higher reaction temperatures greatly favor 1-substitution, so much so that it was possible to reverse completely

Absence of Copper(II)^a*Hydrogenated Product Distribution*

Temp., °C.	Hexanol-			Yield, %
	1-Acetate	2-Acetate	3-Acetate	
25	10.6	87.4	2.0	44.8
100	11.3	87.9	0.8	27.6
25	38.2	60.6	1.2	64.1
100	32.4	65.8	1.8	43.0
25	40.5	55.7	3.8	93.9
100	57.5	38.2	4.3	79.8
25	38.7	54.7	6.6	73.8
100	66.2	29.2	4.6	96.2
25	47.8	52.2	0.0	29.8
100	74.0	22.2	3.8	76.9
25	67.6	27.2	5.2	96.2
100	84.0	14.2	1.8	98.0

10 ml. hexene were used. Yields are based on palladium(II) input.

the ratio of 1- and 2-acetates found using the technique reported by Kitching *et al.* (29) (*cf.* Table I, lines 1a and 6b). Increasing amounts of acetate and chloride relative to palladium favor primary acetate (Table I, lines 6a and b). The optimum acetate/chloride ratio for 1-substitution was found to be 2.5. It is possible that chloride-bridged dimeric structures are involved in this drastic change in reaction pathway.

During the reaction, palladium metal precipitation was observed as would be expected in the vinylation reaction (Reaction 1). During product isolation, water is added to the reaction system. In most of the reactions run at 25°C. this addition resulted in further precipitation of palladium metal from the brown solution, probably owing to decomposition of the trace of π -olefin complex of palladium(II) present. However, the acetic acid solutions of products obtained from 100°C. reactions containing chloride were bright yellow and did not precipitate more palladium when water was added. This color is typical of π -allylpalladium chloride complexes and indeed di- μ -chloro-di- π -(methyl-3-ethylallyl)di-palladium(II) could be isolated from the reaction mixture. Formation of these complexes, π -olefin or π -allyl would, of course, result in decreased yields of vinylation products.

Vinylation Studies in the Presence of Copper(II). The majority of reaction studies were performed with a palladium(II)-copper(II) system (Reactions 5a and b). In this way much more vinylation product

could be obtained from a given charge of palladium, and a closer comparison could be made with previously reported reactions. There was no substantial change in product distribution under these conditions from that obtained in systems without added copper.

Table II. Effect of Varying Acetate/Chloride Ratio on the Vinylation Reaction for Sodium Acetate System^a

Acetate/Chloride Ratio	Distribution of Products, %		% 1-Acetate in	
	Hexenyl Acetates	High Boilers	Hexenyl Acetates	Total Product
0.15	20.0	80.0	66.3	13.3
0.30	19.9	80.1	78.3	15.6
0.45	40.1	59.9	61.8	24.7
0.50	59.2	40.8	59.0	34.9
0.62	69.7	30.3	50.2	35.0
0.75	73.5	26.5	50.7	37.2
1.00	91.7	8.3	38.5	35.5
1.25	100	0		41.0
1.50	100	0		57.5
1.75	100	0		68.8
2.00	100	0		67.5
2.25	100	0		72.0
2.45	100	0		73.8
2.75	100	0		68.8
3.20	100	0		71.8
3.70	100	0		70.0
30 ^b	100	0		55.5

^a All reactions run with PdCl₂-CuCl₂-NaOAc-hexene-1-acetic acid at 115°C. for 15 min.

^b Cu(OAc)₂ used in place of CuCl₂.

Using standard reaction conditions (15 minutes at 115°C.), a further study using sodium acetate was made of the previously noted effect of acetate to chloride ion ratio on product distribution (Table II). At acetate/chloride ratios of 1.25 or higher, only hexenyl acetates—no high boiling products—were isolated. As the ratio was increased beyond this value, an increasing amount of primary acetate was found in the hexenyl acetates until a maximum of 74% was obtained at an acetate/chloride ratio of 2.45. Beyond this ratio, a slow decline in relative amount of primary acetate was noted (*see* Figure 1). However, at acetate/chloride ratios of less than 1.25, high boiling products were found in increasing amounts as the ratio was decreased, until at a ratio of 0.15/0.30 80% of the isolated product consisted of high boiling materials (Figure 1 and Table II). At these lower acetate/chloride ratios the amount of 1-acetate in the hexenyl acetates increased from a minimum of 38.5% at a ratio of 1.0 to values as high as 78% at a ratio of 0.3. However, if one expressed

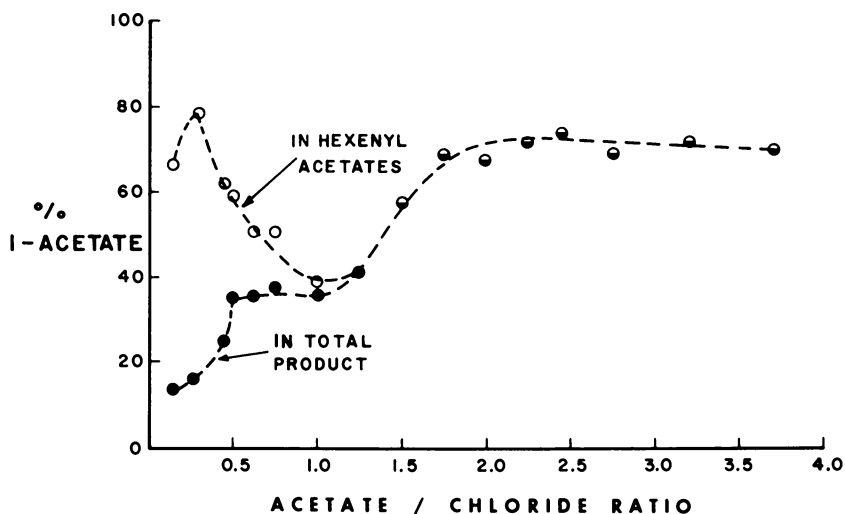


Figure 1. Effect of acetate/chloride ratio on 1-acetate content of vinylation products

Table III. Effect on the Vinylation Reaction of Varying Acetate/Chloride Ratio for Calcium and Magnesium Acetate Systems

AcO/Cl Ratio	Distribution of Products, %		% 1-Acetate	
	$C_6H_{11}OAc$ Isomers	High Boilers	in $C_6H_{11}OAc$	in Total Product
Mg[OAc]₂ Systems				
0.3	26.0	74.0	82.0	21.3
0.6	25.4	74.6	87.5	22.4
1.2	31.0	69.0	79.8	24.8
1.8	37.2	62.8	75.9	28.2
2.4	48.0	52.0	67.2	32.2
3.0	53.8	46.2	65.3	35.2
Ca[OAc]₂ Systems				
0.3	21.3	78.7	88.0	18.7
0.6	53.8	46.2	79.3	42.6
1.2	68.0	32.0	59.5	40.5
1.8	82.6	17.4	54.0	44.6
2.4	96.2	3.8	51.8	49.8
3.0	100	0	52.0	52.0

the amount of 1-acetate present as a function of the total product obtained, a decreasing amount was found with decreasing acetate/chloride ratio (Figure 1). Probably competition is occurring between acetate and chloride for ligand positions on the palladium, and the changing product distribution reflects this competition.

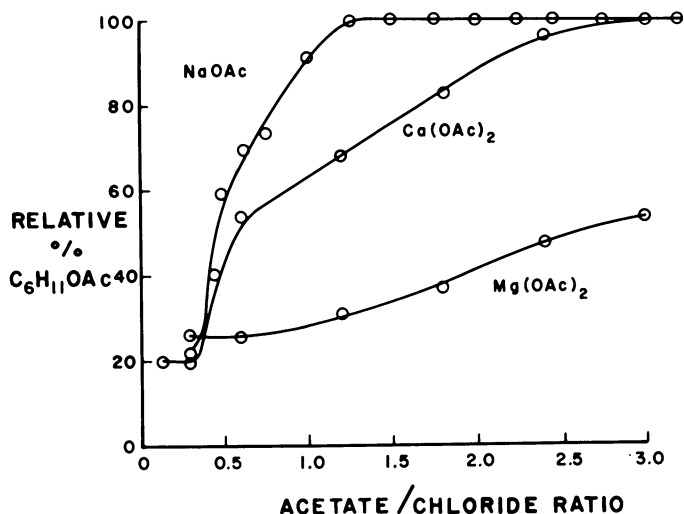


Figure 2. Effect of acetate/chloride ratio on relative amount of hexenyl acetates

Table IV. Effect of Variation in Metal Acetates in the Vinylation of Hexene^a

Acetate Salt	Distribution of Products, %		% 1-Acetate	
	<i>C</i> ₆ <i>H</i> ₁₁ <i>OAc</i> Isomers	High Boilers	in <i>C</i> ₆ <i>H</i> ₁₁ <i>OAc</i>	in Total Product
LiOAc	99.1	0.9	35.6	35.3
NaOAc	100	0	41.0	41.0
Mg[OAc] ₂	31.0	69.0	79.8	24.8
Ca[OAc] ₂	68.0	32.0	59.5	40.5
Sr[OAc] ₂	74.4	25.6	52.2	38.8
Ba[OAc] ₂	91.5	8.5	28.0	25.6
Zn[OAc] ₂	71.7	28.3	14.8	10.6
Cd[OAc] ₂	100	0	23.8	23.8
Hg[OAc] ₂	100	0	0 ^b	0
Al[OAc] ₃	59.4	40.6	55.9	33.2

^a All reactions run using PdCl₂-CuCl₂-Mⁿ⁺[OAc]_n-1-hexene for 15 min. at 115°C. at an AcO/Cl ratio of 1.24.

^b Product 100% hexanol-2-acetate.

Similar studies using calcium and magnesium acetates at varying acetate/chloride ratios gave results which were specifically different but showed the same general trends as observed with sodium acetate (Table III, Figure 2). In general, increasing amounts of hexenyl acetates along with increasing amounts of primary acetate within the hexenyl acetates were found as the acetate/chloride ratio was increased, but these increases were not as rapid as with sodium acetate. Whether this is caused

by a decreased amount of dissociation of the metal acetates or by formation of other types of complexes is not known. When other metal acetate salts were evaluated, none was superior to sodium acetate (Table IV). Some trends appeared (*—e.g.*, the Group II-A elements), but no generalizations could be made. For mercuric acetate, oxymercuration apparently occurred since 2-acetate was the only product isolated.

Table V. Effect of Reaction Time and Temperature on Primary Acetate Content^a

Acetate/Chloride Ratio: 2.25

	<i>Reaction Time, min.</i>						
	0	5	10	15	22	30	420
Reaction Temp., °C.							
80	83.5			78.8		80.2	
90							
95			77.0		75.0		73.2
100				74.2			
115	71.4	72.5	71.0	73.8		74.7	
130				71.4	72.4		
135			72.2				
150				70.8		71.7	

^a All reactions with hexene, acetic acid, PdCl₂, CuCl₂, NaOAc; All products 100% C₆H₁₁OAc; Values are % 1-acetate content.

When reaction time and temperature effects were studied in copper(II)-containing systems, the acetate/chloride ratio affected these results as it did in the copper-free systems. When reaction time and temperature changes were studied on a system with an acetate/chloride ratio of 2.25 (a ratio which led to a maximum amount of 1-acetate in a product free of high boilers), only slight variation in product composition occurred. The selectivity towards primary acetate seemed to decrease slightly as reaction temperature was increased over the range 80°–150°C., but no change in selectivity was noted as the reaction time was varied (Table V). On the other hand, at an acetate/chloride ratio of 0.62, large variations in both primary acetate and high boiling product content were observed (Table VI). A surprising result is that short reaction times led to greatly increased amounts of high boiling products compared with studies at longer reaction times. This would imply that these high boiling isomers are not products of reaction of the vinylated products but are formed either in a different reaction or by interception of one of the vinyl ester precursors. Such an interception has also been proposed by Moiseev and Vargaftik (36) to account for the formation of undeuterated ethylidene diacetate from ethylene in deuterioacetic acid.

In some preliminary studies on the effect of the metallic anion a series of reactions was run in which chloride in both the palladium and copper salts was replaced by other anions. When acetate was used, results similar to the chloride systems were obtained although product distribution was somewhat different (*see also* Table I). Both bromide and iodide were found to inhibit the reaction, and no products were isolated. For the oxyanions, nitrate, sulfate, and acetylacetonate, vinylation products of these oxyanions in addition to the acetate vinylation products were found. Because of the increased complexity of these systems, they were not investigated further. All chloride-containing systems investigated—PdCl₂, Na₂PdCl₄, (NH₃)₂PdCl₂, and π -allylpalladium chloride—had similar reactivities and vinylation-product distributions.

Table VI. Effect of Reaction Time and Temperature on Primary Acetate Content^a

Acetate/Chloride Ratio: 0.62

<i>Reaction Temp. °C.</i>	<i>Reaction Time, min.</i>	<i>Distribution of Products, %</i>		<i>% 1-Acetate in</i>	
		<i>Hexenyl Acetates</i>	<i>High Boilers</i>	<i>Hexenyl Acetates</i>	<i>Total Product</i>
115	0	21.9	78.1	85.3	18.7
115	5	37.2	62.8	57.1	21.2
115	15	40.1	59.9	57.5	23.0
115	30	57.6	42.4	57.9	33.4
80	15	16.3	83.7	83.6	13.6
115	15	40.1	59.9	57.5	23.0
130	15	67.1	32.9	49.2	33.0
150	15	78.6	21.4	52.5	41.2

^a All reactions run using hexene, acetic acid, PdCl₂ and CuCl₂.

The reactions and product distributions thus far reported have been exclusively concerned with hexene. It was of interest to see whether the high specificity of positional substitution could be maintained with the other hexene isomers. By positional substitution specificity is meant ester attachment on either of the carbons involved in the original carbon-carbon double bond. Table VII shows the results of these studies. The internal olefins reacted more slowly than the α -olefin, and with both palladium chloride-cupric chloride and π -hexenylpalladium chloride-cupric chloride systems high substitutional specificity (> 95%) was also maintained with 2-hexene (Table VII). However, with 3-hexene the specificity is considerably lower (80%). Whether this is caused by 3-hexene isomerization prior to vinylation or by allylic ester isomerization is not known. A surprisingly high ratio of 2-substitution to 3-substitution is found (\sim 7:1) in the products from 2-hexene. An effect this large

cannot be ascribed to polar effects and, in fact, is larger than would have been expected from steric effects in the previously postulated oxypalladation.

Because the possibility of olefinic isomerization still loomed important in considering product distributions, we decided to add the powerful olefin isomerization catalyst (17), rhodium trichloride, to the system. No change in product distribution from that of palladium chloride alone was found with either hexene or 2-hexene when a 1:1 molar ratio of rhodium trichloride/palladium chloride was used (Table VII). This is further evidence that the relative rate of vinylation is greater than that of isomerization. When rhodium chloride was used with hexene without any added palladium chloride at 115°C., only slight reaction occurred, and the product contained 85.7% 2-acetate, 10.2% 1-acetate, and 4.1% 3-acetate. Apparently, vinylation had occurred with rhodium trichloride in a manner analogous to oxymercuration and the low-temperature palladium vinylation reaction.

Table VII. Effect of Variation of Olefin Isomer on Product Distribution in the Vinylation Reaction^a

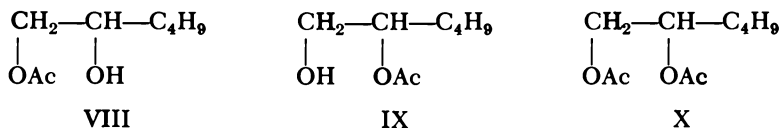
System	Olefin	Hexenyl Acetate Distribution, %		
		1-Acetate	2-Acetate	3-Acetate
PdCl ₂ + CuCl ₂	Hexene	73.8	23.3	2.9
	<i>cis</i> - and <i>trans</i> -2-Hexene	4.2	83.3	12.5
	3-Hexene	0	19.3	80.7
[C ₆ H ₁₁ PdCl] ₂ ^b + CuCl ₂	Hexene	64.0	32.9	3.1
	<i>cis</i> - and <i>trans</i> -2-Hexene	0	87.5	12.5
PdCl ₂ :RhCl ₃ [1:1] + CuCl ₂	Hexene	71.4	25.1	3.5
	<i>cis</i> - and <i>trans</i> -2-Hexene	3.0	83.8	13.2

^a All reactions run at 115°C. for 15 min. using NaOAc in HOAc. Acetate/Chloride Ratio, 2.45; product 100% hexenyl acetates.

^b Di- μ -chloro-di- π -(1-methyl-3-ethylallyl)dipalladium(II).

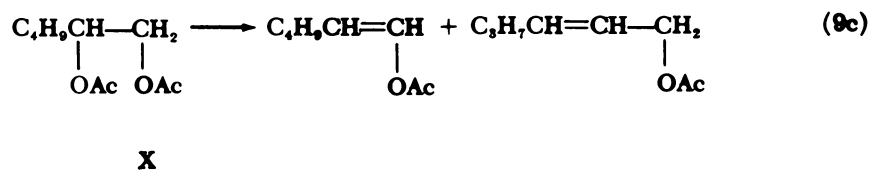
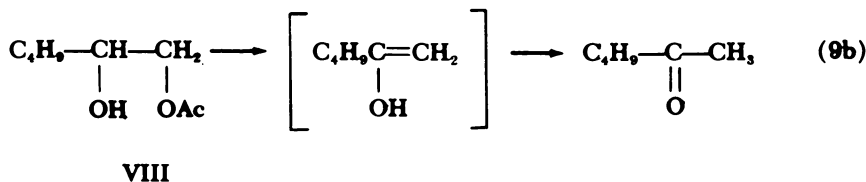
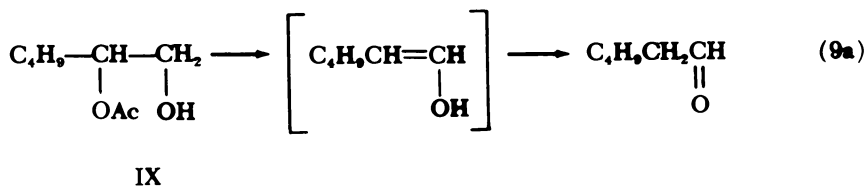
Structure Elucidation of the High Boiling Products. Under certain conditions, vinylation with ethylene gives, in addition to or instead of vinyl acetate, ethylidene diacetate, ethylene glycol monoacetate, and ethylene glycol diacetate (9, 10, 24, 25, 26). In all reported examples of the formation of dioxygenated species, cupric salts have also been present in the reaction medium. For higher olefins, only once has the formation of high boiling products been reported (20). In our current studies, using hexene, under certain conditions (*see above*) high boiling fractions were found, which were mixtures of products. The major component was tentatively identified by NMR as either 1-acetoxy-2-hydroxyhexane (VIII) or 1-hydroxy-2-acetoxyhexane (IX) or a mixture of both.

In addition, 1,2-diacetoxyhexane (X) was also found.



When the mixture of high boiling products was acetylated, VIII and IX were smoothly converted to the diacetate, X. This proved that both the hydroxyacetates and the diacetate had the same oxygen attachment positions. However, these results do not preclude a 1,3-diol type structure.

Pyrolysis of the high boiling products obtained from hexene afforded hexanal (Reaction 9a), 2-hexanone (Reaction 9b) and hexenyl acetates (Reaction 9c).



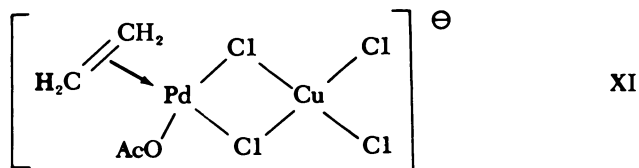
No 3-hexanone was observed. This lack of 3-hexanone and the absence of any unsaturated alcohol products in the pyrolyzate are further arguments for vinylation at the olefinic rather than the allylic position and for the 1,2- rather than 1,3-glycol structure for the diol monoacetates. It is still possible that a 1,3-diol diacetate was formed specifically, without the formation of a 1,3-diol monoacetate, but this is at best unlikely. Reduction of the hexenyl acetate portion of the pyrolyzate showed the product to be 100% primary acetate.

Pyrolysis of the acetylated high boiling fraction under the same conditions gave a product rich in primary hexenyl acetates with almost no aldehydes or ketones present. These observations further support our

structural assignments. However, it is entirely possible that the component identified as hexan-1,2-diol diacetate (X) could contain some hexylidene diacetate, $C_7H_{11}CH[OAc]_2$ hidden under the other diacetate peak. Its pyrolysis would, of course, also give primary hexenyl acetates. The production of high levels of primary acetate from 1,2-glycol diacetates has also been observed in the pyrolysis of propylene glycol diacetate (3). In this case the primary/secondary acetate ratio in the unsaturated ester products was 30/1.

Reaction Mechanism. Any mechanism proposed for the vinylation of acetic acid by the hexenes must be able to account for the production of the high boiling products, 1,2-hexandiol mono- and diacetates (VIII, IX and X), and possibly hexylidene diacetate, as well as the hexenyl acetates. The currently accepted mechanism for synthesizing vinyl acetate from ethylene and acetic acid is derived from that postulated by Henry (1, 19), based on studies of the Wacker acetaldehyde synthesis. The key step in this mechanism is an insertion reaction (18).

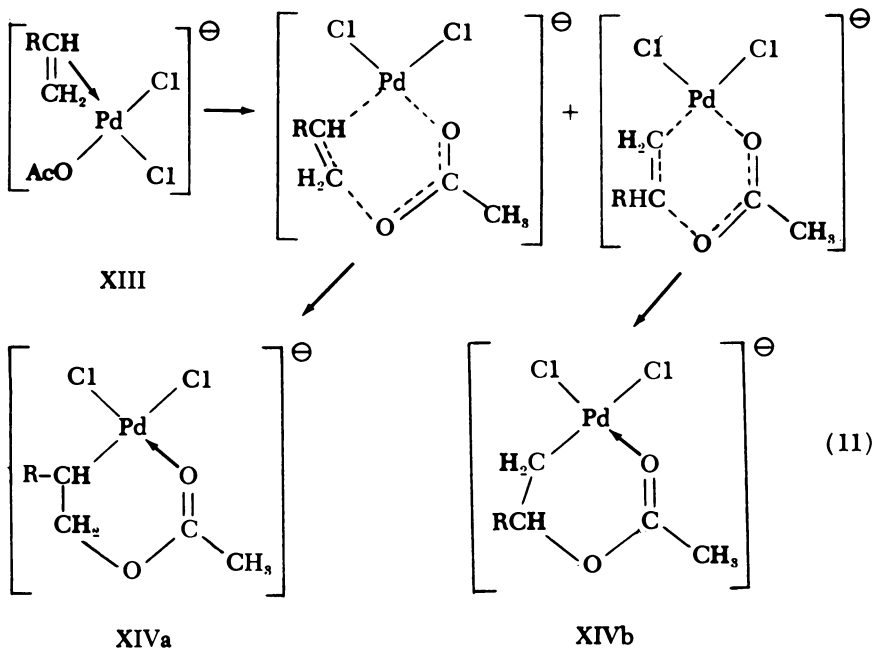
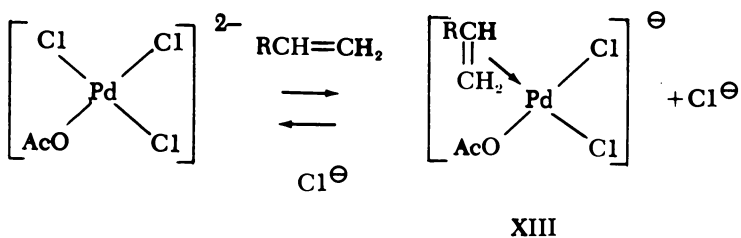
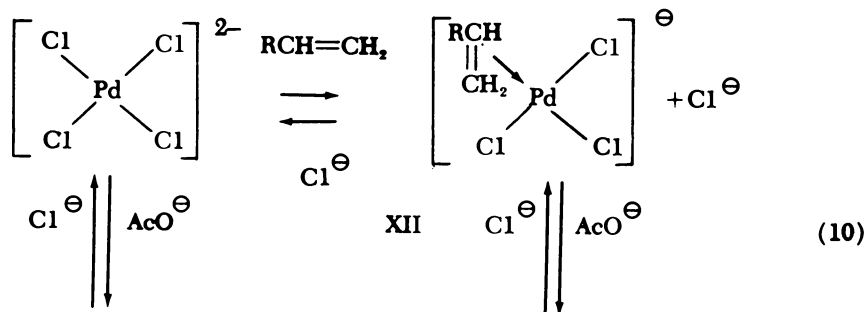
In the following mechanistic proposals, monomeric species have been written for economy of space. In the absence of cupric salts, with large excesses of acetate present, it is unknown whether the species are monomeric or dimeric in palladium although the monomeric species seem most probable. However, in the presence of cupric salts, the most likely species are those like XI, dimeric in palladium and copper. In these



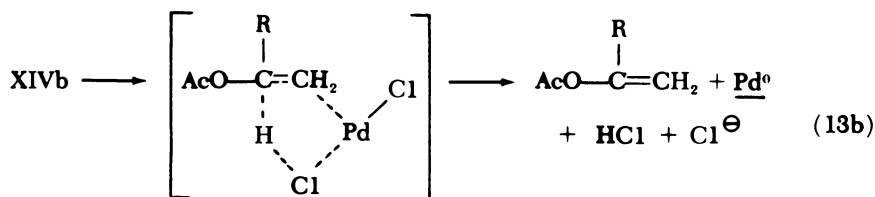
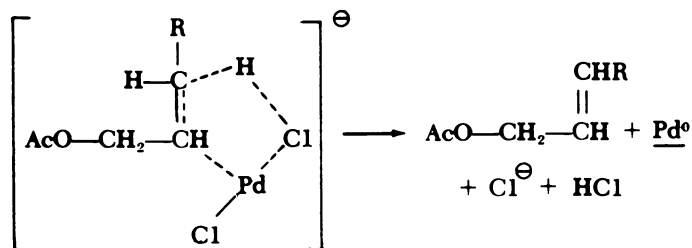
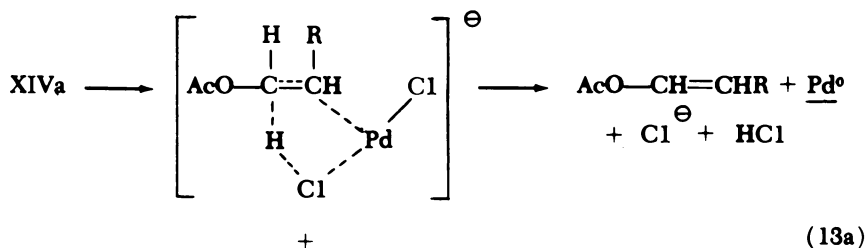
systems, the lack of palladium metal formation can be explained by the electron transfer reactions through the chloride bridges from the cupric halide.

The initial reactions in the vinylation process are probably the establishment of a series of equilibria (—*e.g.*, as shown in Reaction 10) in which a cis configuration of olefin π -complex and acetate in the complex (XIII) is attained.

Similar equilibria and cis complexes have been proposed in related systems (1, 27, 28, 48). The next step in the reaction pathway has been thought to be a two-carbon insertion reaction. Usually this insertion has been formulated as a four-center reaction. However, for acetate system reactions it is possible to write a more satisfying six-center reaction intermediate (Reaction 11).



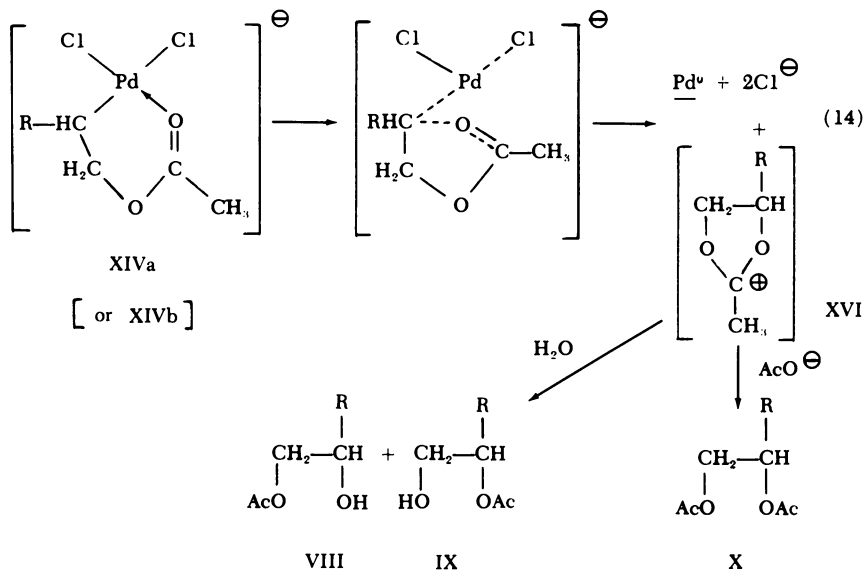
The intermediates XIVa and XIVb are analogous to those previously proposed (27, 29, 48). The selectivity for XIVa and XIVb has been rationalized in terms of Markovnikov and anti-Markovnikov additions (29).



The formation of high boiling products, not previously considered in mechanistic studies of this reaction, presents several problems. Simple addition of the elements of water or acetic acid to the vinylation product to form the hydroxy acetates and the diacetates is unsatisfactory for several reasons. First, there is no analogy in the literature for this type of reaction; second, this type of addition cannot explain the increased amounts of high boiling products found as reaction time is shortened, and finally, simple addition of the elements of acetic acid to the vinyl ester would not explain the results obtained in some of the deuterium studies (36).

A possible route for forming the high boiling products which satisfies all the conditions above is given in Reaction 14.

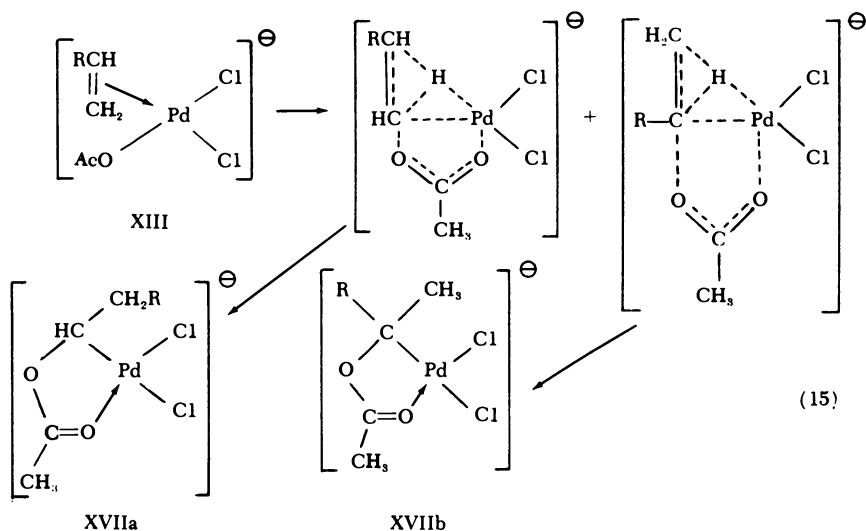
In this case, under conditions which favor high boiler formation—*i.e.*, low acetate/chloride ratio, presence of cupric salts and short reaction times—a neighboring group displacement of palladium by acetate instead of proton loss or hydride transfer could occur to give the intermediate XVI, which then would undergo an acetate displacement reaction to give the diacetate (X) or would react with water during the reaction workup to afford the hydroxyacetates (VIII and IX). Reaction during workup



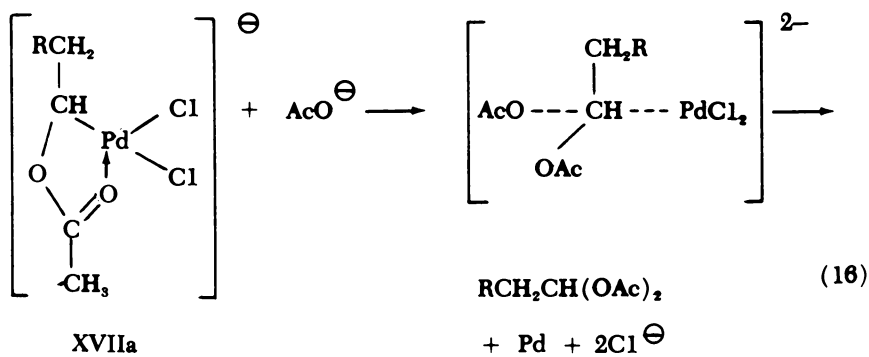
with water is the best way to explain the formation of hydroxyl-containing products in an anhydrous system. This type of neighboring group acetate displacement reaction has also been proposed by Anderson and Winstein (2) in the oxidation of cyclohexene by thallic acetate and by Olson (38) in the selenium dioxide oxidation of ethylene. The need for cupric ion to obtain dioxygenated products is unclear. Perhaps cupric chloride, by forming complexes such as XI, influences the polarity or stereochemistry about the palladium center so as to inhibit proton loss or hydride transfer.

A satisfactory method of explaining gross changes in product distribution as reaction conditions are changed is to invoke two separate and competing reaction mechanisms. In the present situation a second mechanism which also fits all the observed data is a one-carbon insertion reaction. After the equilibria are established (Reaction 10), an insertion reaction could occur (Reaction 15) with concomitant hydrogen shift, resulting in insertion products in which both acetate and palladium are attached to the same carbon (XVIIa and XVIIb).

Rearrangement of a two-carbon insertion product could also lead to intermediates of these structures. Similar one-carbon insertion products have recently been proposed for the Wacker acetaldehyde synthesis (1, 27, 39). Elimination of a proton and palladium could occur from the intermediates XVIIa and XVIIb in a manner analogous to that proposed for the two-carbon insertion product in Reaction 13. This proposed pathway conforms with all observations, including the deuterium studies (36, 54).

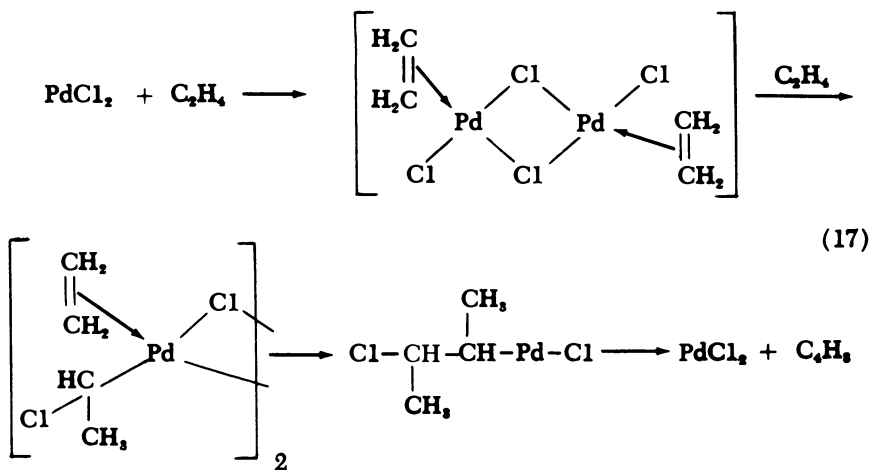


Formation of 1,1-diacetates—*e.g.*, ethylidene diacetate from ethylene or hexylidene diacetate from hexene—by simple acetate displacement of palladium (Reaction 16) is a much more satisfactory reaction scheme than any previously proposed. On the other hand, accounting for 1,2-diol type products is difficult by this scheme, necessitating a reverse hydrogen transfer to form a two-carbon insertion product intermediate. This type



of difficulty serves to emphasize again the possible dual mechanism in this reaction system. Slight changes in reaction conditions or reactant ratios could cause a shift between the one-carbon and two-carbon insertion pathways. At present, 2-substitution products from olefins (hexen-2-yl acetates from hexene) and 1,2-diol mono- and diesters would appear to be formed *via* a two-carbon insertion pathway, while the one-carbon insertion pathway would be favored in forming 1-substitution products and 1,1-diacetates from olefins.

A one-carbon insertion reaction similar to that proposed above could also be used to account for the observed dimerization of ethylene and propylene by palladium(II) systems (28, 56). A possible route for this reaction is given in Reaction 17.



The exact natures of the active species in these reactions are unknown, but undoubtedly differ considerably at the extremes studied. In one case—the low temperature chloride-free system— π -olefin complexes of palladium salts seem to be favored, while in the other case—the high temperature chloride-containing systems—chloride-bridged π -allyl complexes or their precursors seem to be favored. In addition, the presence of cupric ion, which would not be expected to take a direct part in the vinylation reaction, appears to influence the course of the reaction strongly. Whether these changes alter the steric course of the olefin insertion or whether other factors influence this course are unknown. The role of the π -allylpalladium chloride complexes formed in the high temperature reactions is uncertain. While it has been shown that under these conditions they possess apparent activity in the vinylation reaction and can be recovered unchanged from the reaction mixture, it is not known whether the π -allyl group continues to occupy two ligand positions during the reaction. This activity of π -allyl complexes is under continuing investigation.

Acknowledgment

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Oxidizing Olefins by Pd(II) and Tl(III)

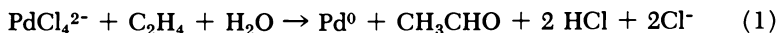
P. M. HENRY

Hercules Research Center, Hercules Inc., Wilmington, Del.

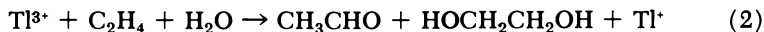
In aqueous solution the kinetics of oxidizing olefins by Pd(II) and Tl(III) are best explained by mechanisms involving oxymetallation adducts with oxymetallation—the rate-controlling step. However, important differences exist between the two oxidations. These are: (1) Pd(II) gives carbonyl compounds whereas Tl(III) gives carbonyl compounds and glycols; (2) π -complex formation is detected in the Pd(II) oxidation but not in the Tl(III) oxidation; (3) the effect of olefin structure on rate is quite different; (4) salt effects are different. These differences can be explained by the different tendencies of the two metal ions to form stable π -complexes and the differences between Pd(0) and Tl(I) as leaving groups. The comparison is extended to non-aqueous systems, and a novel oxidation requiring the presence of both Pd(II) and Cu(II) is discussed.

This paper compares the oxidation of olefins by Pd(II) and Tl(III) because the two oxidations, although apparently proceeding by similar routes, still display considerable differences in their detailed mechanisms. Such a comparison is an effective way to emphasize the important individual features of each oxidation.

Aqueous PdCl₂ oxidizes olefins to carbonyl compounds—e.g., ethylene gives acetaldehyde (Reaction 1).



On the other hand, thallic ion oxidizes olefins to a mixture of glycols and carbonyl compounds—e.g., ethylene gives acetaldehyde and ethylene glycol (Reaction 2).



First the kinetics of each oxidation in aqueous solutions are reviewed, and mechanisms which the author believes best fit all the experimental

data are proposed for each oxidation. Next, the two oxidations are compared, and the common features of both mechanisms are pointed out. The differences are discussed, and an attempt is made to correlate these differences with the known chemistry of each metal ion.

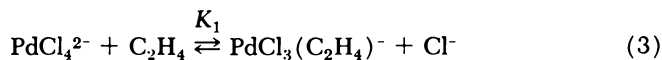
The results in aqueous solutions are extrapolated to nonaqueous systems to demonstrate that the oxidations by these metal ions in these systems are analogous to the oxidations in water.

Finally, a novel oxidation which requires the presence of both Pd(II) and Cu(II) is described, and possible reaction paths are considered in light of the mechanisms proposed for the oxidations involving Pd(II).

Oxidation by Palladium(II)

The oxidation of ethylene to acetaldehyde by aqueous Pd(II) is, of course, the Wacker process developed by Smidt and co-workers (37). The kinetics of this reaction, as studied by several investigators (12, 19, 32, 37, 40), are first-order in ethylene and Pd(II) and strongly inhibited by chloride ions and protons. Olefin-Pd(II) π -complexes have been suggested as intermediates, but in most cases the experimental technique did not permit measurement of π -complex formation under the reaction conditions. However, by using a reactor of high gas-liquid mixing efficiency, we were able to detect initial ethylene uptakes greater than that required to saturate the solution with gas. An example of the type of plots obtained at a constant ethylene pressure of 1 atm., $\log(V_{\infty} - V)$ vs. time, is shown in Figure 1. The double arrows represent the volume of gas required to saturate the solution. After the initial ethylene uptake, the plot is straight, indicating a first-order reaction. Since the volume of ethylene consumed in excess of solubility always corresponded to the amount of Pd(II) reduced, this plot represents a reaction which is first order in Pd(II). The order in ethylene cannot be determined from this run since the ethylene pressure, and therefore the ethylene concentration in solution, is kept constant during the run. However, by running reactions at different olefin pressures, it could be shown that the reaction is also first order in ethylene.

When the chloride ion concentration was varied, not only did the rate of the oxidation change but also the amount of ethylene initially taken up in excess of that required to saturate the solution. By assuming that the net initial ethylene uptake resulted from the following equilibrium,



values of K_1 which did not vary with either chloride ion or proton concentration could be calculated.

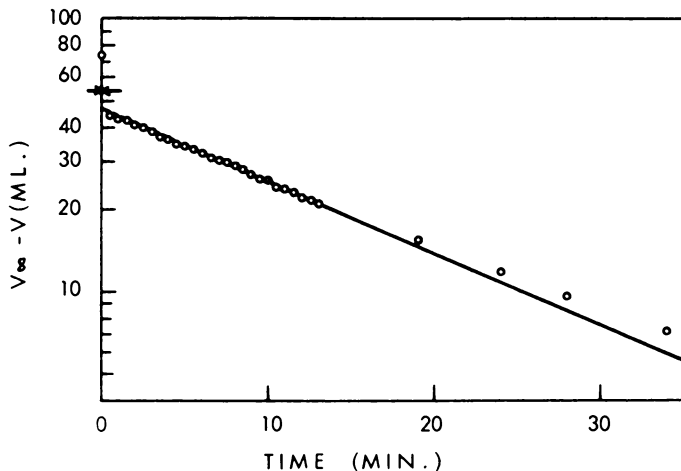


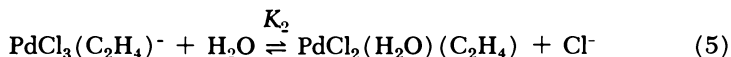
Figure 1. Pd(II) oxidation of ethylene. Plot of $\log(V_{\infty} - V)$ vs. time at constant atmospheric ethylene pressure

By determining the variation of rate with chloride ion and proton concentration, it is possible to show that the complete rate expression is:

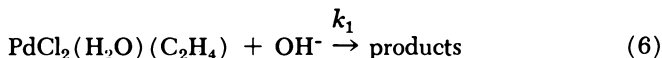
$$-d[\text{C}_2\text{H}_4]/dt = \frac{k[\text{PdCl}_3(\text{C}_2\text{H}_4)^-]}{[\text{Cl}^-][\text{H}^+]} = \frac{kK_1[\text{PdCl}_4^{2-}][\text{C}_2\text{H}_4]}{[\text{Cl}^-]^2[\text{H}^+]} \quad (4)$$

where the value of k is $2.03 \pm 0.2 \times 10^{-4} \text{ M}^2 \text{ sec.}^{-1}$, and K_1 is 17.4 at 25°C .

This rate expression implies that the first step in the reaction is the formation of π -complex (Reaction 3), followed by loss of another chloride to give an aquated π -complex.



The proton inhibition can be explained in several ways. The next step could be the attack of hydroxide ion on the complex.



This possibility can be eliminated on kinetic grounds. The rate expression would be:

$$-d[\text{C}_2\text{H}_4]/dt = k_1[\text{PdCl}_2(\text{H}_2\text{O})(\text{C}_2\text{H}_4)][\text{OH}^-] \quad (7)$$

However, since:

$$[\text{OH}^-] = K_w/[\text{H}^+] \text{ and } [\text{PdCl}_2(\text{H}_2\text{O})(\text{C}_2\text{H}_4)][\text{Cl}^-] = K_2[\text{PdCl}_3(\text{C}_2\text{H}_4)^-], \quad (8)$$

the complete rate expression becomes:

$$-d[\text{C}_2\text{H}_4]/dt = \frac{k_1 K_2 K_w [\text{PdCl}_3(\text{C}_2\text{H}_4)^-]}{[\text{H}^+][\text{Cl}^-]} \quad (9)$$

The equilibrium corresponding to Reaction 5 was not detected in our measurements of K_1 ; hence, the value of K_2 could not be determined. However, allowing for experimental error we can assume it was less than 10^{-2} .

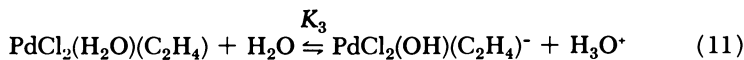
Equating Reaction 9 to Reaction 4, we find:

$$k = k_1 K_2 K_w = 2.03 \times 10^{-4} \text{ M}^2 \text{ sec}^{-1} \quad (10)$$

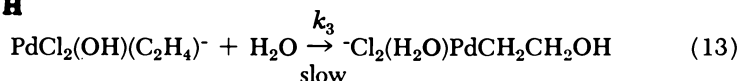
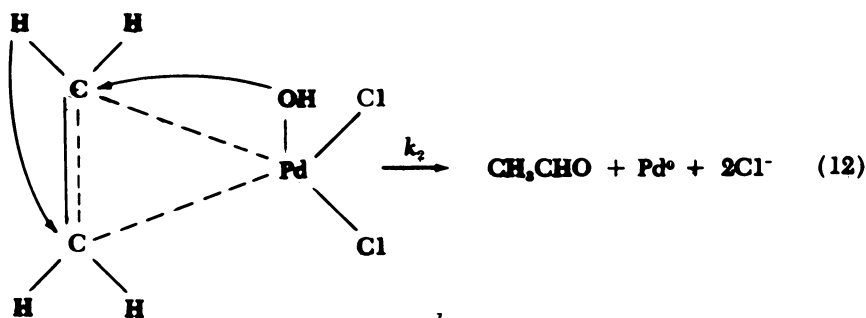
Since K_w is known, we can substitute the value of 10^{-2} for K_2 in Equation 10 and obtain the minimum value of k_1 . This value is $10^{12} \text{ M}^{-1} \text{ sec}^{-1}$ which is 10^3 larger than the rate for a diffusion-controlled process in solution. These calculations demonstrate that the value of k_1 in Reaction 6 must be too large to be reasonable, and thus the reaction cannot proceed by hydroxide ion attack.

Three other plausible paths can be written.

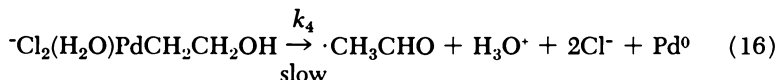
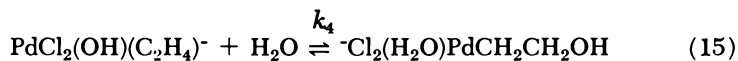
PATH 1



PATH 2



PATH 3

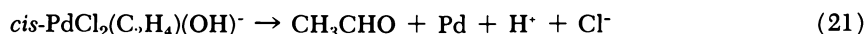
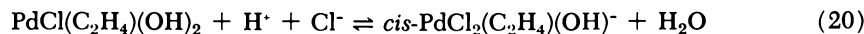
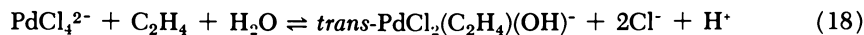


Isotope effects can be used to choose the most likely path. When ethylene is oxidized in deuterated water, the acetaldehyde contains no deuterium; hence, all four hydrogens in the acetaldehyde must come from the ethylene. Thus, if the slow step of the reaction involves the formation of acetaldehyde, the activated complex for this slow step would involve a hydride transfer, and a primary isotope effect would be expected when deuterated ethylene is used. Actually, the isotope effect k_H/k_D was found to be only 1.07. In Paths 1 and 3, the slow step is, respectively, the decomposition of a π -complex and a σ -complex to product, and they would be expected to display a primary isotope effect. However, in Path 2, the rate-determining step is the rearrangement of a π -complex to a σ -complex. Since no carbon-hydrogen bonds are broken, no primary isotope effect would be expected. Thus, Path 2 is consistent with all the experimental facts. Paths involving oxypalladation adducts, first suggested by the Russian workers (32), are now generally accepted (19, 28, 32).

Jira, Sedlmeier, and Smidt (28) recently proposed a kinetic expression and sequence of steps somewhat different from those listed above. They found that a plot of rate *vs.* $[\text{Cl}^-]$ or $[\text{H}^+]$ first increases, reaches a maximum, and then decreases. The following expression was found to fit the families of curves depicting rate *vs.* $[\text{Cl}^-]$ and $[\text{H}^+]$ (where $a = c [\text{Pd}(\text{II})][\text{C}_2\text{H}_4]$):

$$\text{rate} = \frac{a \cdot [\text{H}^+][\text{Cl}^-]}{b + [\text{H}^+]^2[\text{Cl}^-]^3} \quad (17)$$

At high $[\text{Cl}^-]$ and $[\text{H}^+]$ this expression reduces to Equation 4. These workers interpreted this rate expression to mean that the following series of steps are occurring.



They reasoned that the $[\text{H}^+]^2$ and $[\text{Cl}^-]^3$ terms in the denominator arise from Reactions 18 and 19 and the $[\text{H}^+]$ and $[\text{Cl}^-]$ terms in the numerator from Reaction 20. These steps are proposed to arrive at *cis*- $\text{PdCl}_2(\text{C}_2\text{H}_4)(\text{OH})^-$ since it was felt that this stereochemistry was required for the further reaction of the hydroxo π -complex. Because of the *trans* effect of the ethylene, the original complex would be expected to be *trans*.

This analysis is unlikely from a kinetic standpoint and invalid from thermodynamic considerations. First, the only way that the reaction scheme represented by Reactions 18–21 could obey a rate expression in

the form of Equation 17 would be if almost all the Pd(II) were in the form of the dihydroxy π -complex at low $[H^+]$ and $[Cl^-]$. It is extremely unlikely that Pd(II) would eject two protons to form any large concentrations of this material. In any case, if the dihydroxy complex did form in high yield, it could be detected by measuring pH and ethylene uptake at high $[Pd(II)]$, low $[Cl^-]$, and low $[H^+]$. Almost certainly the differences in kinetics in the two ranges merely result from the fact that Pd(II) is not present as $PdCl_4^{2-}$ in the lower $[Cl^-]$ and $[H^+]$ regions but rather exists as $[PdCl_m(H_2O)_n(OH)_p]_r$ species (where $m + n + p = 4$ and $r = 1$ or 2). It has already been pointed out (19) that Equation 4 is valid only in the range of $[Cl^-]$ in which Pd(II) exists as $PdCl_4^{2-}$. Henry reports (22) that the values of *both* k and K_1 in Equation 4 drift when $[Cl^-] < ca. 0.08$.

Second, Reactions 18, 19, and 20 represent equilibria, and thus all species in these equations are in equilibrium with each other. Hence, the *trans*- $PdCl_2(C_2H_4)(OH)^-$ is in equilibrium with *cis*- $PdCl_2(C_2H_4)(OH)^-$, and it is meaningless to speak of intermediate equilibria such as Reactions 19 and 20. In any case, if the *cis*- $PdCl_2(C_2H_4)(OH)^-$ is required for reaction, it is certain that kinetically significant amounts are in equilibrium with the *trans* isomer (19).

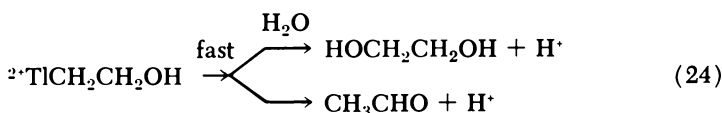
No detailed kinetic studies have been carried out on this reaction in aqueous solution containing no chloride ion, but qualitatively the results are similar. Since no chloride ion is present to inhibit π -complex formation, the initial uptake of ethylene in excess of that required to saturate the solution is much greater than the uptake in chloride-containing solutions. In fact, more than one ethylene is taken up for each Pd(II); hence, some diolefin π -complexes must be formed. The excess ethylene is gradually released as Pd^0 , and acetaldehyde is formed (37).

Oxidation by Tl(III)

The kinetics of this oxidation, first reported by Grinstead (15), are much simpler than the Pd(II) oxidation. The rate expression is (20):

$$-d[C_2H_4]/dt = [Tl^{3+}][C_2H_4] \quad (22)$$

Although it is impossible to demonstrate by kinetics alone, the only mechanism compatible with the experimental facts is one involving an oxythallation adduct which decomposes to give the observed products.



In several cases, the oxythallation adducts have been isolated (11, 29, 35) in nonaqueous solutions, and we have found that even in aqueous solution some intermediates can be isolated if the solution contains excess acetate ion (24). Also stereochemical results (2), as well as the effect of olefin structure on product distribution, are consistent with such an intermediate (21).

The oxymetallation step (Reaction 23) must be rate determining for two reasons:

(1) The lack of proton inhibition means that the oxymetallation adduct cannot be in equilibrium with Tl^{3+} and ethylene. Thus, if the mechanism were:



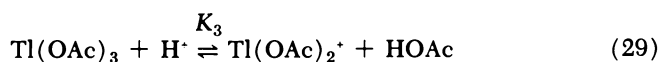
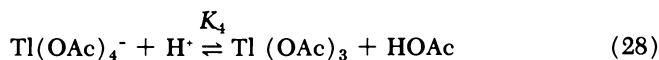
the rate expression would be:

$$-d(C_2H_4)/dt = k_5[2 \cdot TlCH_2CH_2OH] = k_5 K_5 \frac{[Tl^{3+}][C_2H_4]}{[H^+]} \quad (27)$$

(2) No primary isotope effect is observed when deuterated ethylene is used (24). An effect would be expected if Reaction 26 were the rate determining step.

To compare Pd(II) and Tl(III) under identical conditions, it would be desirable to measure the Tl(III) kinetics in chloride solution. Since the insoluble thallium sesquichloride precipitates as thallos ion is formed, this is difficult to do. In any case, it is known that thallic chloride is unreactive (15).

Acetate ion, however, complexes thallic ion about as well as chloride, and with aqueous thallic acetate there is not the complication of thallic- and thallos-containing species precipitating as the reaction proceeds. Thallic acetate itself is unreactive towards ethylene, but if strong acid is added to the solution, the oxidation rate of ethylene increases. The values of K_3 and K_4 for the equilibria represented by Reactions 28 and 29 were determined by pH measurements (23).



Using the values of K_3 and K_4 and kinetic data at various free acetate ion concentrations, it is possible to show that over a range of acetate ion concentrations of 10^4 the only important reactive species is $Tl(OAc)_2^+$.

Of course, at very low acetate ion concentrations the oxidation by Tl^{3+} and by $Tl(OAc)_2^+$ becomes appreciable.

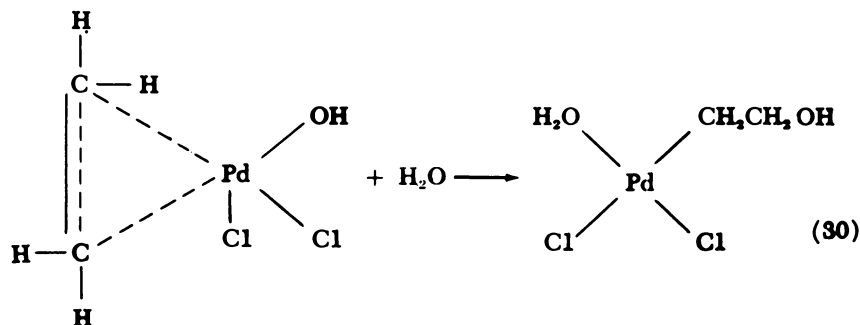
The most important result of this study is that $Tl(OAc)_2^+$ is similar to Tl^{3+} in oxidizing olefins. The absolute values of their rates of oxidation are quite close, and the effect of olefin structure on relative rates (with respect to ethylene as one) and product distribution are almost identical. Thus, complexing $Tl(III)$ with two acetates does not change the nature of its oxidation of olefins. Higher complexing does inhibit its reactivity, but $Pd(II)$ complexed with more than two chlorides is likewise not reactive. It is interesting that the activated complexes in the two systems [$Tl(III)$ in aqueous acetate and $Pd(II)$ in aqueous chloride] resemble each other in that both contain one metal ion, one ethylene, and either two chlorides or acetates. $Pd(II)$, of course, also contains a hydroxyl.

Comparison of Pd(II) and Tl(III)

The mechanisms proposed for the $Pd(II)$ and $Tl(III)$ oxidations are similar in that both involve oxymetallation adducts as intermediates, and the rate-determining step in each oxidation is the formation of the σ -bonded adduct (oxymetallation).

The second is important because it permits the comparison to be broken down into two parts—oxymetallation and decomposition of the oxymetallation adduct. Since decomposition occurs after the rate-determining step, it cannot be studied by kinetics but rather by product distribution. Oxymetallation, on the other hand, which can be studied kinetically, does not affect product distribution.

Oxymetallation. The important kinetic differences between the two reactions are given below. The kinetic expressions themselves are quite different. The rate determining step for the $Pd(II)$ oxidation most likely (but not necessarily; *see below*) involves rearrangement of a hydroxy π -complex to a σ -compound.



The Tl(III) involves the attack of Tl^{3+} on an olefin. No π -complex is detected although one may be a transient intermediate.

The effect of olefin structures on rate for the two oxidations are different. The relative rates with ethylene taken as one in each case, are shown in Table I. Pd(II) oxidation is relatively insensitive to olefin structure while the Tl(III) oxidation is greatly accelerated by methyl substitution on the vinyl carbon.

Table I. Effect of Olefin Structure on Rates of Oxidation

Olefin	Relative Rate	
	Pd(II) ^a	Tl(III) ^b
$CH_2=CH_2$	1 ^c	1
$CH_3-CH=CH_2$	0.3 ^c	160
$\begin{array}{c} CH_3 \\ \\ CH_3-C=CH_2 \end{array}$	<0.05	200,000 ^d

^a Data from Henry (22).

^b Data from Henry (21).

^c This is the relative value of k (see Equation 4) and thus is the rate of decomposition of (olefin) $PdCl_3^-$.

^d Estimated by slowing the reaction by adding acetate ion.

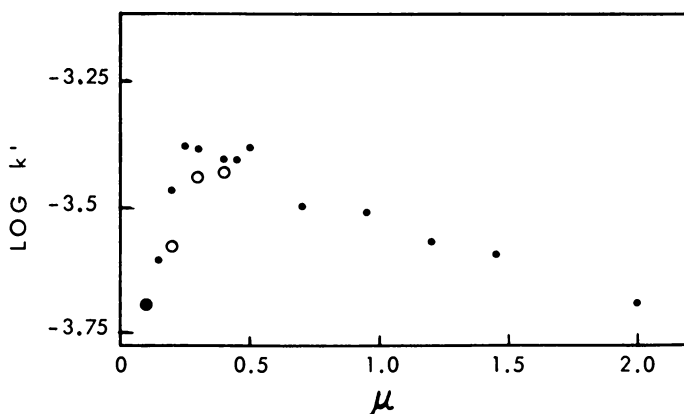


Figure 2. Salt Effect on the Pd(II) oxidation of ethylene

● μ varied by adding NaCl or NaClO₄,

○ μ varied by adding HClO₄,

Salt effects on the two oxidations are different. Pd(II) oxidation (Figure 2) is relatively insensitive to increasing electrolyte concentration; Tl(III) oxidation (Figure 3) is greatly accelerated by increasing electrolyte concentration.

The first difference is not surprising since many stable Pd(II)-olefin π -complexes have been prepared in nonaqueous solutions, while no such Tl(III) π -complex preparations have ever been reported. Moreover, it is the most important difference between the two oxymetallations since the other two follow logically from it.

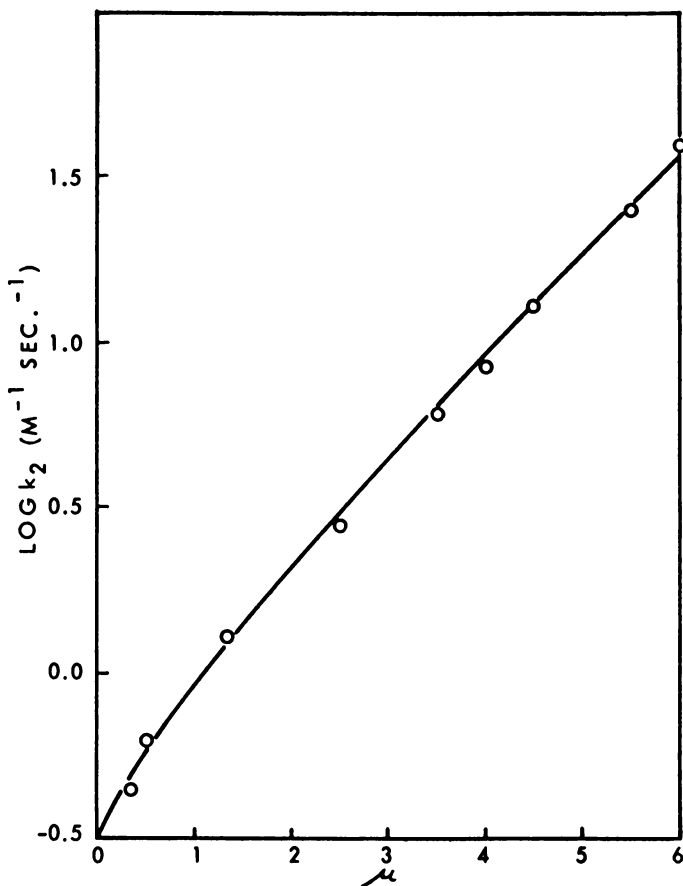


Figure 3. Salt effects on the Tl(III) oxidation of ethylene. μ varied with NaClO_4 . ($\text{HClO}_4 = 0.35$ or 0.5M)

Thus, if the olefin is strongly bonded to Pd(II) before the transition state, Pd(II) attack cannot be a simple electrophilic attack on the olefin, such as is the proton attack in olefin hydration. It is rather a rearrangement of a π -bonded to a σ -bonded adduct. There is no reason to expect that the transition state for this rearrangement would have much polar character. The small effect of olefin substitution on rate indicates that this transition state is, in fact, nonpolar.

Thallic ion, on the other hand, does not form stable π -complexes and has a high positive charge. Thus, its attack on olefins would be expected to be electrophilic, and the transition state would have considerable polarity, analogous to a proton in the hydration of an olefin, and the effect of structure on rate for the Tl(III) oxidation of olefin parallels that of olefin hydration. Alkyl substitution on vinyl C—2, which stabilizes the positive charge, greatly accelerates the rate, and dialkyl substitution on C—2 (isobutene) increases the rate still further.

By the same reasoning, the effect of electrolyte concentration on Pd(II) oxidation would not be expected to be large. In fact, since the equilibrium shown in Reaction 5 would not be expected to be greatly affected by ionic strength, ionization of the proton from the aquo complex (Reaction 11) would be expected to be the step most affected by ionic strength. Actually the effect of ionic strength on rate (Figure 2) does parallel that found for the ionization of weak acids (19). On the other hand, the thallic ion is highly solvated in aqueous solution, and increasing electrolyte concentration, which lowers the water activity, would "dehydrate" the thallic ion and make it more reactive. Using the analogy with the proton once again, this effect corresponds to the H_0 function and is attributed to an increasing activity of the proton by lowering the water activity. A similar effect has been observed in the mercuration of aromatics (36).

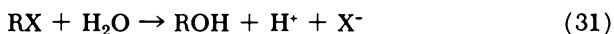
One may ask: does π -complex formation aid Pd(II) oxidation? Certainly in chloride solution $PdCl_4^{2-}$ is so strongly complexed by chloride that if ethylene were not able to displace chloride, Pd(II) would probably be as unreactive as Tl(III) in chloride solution. However, even in a chloride-free system, Pd(II) is more reactive than Tl(III), probably because π -complexes activate the olefin for further reaction (16).

Another question: why must the aquated π -complex lose a proton before it rearranges to a σ -complex? It could be simply that π -complexing makes the olefin susceptible to nucleophilic attack, and the OH^- group is more nucleophilic than the H_2O group. An alternative explanation is that the loss of a proton makes the complex more labile so that it rearranges more easily to a σ -complex. Loss of a proton from an aquo Rh(III) ion greatly accelerates water exchange (13). In noble metal ion complexes the hydroxo complex may be more labile than the aquo complex. If this is the reason for need of losing a proton, the olefin may be reacting with the solvent rather than being inserted into a palladium-hydroxide bond.

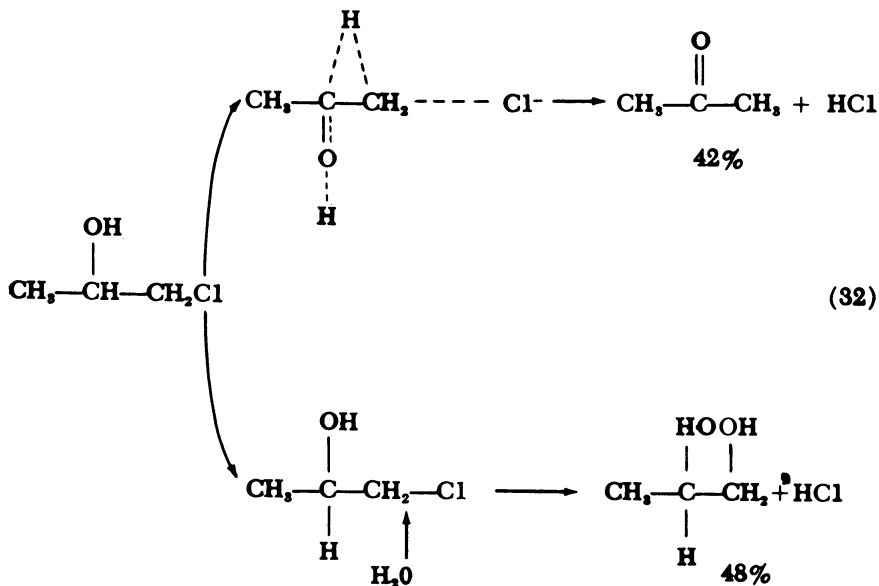
Decomposition of the Oxymetallation Adduct. The most important difference between the two oxidations concerns the oxidation products

themselves. The fact that Pd(II) gives only carbonyl compounds while Tl(III) gives glycols and carbonyl compounds can be explained only by different modes of decomposition of the organometallic intermediates.

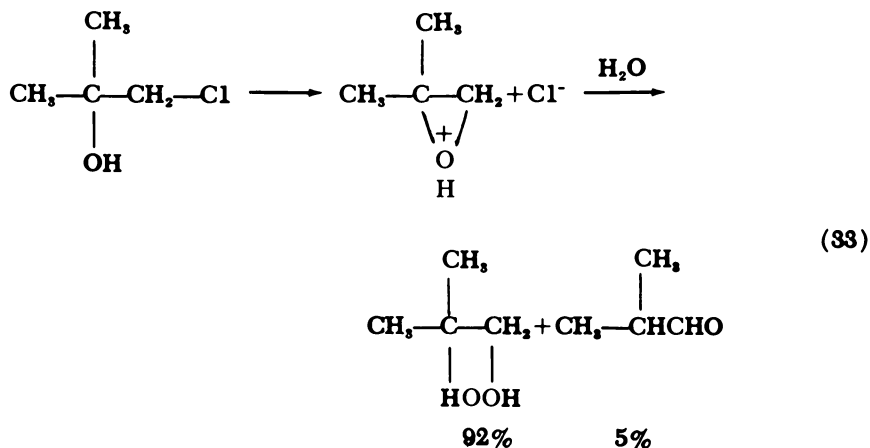
One reasonable mode of decomposition of the oxymetallation adduct is by heterolytic splitting of the metal-carbon bond in a manner analogous to the bond splitting of carbon-halogen bonds in alkyl halides or carbon-oxygen bonds in alkyl tosylates. Thus in water, where R is a simple alkyl and X⁻ is the leaving group (39), solvolysis usually occurs to give an alcohol.



If R has a β -hydroxyl group, two other modes of decomposition can occur—neighboring group participation by either hydrogen or hydroxyl. Thus, the acid hydrolysis of propylene chlorohydrin gives not only glycol by solvolysis of the carbon-chlorine bonds, but also acetone by a hydrogen shift simultaneous with the departure of X⁻ (14).

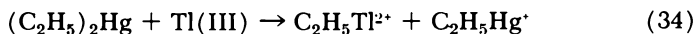


In systems where the hydroxyl is on a secondary or tertiary carbon, neighboring hydroxyl participation can occur. For example, the acid hydrolysis of 1-chloro-2-methyl-propan-2-ol gives isobutyraldehyde as well as isobutylene glycol (18).



Since Tl(III) oxidation gives both glycols and carbonyl compounds, decomposition of the oxythallation intermediate most likely occurs by routes analogous to that of the chlorohydrins mentioned above. However, for oxythallation adducts, the leaving group is the positive Tl⁺ rather than Cl⁻.

This type of decomposition of the oxythallation adduct is entirely consistent with the chemistry of monoalkyl thallium(III) compounds. As expected from the fact that thallium(III) is a vigorous oxidizing agent and Tl(I), a stable species in water, is a good leaving group, these alkyls are very unstable and seem to decompose by solvolysis. No thallium alkyls have been prepared in aqueous solution, but their mode of decomposition can be demonstrated by the reaction of diethyl mercury and Tl(III) in strong aqueous acid to form presumably ethyl thallium(III) (24). The only products are ethanol and Tl(I), indicating a heterolytic decomposition of the carbon-Tl(III) bond.



Further evidence for heterolytic decomposition is obtained from the effect of olefin structure on product distribution. Table II shows the ratio of carbonyl to glycol product for three olefins. Listed for comparison is the carbonyl/glycol ratio for the chlorohydrin, which corresponds to the structure of the oxythallation adduct from ethylene and propylene. The effect of structure on the ratio is qualitatively the same for the thallic ion oxidation and the hydrolysis of the corresponding chlorohydrin. Since the product distributions for both are inconsistent with neighboring hydroxyl participation (Reaction 33) the carbonyl/glycol ratio is a measure of the competition between hydride shift *vs.* water attack in

Reaction 32. The order of increase of carbonyl/glycol ratio in going from ethylene to propylene is expected as hydride shift tendencies on secondary carbon is greater than on primary carbon (5).

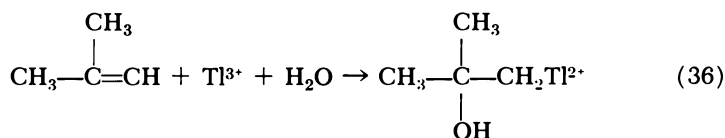
Table II. Product Distribution in the Thallous Ion Oxidation of Three Olefins

Olefin	Structure of Adduct	Carbonyl/Glycol	
		Tl(III) Oxidation	Hydrolysis of Corresponding Chlorohydrin
CH ₂ =CH	HOCH ₂ CH ₂ Tl ²⁺	0.8	0.01 ^a
CH ₃ -CH=CH ₂	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3-\text{CH}-\text{CH}_2\text{Tl}^{2+} \end{array}$	4.0	0.9 ^b
CH ₃ -CH=CH-CH ₃	$\begin{array}{c} \text{OH} \quad \text{Tl}^{2+} \\ \quad \\ \text{CH}_3-\text{CH}-\text{CH}-\text{CH}_3 \end{array}$	>200	—

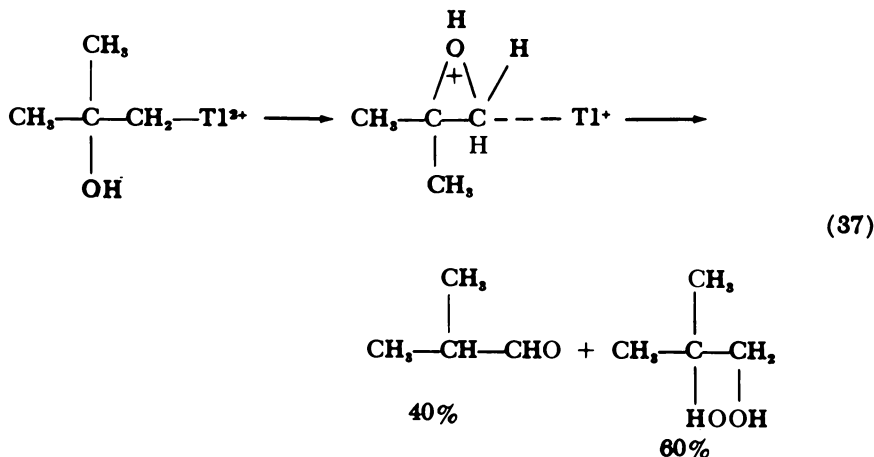
^a Data from Cowan *et al.* (9).

^b Data from Gregor *et al.* (14).

Data for 2-chloro-3-butanol is unavailable, but the low glycol yield for Tl(III) oxidation is understandable on the basis of steric hindrance to S_N2 attack of water on the carbon-thallium bond. With ethylene and propylene, the thallium(III) is attached to a primary carbon while with 2-butene it is attached to a secondary carbon. The situation with 2-butene is somewhat different from that found with the other olefins. In the oxythallation adduct from this olefin,



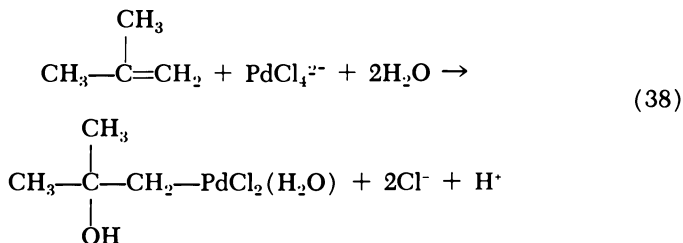
there is no hydrogen on the carbon adjacent to the carbon containing the thallium(III). Thus, it cannot decompose by hydride shift to give carbonyl. A methyl group could migrate to give 2-butanone, but this compound was not detected. Rather a 40% yield of isobutyraldehyde was obtained (21). This compound could have arisen only from neighboring hydroxyl participation. It is interesting that in the acid hydrolysis of the chlorohydrin corresponding to the oxythallation adduct from 2-butene, 1-chloro-2-methyl-2-propanol also decomposes by neighboring hydroxyl participation (18) (*see* Reaction 33).



Mercury alkyls also have been shown to decompose by solvolysis (25, 26, 27). This similarity between Hg(II) and Tl(III) alkyls is not surprising since they are isoelectronic. Tl(III) alkyls are much less stable than Hg(II) alkyls, as would be predicted from their relative oxidative powers and the fact that Tl(I) is a better leaving group than Hg(0) [Hg(0) is unstable in aqueous solution]. Oxymercuration adducts, for instance, can be prepared (6) in strong aqueous acid while oxythallation adducts cannot.

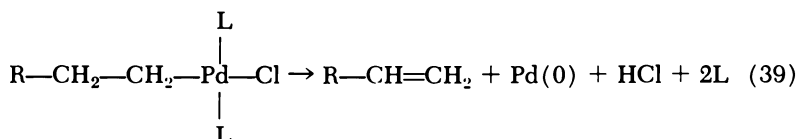
On the other hand, Pb(IV) alkyls are less stable than Tl(III) alkyls toward solvolytic decomposition, and no monoalkyls of lead(IV) have been isolated. This is expected since Pb(IV) is a more vigorous oxidizing agent than Tl(III) (11).

While the products from the Tl(III) oxidation are entirely consistent with a simple heterolytic splitting of the Tl(III)-carbon bond in the oxythallation intermediate, the products of the Pd(II) oxidation are not consistent with this type of decomposition of the oxypalladation intermediate. If heterolytic splitting of the Pd(II)-carbon bond were taking place in aqueous solution, some glycol products would be expected; yet none is ever found, even when a hydride shift is impossible—e.g., the oxypalladation adduct obtained by normal Markovnikov addi-



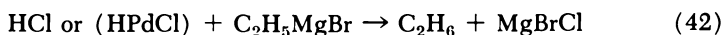
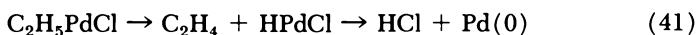
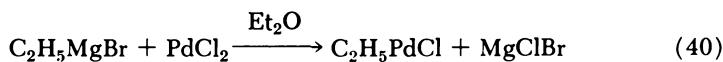
tion to 2-butene (Reaction 38). The only product obtained with 2-butene is isobutyraldehyde (37), which would result from non-Markovnikov addition followed by hydride shift.

Fortunately, we can postulate a plausible decomposition route from the known chemistry of Pd(II) alkyls. Pd(II) with a stabilizing ligand, such as phosphine, forms methylpalladium(II), but alkyls with a β -hydrogen are unstable (4). The reason for this instability is not solvolytic decomposition but probably β -hydrogen elimination to give olefin and apparently an unstable palladium(II) hydride, which decomposes to Pd(0) and H \cdot .

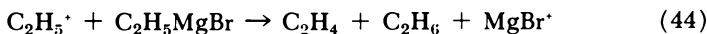
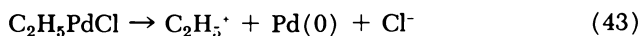


The stability of Pd(II) alkyls to heterolytic decomposition is not surprising since Pd(0) is unstable in aqueous solution and would thus be a poor leaving group.

Recent results of Moiseev and Vargaftik are consistent with this picture of a hydride shift decomposition of palladium(II) alkyls. These workers allowed ethyl magnesium bromide to react with PdCl₂ in ether (34), and they obtained equal amounts of ethylene and ethane. This result is consistent with the following scheme.

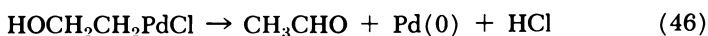


Unfortunately these results are not definitive since they are also consistent with heterolytic splitting of the palladium(II)-carbon bond to give an ethyl carbonium ion, which in the absence of a nucleophile



would react with C₂H₅MgBr to give ethylene and ethane. It would be interesting to repeat these experiments in the presence of a nucleophile which would react with any intermediate carbonium ions.

These workers also allowed β -hydroxyethyl mercuric chloride to react to form supposedly the oxypalladation adduct postulated in the Pd(II) oxidation; they obtained acetaldehyde as the product (34).

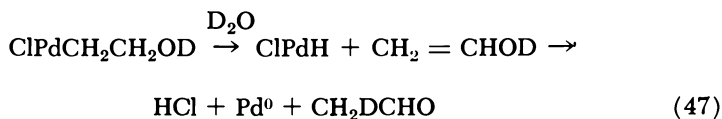


Thus, the essential feature of the Pd(II) oxidation is that the decomposition of the oxypalladation adduct does not occur by simple heterolytic cleavage of the Pd(II)-carbon bond, but rather Pd(II) somehow aids the transfer of the proton from the hydroxyl carbon to the carbon which originally held the Pd(II). This transfer results in only carbonyl product.

It is important to emphasize this difference between Pd(II) and Tl(III) oxidations since some workers (32, 33) have suggested that the decomposition of the oxypalladation adduct occurs, in effect, by heterolytic splitting of the Pd(II)-carbon bond with simultaneous hydrogen shift and no Pd(II)-hydrogen interaction. The fact that Tl(III) and Pb(IV) oxidations give glycol products while the Pd(II) oxidations do not is explained by the greater stability of the Tl and Pb organometallic intermediates allowing them to decompose by S_N2 attack of water on the metal-carbon bond (33). However, this picture is not consistent with all the facts. First, as mentioned above, there is the oxypalladation adduct which has no β -hydrogen. For example, in the 2-butene oxidation (Reaction 33), if heterolytic bond splitting were so rapid with Pd(II), decomposition of the carbonium ion formed would have to occur by some path other than hydride shift. Possibilities are methyl shift to give methyl ethyl ketone; neighboring hydroxyl participation (Reaction 32) to give isobutyraldehyde and isobutylene glycol; water attack to give isobutylene glycol. The product distribution is not consistent with any of these paths. Second, if some Pd(II)-hydrogen interaction is not responsible for the instability of Pd(II) alkyls, how can we explain the stability of methyl Pd(II) as opposed to Pd(II) alkyls with β -hydrogens? Third, there is no evidence that Pd(II)-carbon bonds are more prone to heterolytic decomposition than Tl(III)-carbon bonds. Fourth, even if Pd(II)-carbon bonds were much weaker than Tl(III)-carbon bonds, oxidation of ethylene would be expected to give some ethylene glycol. Treating $\text{HOCH}_2\text{CH}_2\text{NH}_2$ with nitrous acid gives $\text{HOCH}_2\text{CH}_2\text{N}_2^+$. This intermediate is analogous to the oxymetallation adduct intermediates in the Pd(II) and Tl(III) oxidations. However, N_2 is the best leaving group known and would be expected to come as close as possible to giving $\text{HOCH}_2\text{CH}_2^+$, yet this reaction gives ethylene glycol as well as acetaldehyde (19).

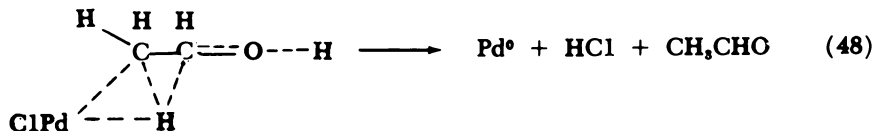
There is, however, one problem which arises from the Pd(II)-hydrogen interaction picture of the decomposition of the oxypalladation adduct. Based on analogy with Pd(II)-alkyl chemistry, the most likely mode of decomposition of the oxypalladation adduct would be palladium(II) hydride elimination to give vinyl alcohol, which would re-

arrange to acetaldehyde. However, if the reaction were run in D_2O , acetaldehyde would be expected to contain one deuterium.

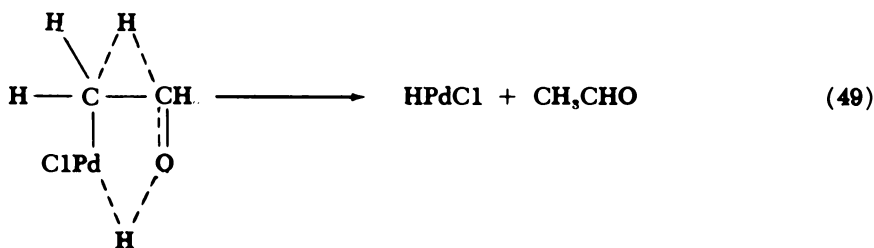


Actually it is found that the ethylene contains no deuterium (37). Three decomposition mechanisms have been proposed to account for this experimental result.

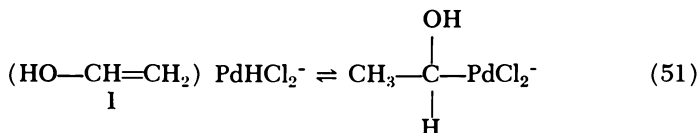
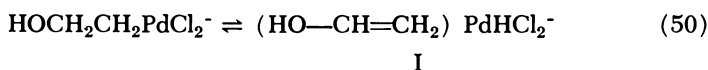
In the first, palladium(II)-hydride elimination is not completed before rapid electron rearrangement gives acetaldehyde. Thus, we could picture the transition state as a Pd(II)-*assisted* shift of the hydride (19).

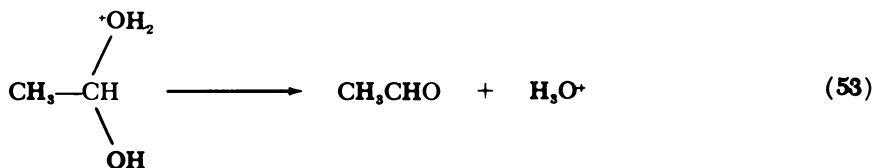
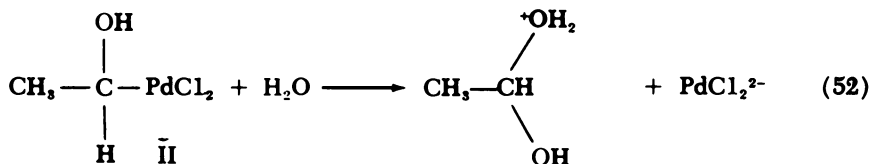


Another possibility is for the palladium(II) to take the proton from oxygen and to leave as palladium(II) hydride (17).



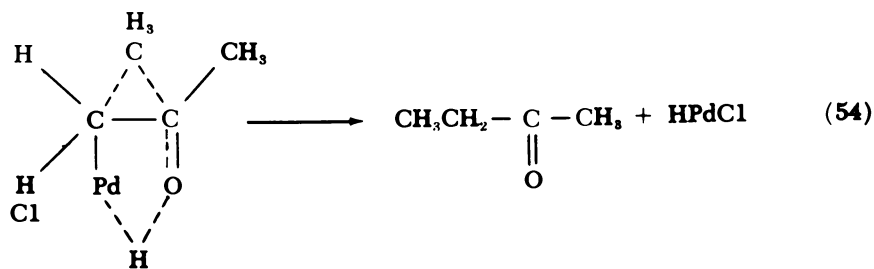
A third mode of decomposition of the oxypalladation adduct has been suggested recently (28). This involves Pd(II) hydride elimination followed by readdition.



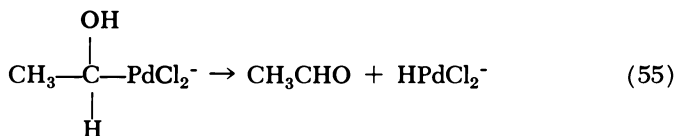


Each mechanism has its unsatisfactory features. Thus, in the first, Pd(0) is a leaving group. Monomeric Pd(0) would be a poor leaving group since it is unstable in aqueous solution. On the other hand, the Pd(0) would be complexed with ligands such as chloride and water. These ligands would increase its stability.

The second mechanism avoids the necessity of postulating Pd(0) as a leaving group but the removal of a hydroxylic proton by Pd(II) to form a hydride has no analogy in Pd(II) chemistry while removal of hydrogen from the β -carbon does have precedent. Furthermore, since a Pd(II)-assisted hydride shift is not a feature of this mechanism, the adduct from 2-butene might be expected to undergo methyl shift to give 2-butanone.



The third possibility involves solvolysis of a Pd(II)-carbon bond (Reaction 52). Although, as mentioned above, this type of decomposition does not seem to occur in simple Pd(II) alkyls, the presence of an α -hydroxyl would be expected to increase solvolysis rates greatly. However, the fact that the reaction of $\text{ClHgCH}_2\text{CH}_2\text{OH}$ with PdCl_2 in non-aqueous solvent gives acetaldehyde (34) suggests that adduct decomposition does not occur by solvolysis. However, the decomposition of II could occur by removal of hydrogen by Pd(II) from the α -hydroxyl.



Of the three possibilities, the second is probably least likely since all evidence points to some interaction between the β -hydrogen in the oxypalladation adduct and the Pd(II). The remaining two are actually quite similar, and it would be difficult to distinguish between them experimentally in aqueous solution.

However, if in nonaqueous solutions (discussed next) the oxidations also proceed through oxypalladation adducts, then the two mechanisms of decomposition of the oxypalladation adducts would predict different products. First, let us consider the mechanism of Jira, Sedlmeier, and Smidt (Reactions 50–53). In this case OH in II (Reaction 52) is replaced by OR. Decomposition *via* Reaction 55 is impossible, so II must decompose by solvolysis. This would give 1,1-disubstituted ethanes from ethylene oxidation. On the other hand, the first suggestion (Reaction 48) would probably be more consistent with formation of the vinyl compounds since hydride elimination should be completed if a rapid rearrangement of electrons to give acetaldehyde cannot occur. Evidence exists that 1,1-disubstituted ethanes are the initial products in methanol, and in acetic acid it is claimed that both vinyl acetate and 1,1-diacetoxyethane are initial products; this suggests that in this solvent competition exists between palladium(II) hydride elimination and acetate attack. However, until now there have been no detailed studies of the oxidation under conditions where 1,1-disubstituted products are formed. More work is needed before the course of the reaction under these conditions is completely understood.

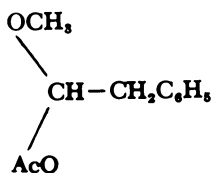
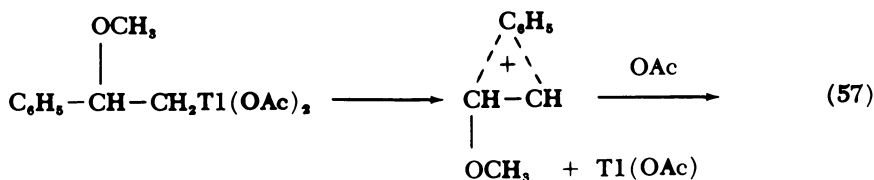
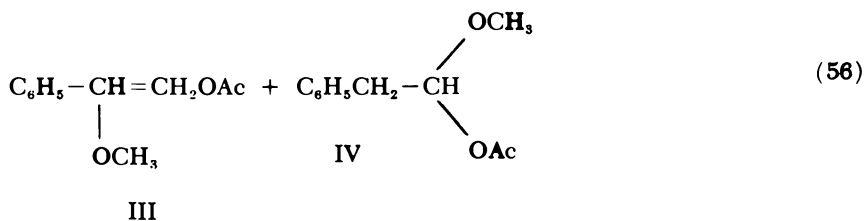
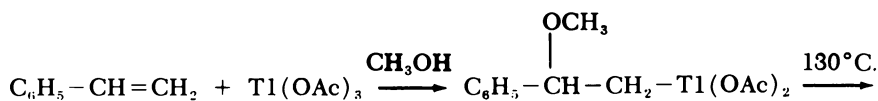
Nonaqueous Systems

Oxidations in nonaqueous systems by Pd(II) and Tl(III) parallel oxidations in aqueous solutions and can be rationalized by mechanisms analogous to those proposed for the aqueous systems.

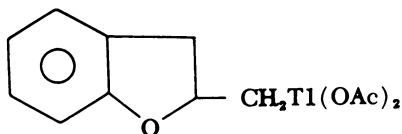
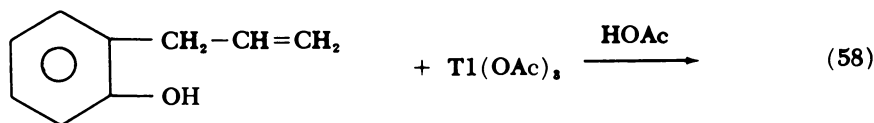
In nonaqueous solvents, the oxythallation adduct can actually be isolated in the oxidation of certain olefins, and in cases where it cannot be isolated, the product can be explained by solvolysis of an oxythallation adduct.

Thus, Criegee (11) prepared the oxythallation adduct of styrene in methanol which he decomposed at 130°C. to give products which result from solvolysis of the carbon-thallium bond with (III) and without (IV)

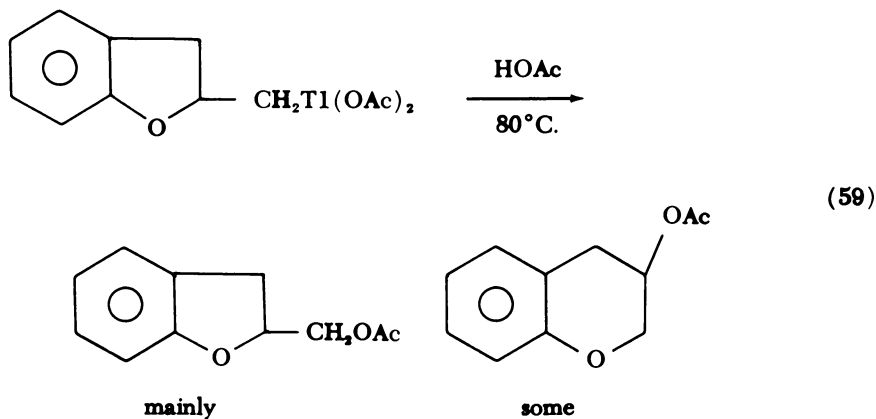
phenyl migration (Reaction 56). The phenyl migration no doubt results from neighboring phenyl participation to give a phenonium ion.



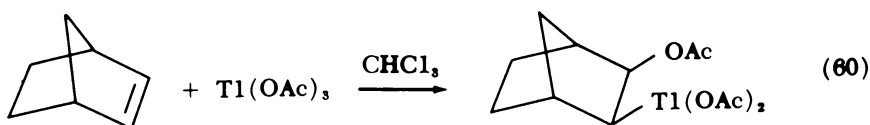
Kabbe (29) prepared an oxythallation adduct from *o*-allylphenol to give an ether-type adduct analogous to the mercury(II) adducts prepared some years ago by Adams (1) (Reaction 59).



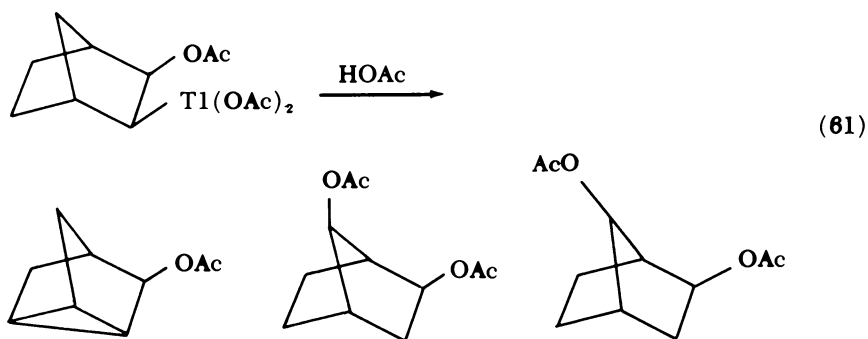
The adduct decomposed at 80°C. to give mainly the unrearranged solvolysis products.



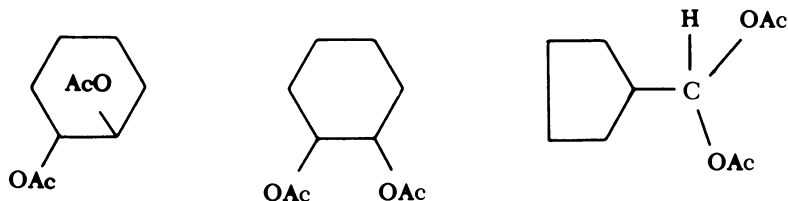
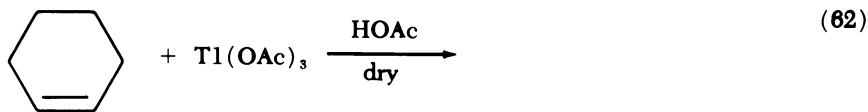
Pande and Winstein (35) prepared the adducts from norbornene and norbornadiene. With norbornene, the *cis*-exoadduct is obtained. This adduct solvolyzes readily in acetic acid:



to give products which are obtained by direct treatment of norbornene with $\text{Tl}(\text{OAc})_3$ in acetic acid.



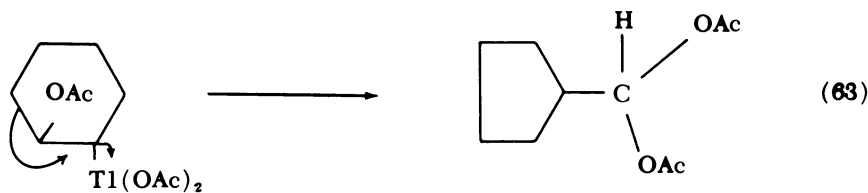
No adduct is isolated in oxidizing cyclohexene in acetic acid, but oxidation in acetic acid gives mostly products which could result from decomposition of a *trans*-oxythallation adduct with neighboring carbon or acetate participation (2) (Reactions 62, 63, and 64).



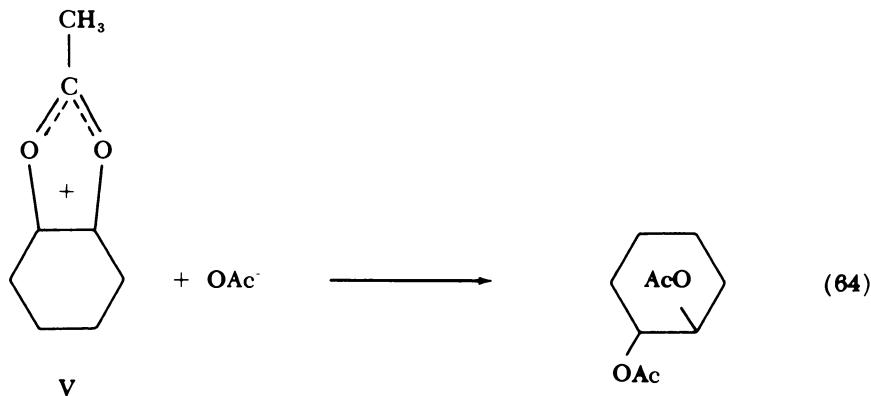
45%

5%

50%



(63)



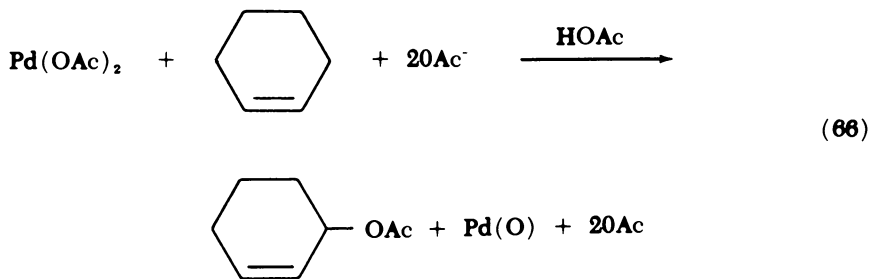
(64)

When moist acetic acid is employed, the monoacetates obtained are mainly *cis* as would be expected from the reaction of the acetoxonium ion, V, with water.

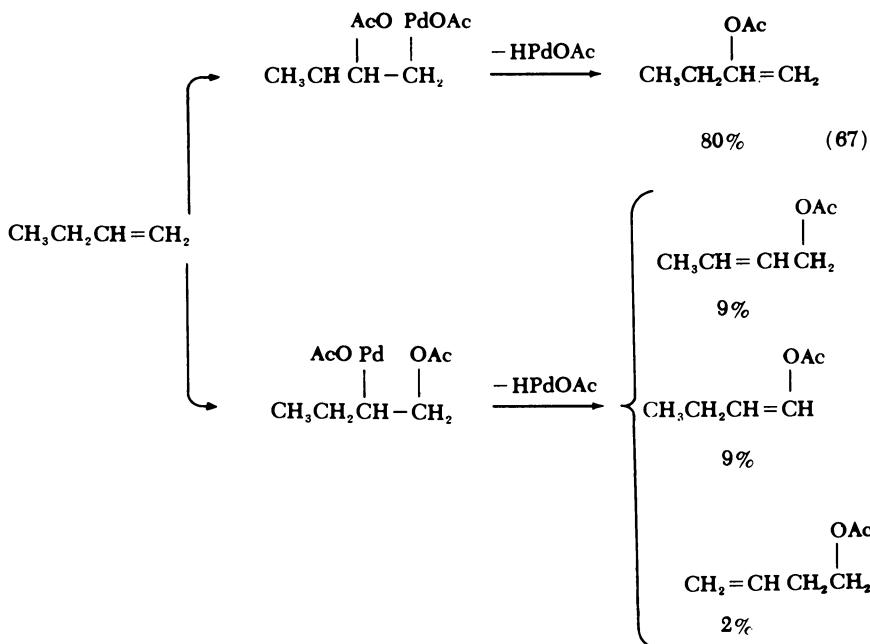
Pd(II) in acetic acid oxidizes ethylene mainly to vinyl acetate. This is the product expected from Pd(II)-hydride elimination from an oxy-palladation adduct. However, 1,1-diacetoxyethane has been reported to be a primary product under some conditions (33). Thus, as discussed above, decomposition of the adduct may not occur by simple Pd(II)-hydride elimination.

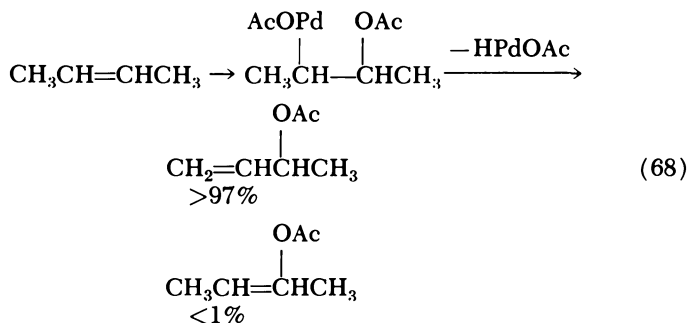


With higher olefins, allylic and vinyl oxidation products are obtained (31). Thus, cyclohexene yields almost exclusively allylic oxidation product (2).



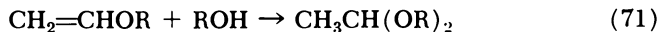
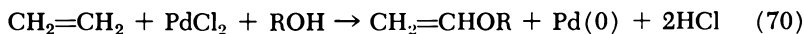
A recent study (30) of the oxidation of several straight-chain olefins reported product distributions which could be explained only by preferential Markovnikov oxy-palladation, followed by HPdOAc elimination, preferentially by abstracting hydrogen from the carbon not containing the acetate. The products obtained with 1- and 2-butene can be used as an example.



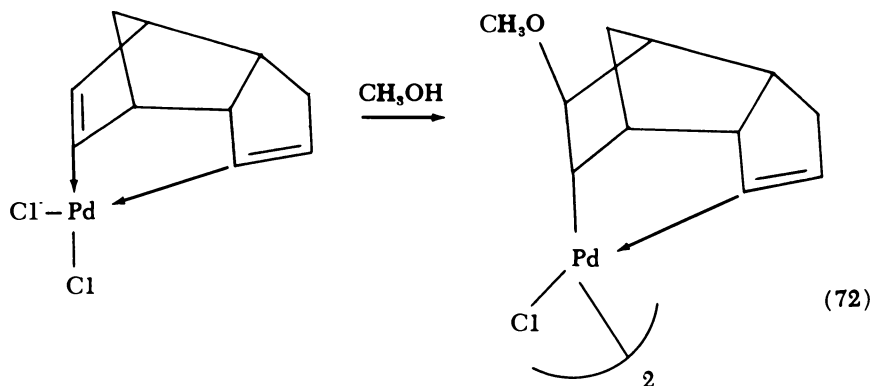


These results eliminate π -allylic type of intermediates since the π -allyl from 1- and 2-butene would be the same and would be expected to give the same allylic oxidation products. Actually the allylic oxidation product from 1-butene is a primary acetate whereas from 2-butene a secondary acetate is obtained. It is worthwhile noting that no 1,1-diacetates were reported in this study.

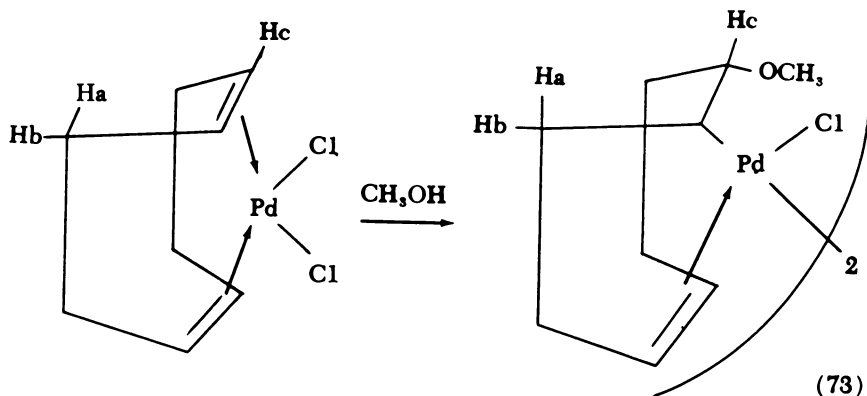
In alcohols the main product is acetal (31) (Reaction 69), but it is not certain if the acetal is the initial product or is formed by the metal ion-catalyzed addition of alcohol to an initial vinyl ether product. There is evidence that the acetal is the initial product (33). Oxidation of ethylene in CH_3OD is reported to give acetal containing no deuterium. This would not be expected if the oxidation occurred by Reactions 70 and 71.



Several oxypalladation adducts, corresponding to the intermediates proposed for the Pd(II) oxidation of olefins, have been prepared (7) from diolefins, and their structures were investigated (38, 39, 42). Thus, dicyclopentadiene PdCl₂ π -complex reacts as follows:



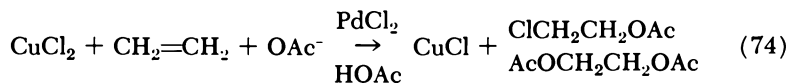
Even though the second double bond provides some stabilization, resistance of the compounds to decomposition by Pd(II)-assisted hydride transfer is interesting. Thus, Pd(II) alkyls with β -hydrogens even when they have phosphine groups (which would be expected to be better than olefin groups in stabilizing Pd(II) alkyls) decompose rapidly. As recently discussed by Stille and Morgan (39), the stability of the adducts from bicyclic olefins such as the one from dicyclopentadiene (Reaction 72) can probably be reasonably attributed to the fact that Pd(II)-hydride elimination would form a strained double bond. However, the stability of the adduct from 1,5-cyclooctadiene cannot be explained in this way.



Elimination of Pd(II) hydride where the origin of the hydrogen is Ha, Hb, or Hc would give a strain-free double bond. However, there is another possible explanation for this stability. If the original oxypalladation is cis and if the Pd(II)-hydride elimination is also cis, then Hc is trans to the Pd(II) and cannot be eliminated. Furthermore, if molecular models are made, one can see that if square-planar Pd(II) is bonded to one carbon and also coordinated to the double bond, then the cyclooctene ring must be twisted so that Ha and Hb are not in position for a cis elimination. Any other combination of cis or trans addition and cis or trans elimination does not give the desired result. Recently it was reported that the adduct from PdCl₂ and 1,5-cyclooctadiene (Reaction 72) does in fact have cis stereochemistry (Anderson, C. B., Burreson, B. J., *Chem. Ind.* 1967, 620).

There have been two reports (3, 8) of a novel reaction of Pd(II) in acetic acid. As mentioned above, under a wide range of chloride and acetate ion concentrations, the only product detected from ethylene oxidation is vinyl acetate. However, if cupric chloride is added to the system, a different reaction occurs. This is the formation of the 2-chloroethylacetate, ethylene glycol diacetate, and, if water is present, ethylene

glycol monoacetate. Since cupric chloride reoxidizes Pd(0), CuCl rather than Pd(0) is produced.



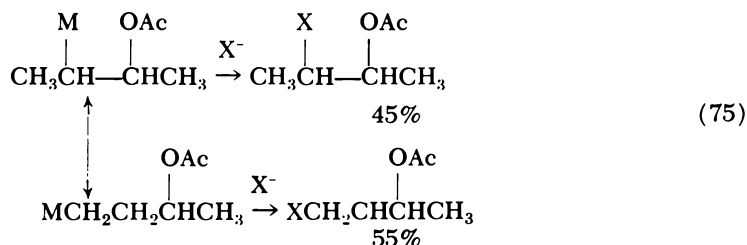
Both PdCl₂ and CuCl₂ are required for this reaction. Cupric chloride alone gives no reaction (24).

One interesting aspect of this reaction is that higher olefins give isomers other than those which would result from 1,2-addition to the double bond. Thus, propylene gives 1,3- as well as 1,2-diacetates and chloroacetates. Admittedly it is premature to suggest a detailed reaction route, but some speculation as to general mechanism can be made from the results of a study of the isomer distribution with 1- and 2-butenes. The results are given in Table III (24).

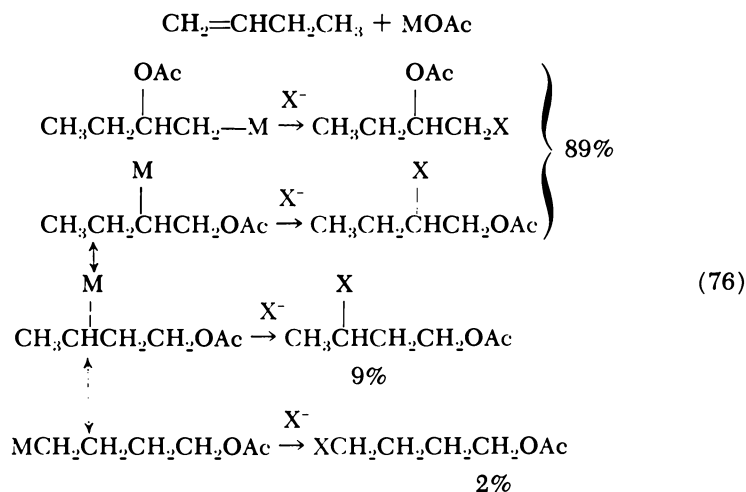
Table III. Isomer Distribution for the Oxidation of 1- and 2-Butene

Isomer	2-Butene	1-Butene
2,3	45	trace
1,3	55	9
1,2	<0.1%	89
1,4	<0.1%	2

These distributions are inconsistent with a π -allyl intermediate since the π -allyl from 1- and 2-butene would be the same and would be expected to give the same products. However, these results are consistent with preferential Markovnikov addition of the elements M-OAc to the double bond to give an oxymetallation adduct. This adduct can then decompose by attack of X⁻ (X⁻=Cl⁻ or OAc⁻) or can isomerize to put the metal on the adjacent carbon or isomerize twice to move the metal two carbons down the chain. Thus, with 2-butene the reaction sequence would be:



Thus, only 2,3- and 1,3-products would be expected from 2-butene. On the other hand, 1-butene can add Markovnikov or non-Markovnikov.



Thus, most of the product with 1-butene would be expected to be the 1,2-isomer since the preferred Markovnikov adduct cannot isomerize. Also reaction of the non-Markovnikov adduct *without* isomerization gives 1,2-isomer. The 1,3-isomer from 1-butene is much less favored than it is with 2-butene, for with 1-butene, non-Markovnikov addition followed by isomerization before decomposition is required. This expectation is confirmed. 1-Butene gives one-sixth as much 1,3-isomer as 2-butene. Of course, 1,4-isomer is even less preferred because it requires non-Markovnikov addition followed by two isomerizations before decomposition, and only traces of 1,4-isomer is detected.

The original oxymetallation is probably oxypalladation, and this reaction is known to occur. Isomerization could occur by palladium(II)-hydride elimination and readdition. Elimination could occur by interaction of Cu(II) with Pd(II) in the oxypalladation adduct to make Pd(II) a good leaving group, or else the alkyl could be transferred from Pd(II) to Cu(II) followed by decomposition. Pd(IV) species could also be involved.

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Organic Syntheses by Means of Noble Metal Compounds

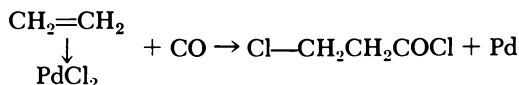
XXXI. Carbonylation of Olefins and Decarbonylation of Acyl Halides and Aldehydes

JIRO TSUJI and KIYOTAKA OHNO

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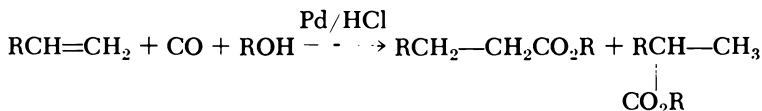
Palladium chloride and metallic palladium are useful for carbonylating olefinic and acetylenic compounds. Further, palladium is active for decarbonylation of aldehydes and acyl halides. Homogeneous decarbonylation of aldehydes and acyl halides and carbonylation of alkyl halides were carried out smoothly using rhodium complexes. An acyl-rhodium complex, thought to be an intermediate in decarbonylation, was isolated by the oxidative addition of acyl halide to chlorotris(triphenylphosphine)rhodium. The mechanisms of these carbonylation and decarbonylation reactions are discussed.

Ethylene-palladium chloride complex reacts smoothly with carbon monoxide in benzene at room temperature to give β -chloropropionyl chloride with the separation of metallic palladium (18).



Some other olefins are carbonylated similarly; carbon monoxide is introduced at the terminal position to form β -chloroacyl halides (10). In addition, it was found that metallic palladium is a versatile catalyst for carbonylating various olefins. Saturated esters are prepared by carbonylating simple α -olefins and some cyclic olefins when the reaction is carried out in alcohol containing hydrogen halide and a catalytic amount

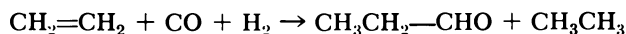
of metallic palladium (12, 13, 14), or the carbonylation of some highly reactive olefinic compounds such as 1,5-cyclooctadiene can be carried out simply by adding palladium chloride to the reaction system. Palladium chloride is reduced easily *in situ* with carbon monoxide in alcohol to form zero-valent palladium and hydrogen chloride.



β , γ -Unsaturated esters are formed by the palladium-catalyzed carbonylation of allylic compounds (15) and conjugated dienes (16, 17).



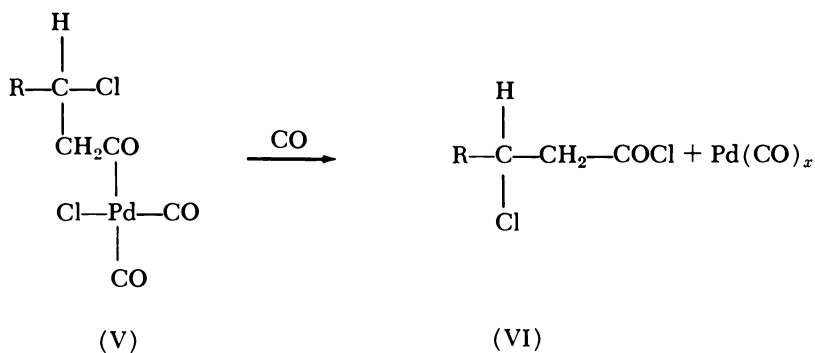
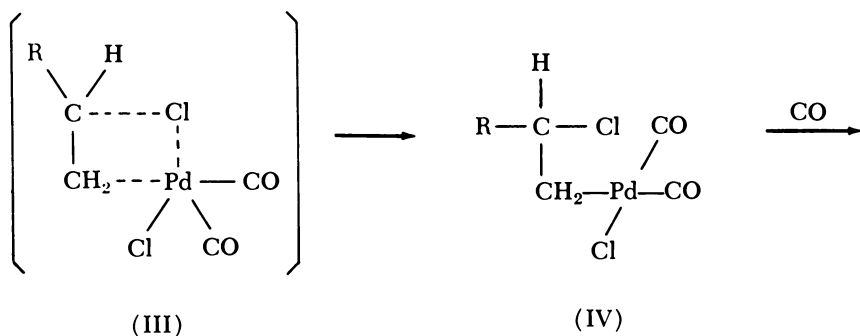
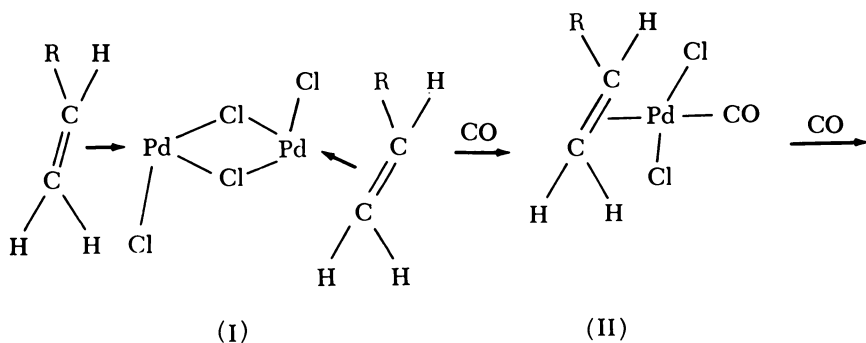
In these catalytic carbonylation reactions, metallic palladium and hydrogen halides are essential for the catalysis. Furthermore, olefins react with carbon monoxide and hydrogen in benzene in the presence of metallic palladium to form aldehydes in a low yield (19).



In addition to the carbonylation of these olefinic compounds, the carbonylation of various acetylenic compounds is also possible by the catalytic action of palladium and hydrogen halide (20, 21, 22).

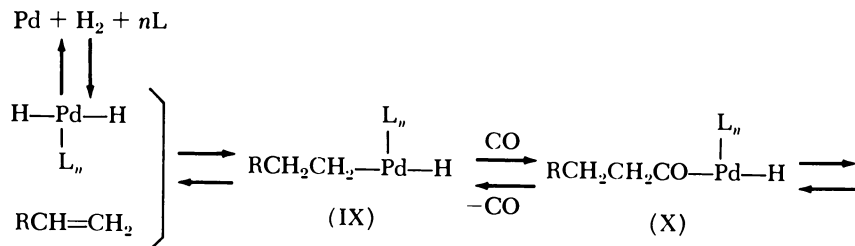
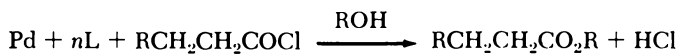
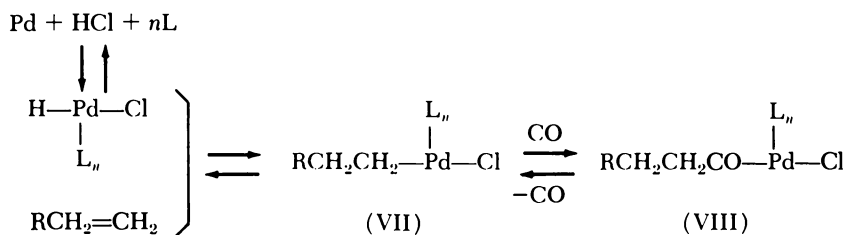
Olefins are usually carbonylated in the presence of metal carbonyls, such as nickel, cobalt, and iron carbonyls under homogeneous conditions, and the mechanism of these carbonylations has been established in several cases. On the other hand, isolation or formation of true palladium carbonyl has not been reported. Since palladium is an efficient and versatile catalyst for various types of the carbonylation mentioned above, the mechanisms of the carbonylation of olefin-palladium chloride complexes and of metallic palladium catalyzed carbonylations seem to be worth investigating.

The following mechanism was proposed for the carbonylation of olefin-palladium chloride complex (10). The first step is coordination of carbon monoxide to the complex. Insertion of the coordinated olefin into the palladium-chlorine bond then forms a β -chloroalkylpalladium complex (IV). This complex undergoes carbon monoxide insertion to form an acylpalladium complex (V), as has been assumed for many metal carbonyl-catalyzed carbonylation reactions. The final step is formation of a β -chloroacyl chloride and zero-valent palladium by combination of the acyl group with the coordinated chlorine.



In the metallic palladium-catalyzed carbonylation of olefins, some hydrogen sources are essential; hydrogen halide and molecular hydrogen were found to be the most effective. The following sequence of reactions was proposed for the reaction mechanism of the ester and aldehyde formation catalyzed by palladium (23). The first step of the metallic palladium-catalyzed carbonylation seems to be the formation of a palladium-hydrogen bond by the oxidative addition of hydrogen chloride

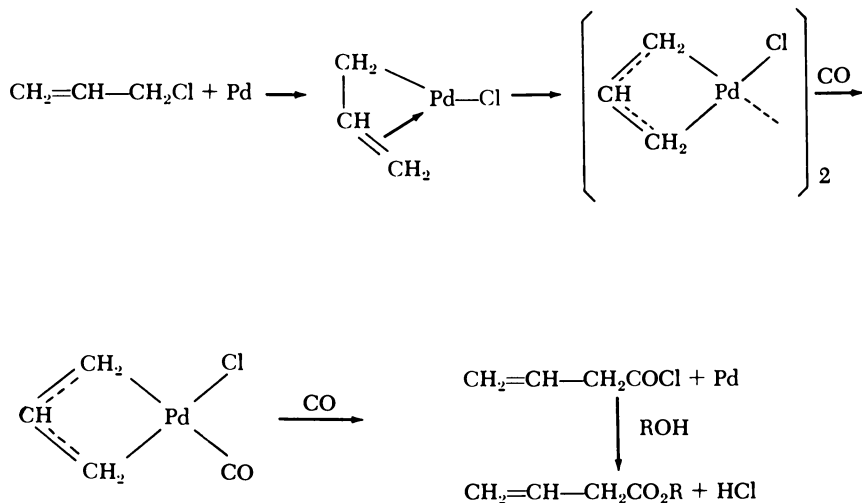
to palladium. Then olefin is coordinated, followed by insertion of the coordinated olefin to the palladium hydride to give an alkylpalladium complex (VII). The alkylpalladium complex (VII) is converted into the acylpalladium complex (VIII) by carbon monoxide insertion. The final process is the splitting of the acyl-palladium bond by the combination of the acyl group with the coordinated chlorine to form acyl chloride and metallic palladium. The acyl chloride then reacts with alcohol to give an ester and hydrogen chloride. Thus, the regeneration of metallic palladium and hydrogen chloride makes the whole reaction a catalytic cycle. In the same way, the reaction of molecular hydrogen, instead of hydrogen chloride, and palladium forms a palladium hydride which leads to the aldehyde formation. Alkyl complex formation (IX) is then followed by carbon monoxide insertion to form the acyl bond (X); and finally, the acyl complex collapses with formation of the aldehyde and metallic palladium.



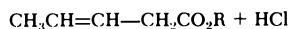
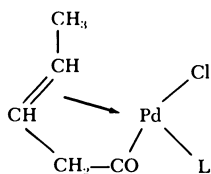
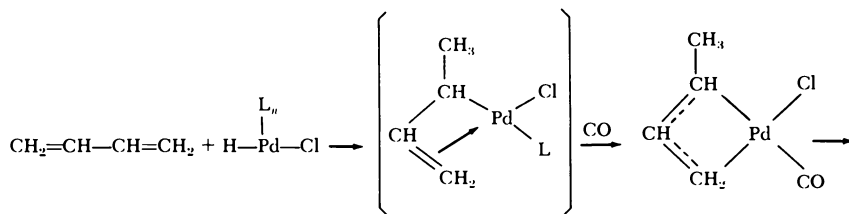
L, used in this mechanism, is a ligand which can stabilize the intermediate palladium complexes and satisfy a coordination number of the palladium whatever it is. L, for example, can be carbon monoxide, phosphines, solvents, or another molecule of palladium. Formation of hydride complexes by the oxidative addition of hydrogen chloride or hydrogen to a metal complex is well known (9, 27), as is formation of alkyl metal complexes by addition of metal hydrides to olefins.

The similarity in the mechanisms of the two carbonylations is apparent. In the β -chloroacyl chloride formation, the first step is the insertion of olefins into the palladium-chlorine bond. For the catalytic carbonylations, the insertion of olefins takes place to the palladium hydride complex formed *in situ*. In both cases, divalent palladiums react with olefins.

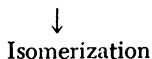
The catalytic carbonylation of allyl chloride to form 3-butenate proceeds through a π -allyl complex which is formed by the oxidative addition of allyl chloride to metallic palladium. The π -allyl complex formation has been reported by Fischer and Bürger (4) with allyl bromide and palladium as a supporting evidence. The carbonylation then proceeds by the insertion of carbon monoxide as before.



Butadiene is carbonylated catalytically to form 3-pentenoate in the presence of palladium and hydrogen chloride in alcohol (16). In this reaction, butadiene forms an unsymmetrical π -allylic complex by the insertion of one of the double bonds into the palladium-hydrogen bond. Then the insertion of carbon monoxide takes place at the less hindered carbon of the complex to give 3-pentenoate.



It is known that insertion of carbon monoxide to form an acyl complex is reversible, in which results depend on the pressure of carbon monoxide and temperature. If the above-mentioned mechanisms are correct, then acyl halides and aldehydes should be decarbonylated to form olefins provided that an acyl-palladium bond is formed by the oxidative addition of acyl halides or aldehydes to metallic palladium. This proved to be the case. When acyl halide was heated with a catalytic amount of metallic palladium or palladium chloride at 200°C. in a distilling flask, carbon monoxide and hydrogen halide were evolved rapidly, and olefin was collected in a good yield. This reaction is a new and useful preparative method of olefins. In the same way, aldehydes can be decarbonylated smoothly, but in this case, both olefin and the corresponding paraffin were obtained. The latter probably arises by the hydrogenation of the olefin. Decarbonylation of certain aldehydes has been reported by several workers (3,6), but no reasonable mechanism has been known. The mechanism of the palladium-catalyzed aldehyde formation discussed above gives clear explanation for the palladium catalyzed decarbonylation of aldehydes.

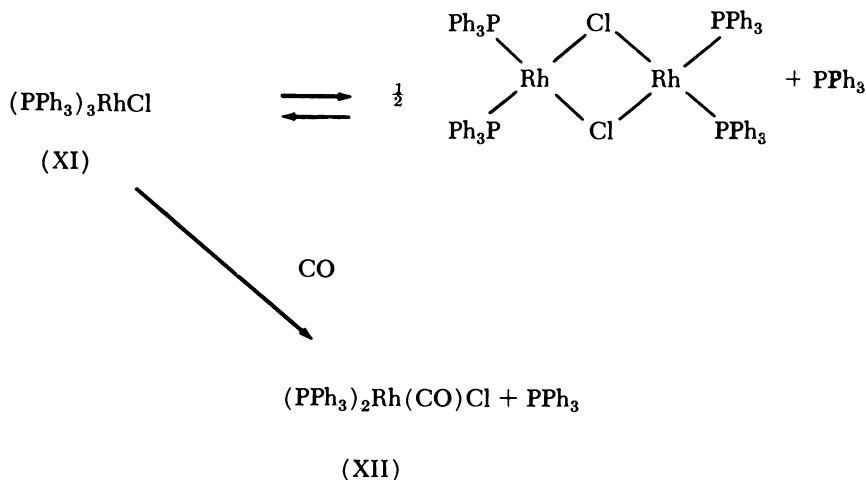


Thus, it was established that metallic palladium catalyzes both carbonylation of olefins to acyl halides or aldehydes in the presence of

carbon monoxide and decarbonylation of acyl halides and aldehydes to olefins in the absence of carbon monoxide. In these mechanisms, the reversible formation of the acylpalladium complex is essential. It seems possible that both aldehydes and acyl halides form the acyl-palladium bond by the oxidative addition when they are contacted with palladium at high temperature. So far, however, we have not been successful in establishing this oxidative addition definitely.

To investigate the oxidative addition of acyl halides to a metal to form the acyl complex and to find a better decarbonylation agent, we selected chlorotris(triphenylphosphine)rhodium (XI) as a model complex. This complex is known to catalyze the oxo reaction (8) and the homogeneous hydrogenation of acetylenes and olefins (7, 28).

The most characteristic property of this complex is its facile liberation of one mole of triphenylphosphine to produce a dimeric structure (I). The dimeric complex can coordinate with other ligands. Specifically, it can easily pick up one mole of carbon monoxide and form chlorocarbonyl-bis(triphenylphosphine)rhodium (XII), which is a very stable complex.



By using this property, decarbonylation of carbonyl compounds was investigated. Smooth decarbonylation of aldehydes was observed even at room temperature; the reaction can be expressed by the following equation (24). Some results are given in Table I.

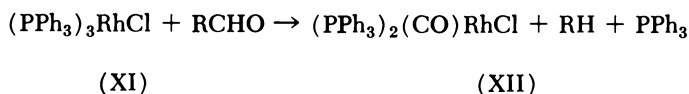


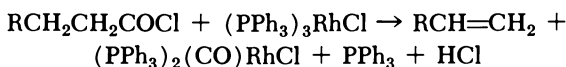
Table I. Decarbonylation of Aldehydes by $(\text{PhP})_3\text{RhCl}^a$

	<i>Solvent</i>	<i>Temp.</i>	<i>Time,</i> <i>Hrs.</i>	<i>Product</i>	<i>Yield,</i> <i>%^b</i>
Ph—CHO	Toluene	Reflux	2	Benzene	83
CH ₃ —CH ₂ —CH ₂ —CHO	Benzene	Room	2	Propane	—
Ph—CH=CH—CHO	CH ₂ Cl ₂	Room	8	Styrene	60
<i>p</i> -Cl—C ₆ H ₄ —CHO	Benzene	Reflux	3	Chloro- benzene	85
<i>o</i> -HOC ₆ H ₄ —CHO	Toluene	Reflux	$\frac{1}{3}$	Phenol	70

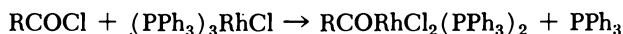
^a In all cases, 1 to 3 grams of $\text{RhCl}(\text{Ph}_3\text{P})_3$ and an excess of the aldehydes were used.

^b Yield based on $\text{RhCl}(\text{PPh}_3)_3$.

Thus, this reaction is a most facile and selective method of decarbonylation of aldehydes. The decarbonylation of acyl halides by using the complex (XI) was then tried, and again decarbonylation proceeded smoothly though it was necessary to warm the solution for complete decarbonylation.



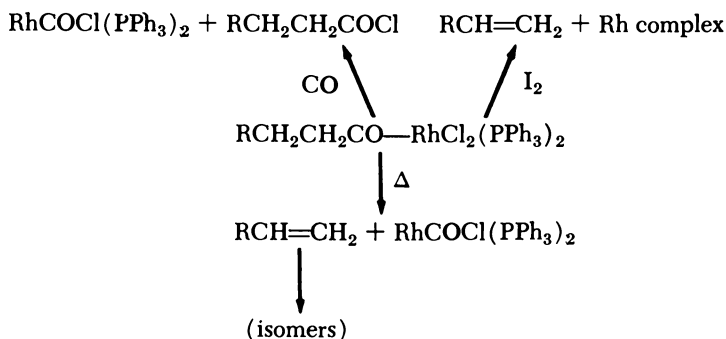
By careful investigation of the reaction between acyl halides and chlorotris(triphenylphosphine)rhodium, we found that a new acylrhodium complex (XIII) could be isolated in good yield. It forms by the oxidative addition of acyl halide, with the elimination of one mole of triphenylphosphine (25). This is the first example of acyl complex formation by direct oxidative addition of acyl halides.



(XIII)

The structure of the acyl complex was supported by analysis and molecular weight determination. The complex showed a sharp infrared band at 1715 cm^{-1} , which was assigned to the acyl rhodium carbonyl. This complex is stable in air and does not react with water or alcohol.

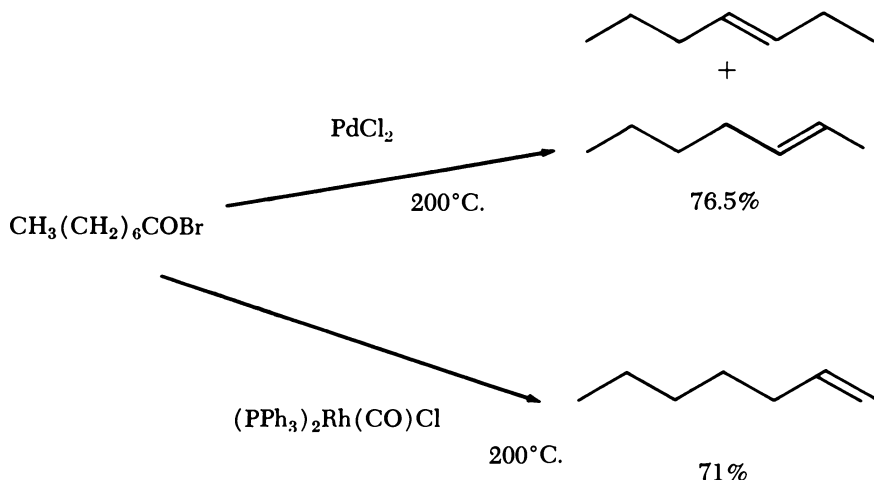
Several chemical transformations of this acyl complex were carried out in order to prove its structure. The reaction of carbon monoxide with the complex gave acyl halide and chlorocarbonylbis(triphenylphosphine)-rhodium (XII). The thermal decomposition of the acyl complex gave rise to a mixture of isomeric olefins. The formation of olefin from the complex can be carried out more smoothly by adding iodine. When iodine was added to the solution of the acyl complex at room temperature, terminal olefin was obtained in high yield. These reactions are summarized below



In the above-mentioned decarbonylation, chlorotris(triphenylphosphine)rhodium (XI) was converted into chlorocarbonylbis(triphenylphosphine)rhodium (XII)—*i.e.*, the reaction is stoichiometric with regard to the rhodium complex (XI).

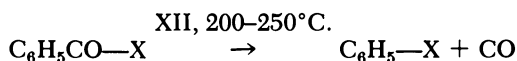
It would be more interesting and useful if the reaction could be made catalytic. Actually, catalytic decarbonylation reaction was found to be possible by using chlorocarbonylbis(triphenylphosphine)rhodium (XII) (26). This complex is reasonably stable, and more importantly it is four-coordinated and coordinately unsaturated, so that it may expand to a six-coordinated complex by the oxidative addition of acyl halides or aldehydes. The oxidative addition of methyl iodide to similar complexes was reported by Heck (5).

Acyl halides were decarbonylated homogeneously to olefins when they were heated to 200°C. in the presence of a catalytic amount of chlorocarbonylbis(triphenylphosphine)rhodium (XII). It is possible to



isolate olefins as a main product of decarbonylation by selecting the proper reaction conditions. This complex is, therefore, superior to metallic palladium which gives olefin mixtures with inner olefins as the main products.

The most characteristic catalytic activity of the rhodium complex was observed with the reaction of aroyl halides. The decarbonylation of aroyl halides was not satisfactory with palladium catalyst whereas they decarbonylated smoothly on heating to 200°C. with the rhodium complex. For example, when benzoyl chloride was heated with the complex at 200°C., chlorobenzene distilled off rapidly with the evolution of carbon monoxide. Benzoyl bromide reacts similarly to give bromobenzene. Phenylacetyl chloride was converted into benzyl chloride. Additional results are in Table II.



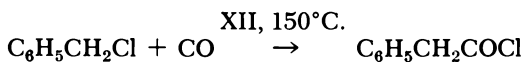
Recently Blum reported that chlorotris(triphenylphosphine)rhodium (XI) is an active catalyst for the decarbonylation of aroyl halides and showed several examples (2). But in this case too, the real catalyst seems to be chlorocarbonylbis(triphenylphosphine)rhodium (XII), which is formed *in situ* from XI by the stoichiometric reaction with acyl halides. Formation of alkyl halides by decarbonylation of acyl halides can be carried out by the Hunsdiecker reaction, but the reaction is unsatisfactory when applied to aroyl halides. Therefore, the decarbonylation reaction of aroyl halides by the rhodium complex is a new and useful means of introducing halogen onto the aromatic ring.

Table II. Decarbonylation Catalyzed by $(\text{PhP}_3)_2\text{Rh}(\text{CO})\text{Cl}$

<i>Acyl Halide,</i> <i>Grams</i>	<i>Catalyst,</i> <i>Gram</i>	<i>Temp.,</i> <i>°C.</i>	<i>Time,</i> <i>Hrs.</i>	<i>Product,</i> <i>Grams</i>	<i>Yield,</i> <i>%</i>
Ph—CH ₂ COCl, 8	0.1	220	2	Benzyl Chloride 3.9	60
Ph—COCl, 8	0.2	200	4	Chlorobenzene 5.1	80
Ph—COBr, 8	0.2	220	1.8	Bromobenzene 5.9	87
CH ₃ —(CH ₂) ₅ —COBr, 4	0.1	200	0.5	Hexene 1.4	80

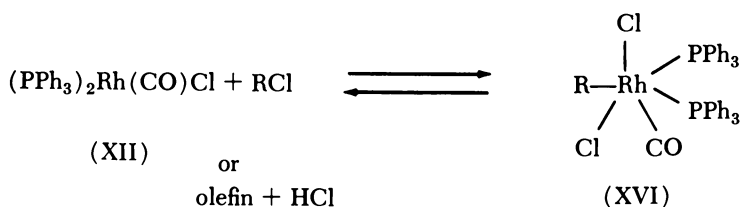
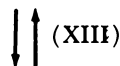
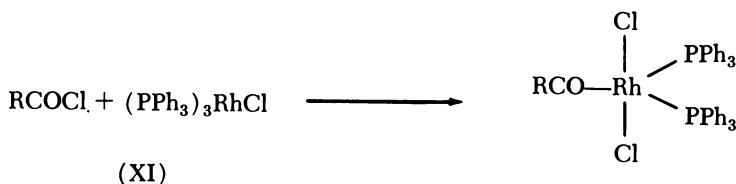
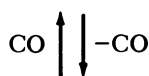
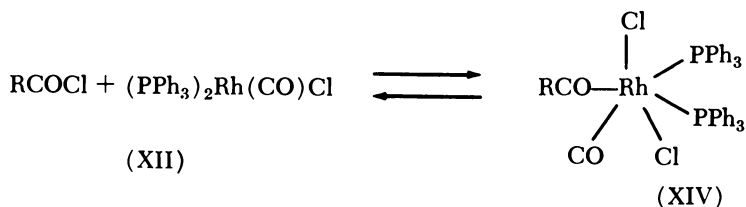
In view of the fact that oxidative addition of alkyl halides and acyl halides to chlorocarbonylbis(triphenylphosphine)rhodium is possible, it was expected that the carbonylation of alkyl halides could be carried out catalytically with this complex. Actually the carbonylation of certain

alkyl halides was observed. For example, benzyl chloride was carbonylated in benzene to form phenylacetyl chloride in the presence of a catalytic amount of the rhodium complex at 150°C. Thus, it was shown that chlorocarbonylbis(triphenylphosphine)rhodium is active for decarbonylation of acyl halides



in the absence of carbon monoxide and for carbonylation of alkyl halides in the presence of carbon monoxide.

From the experimental results, the mechanism of the decarbonylation and carbonylation reactions catalyzed by chlorotris(triphenylphosphine)-rhodium and chlorocarbonylbis(triphenylphosphine)rhodium can be given.

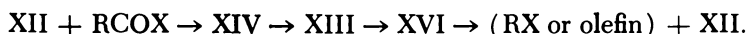


Regarding this mechanism the following can be said:

(1) The reaction of acyl halides with the complex (XI) is irreversible, and the complex (XI) is not recovered under any conditions. Therefore, the decarbonylation by the complex (XI) is stoichiometric.

(2) When (XI) was treated with acetyl chloride or benzoyl chloride, complex (XIII) was not isolated. Instead, (XVI) was isolated, from which (XII) and either CH_3Cl or $\text{C}_6\text{H}_5\text{Cl}$ were formed. The complex (XVI) was isolated as a crystalline substance which exhibited an infrared band at 2080 cm^{-1} .

(3) The course of the decarbonylation reaction catalyzed by the complex (XII) could be:



(4) The course of the carbonylation reaction of RX is:



In this mechanism, the most important point is that the complex (XII) is formed after the carbonylation and decarbonylation, and this complex plays the key role in the reactions.

It is well known that there is a close analogy between a transition metal complex and a transition metal surface with respect to their reactions with hydrogen, hydrogen halides, carbon monoxide and some other reagents. From this consideration, the carbonylation and decarbonylation reactions by metallic palladium and by rhodium complexes discussed in this paper have great significance.

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Liquid-Phase Oxychlorination of Ethylene To Produce Vinyl Chloride

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The M. W. Kellogg Co., Research and Development Division, Piscataway, N. J.

A new technology for producing 1,2-dichloroethane from ethylene, wet or dry hydrogen chloride, and oxygen uses a promoted aqueous solution of copper salts as the catalyst. The process features a selectivity better than 96%, flexibility in the use of HCl or Cl₂ in any proportion, moderate temperature, direct heat removal by vaporization of water and the use of recognized materials of construction. Extensive pilot-plant studies were carried out to determine the mass transfer, chemical kinetics, heat removal and scale-up characteristics of the process and to determine selectivity and the stability of the system as well as appropriate materials of construction. These results, together with extensive engineering design studies provide the basis of the new process for producing dichloroethane. Economics of the process for a commercial size plant are described.

The past 10 years have seen a dramatic change in the technology of poly (vinyl chloride) as the price has dropped from 33 to 14 cents/lb. and as U. S. demand has increased nearly five-fold to an estimated two billion lbs./year in 1966. This has created an unprecedented demand for the monomer, has added to the imbalance in chlorine/caustic demand, and has created large surplus quantities of HCl—a by-product of the ethylene route to vinyl chloride.

In producing vinyl chloride from ethylene, a two-step process is used (6) in which ethylene is first chlorinated to 1,2-dichloroethane (DCE).

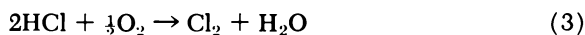


DCE is then thermally cracked to produce vinyl chloride and by-product HCl.



Some producers achieve a balanced operation by a combination of processes in which the by-product HCl reacts with acetylene to yield additional vinyl chloride. This is not generally the most attractive alternative because of the relatively high cost of acetylene compared with ethylene. Acetylene and ethylene can be produced in balanced yield ratios (1, 2), but these processes involve separation problems. Consequently, a very considerable amount of research effort has gone into other techniques to use HCl directly for chlorination purposes.

One obvious method is the historic Deacon process for oxidizing HCl back to chlorine.

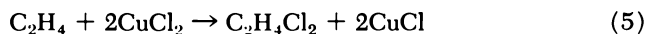


Several modern versions of this process (7) have been proposed. Another technique, which has been used with varying success, is the direct oxychlorination of ethylene to DCE (4) via Reaction 4.



Both of the above processes have normally been carried out over supported metal halide catalysts at elevated temperature and pressure. One of the most difficult problems has been removing the large quantity of heat generated at the surface of the catalyst by the reaction. If temperature is not adequately controlled in oxychlorination, a serious loss in selectivity will result, and catalyst volatilization will occur. In some cases fluidized solids or moving-bed techniques have been used, but these have generally met with difficulties owing to the volatile nature of the more active metal halide catalysts, such as copper chloride and the corrosive nature of the system.

During a series of basic experiments in homogeneous catalysis at the M. W. Kellogg Laboratory, it was discovered that ethylene could be made to react with an aqueous solution of certain metal halides to give 1,2-dichloroethane at moderate temperatures and pressures (*e.g.*, 300°F., 150 p.s.i.g.). The reaction appears to occur between complexed ethylene and the metal halide. For example using copper chloride, ethylene complexed with cuprous chloride is believed to react with cupric chloride to produce dichloroethane. The over-all reaction can be written simply as:



Since the oxidation of aqueous cuprous-cupric solutions is well-known (8):



it appeared that this system might constitute a novel way (3, 5) to carry

out the over-all oxychlorination (Reaction 4) in which precise temperature control could be achieved by vaporizing water from the catalyst.

Homogeneous catalysis of chemical reactions is a fast-growing new technology, which has now achieved a considerable degree of commercial acceptance. Because of its novelty, however, extensive pilot-plant studies were necessary to determine mass transfer, chemical kinetics, heat removal, and scale-up characteristics of the process and to determine selectivity and the stability of the system as well as appropriate materials of construction. Based on these results, together with extensive engineering design studies, a new process for producing DCE has been developed which offers unusual flexibility and selectivity.

Process Description

A flowsheet of the process is shown in Figure 1. It can operate with either HCl/O₂, chlorine, or HCl/O₂ and chlorine in any proportion as regenerants. It offers outstanding flexibility in that it will also accept wet HCl or contaminated by-product HCl from the cracking of DCE in a vinyl chloride plant. These regenerants, along with ethylene, are fed to a prestressed brick-lined reactor containing the promoted, aqueous CuCl₂/CuCl catalyst. Ethylene chlorination and catalyst regeneration occur simultaneously at steady state in the reactor, and DCE is produced at a selectivity of better than 96%. The reactor operates in the ranges 340°–360°F. and 250–275 p.s.i.g. Other reactor conditions, particularly catalyst composition and partial pressures of DCE, HCl, and water vapor have been set to assure high selectivity operation as delineated by pilot-plant studies. Reaction heat is removed simply and smoothly by vaporizing water. No cooling surface is required in the reactor; thus, there are no temperature gradients, and close temperature control is attained.

Reactor effluent gases are quenched with water in a prestressed brick-lined, packed tower. The liquid leaving the tower is cooled further and separated into aqueous and DCE phases. The aqueous phase is split, part being recycled to the tower as quench liquid and the remainder recycled to the reactor, except for a purge equal to the water produced in the oxychlorination reaction. The water recycled to the reactor is first used to absorb part of the HCl feed and enters the reactor as an aqueous HCl solution. DCE product is cooled further and flashed to separate out more water (purged) and dissolved ethylene (recycled).

Uncondensed gases from the quench tower are recycled to the reactor, except for a purge stream to remove inerts. The purge stream goes through an ethylene recovery system to keep the over-all utilization of ethylene high—*i.e.*, better than 95%.

Careful attention has been given to the oxygen level in the reactor effluent and recycle gases. Experimental determinations were made, under severe ignition conditions, of flammability limits for these ethylene- and oxygen-bearing gases at actual process temperature, pressure, and

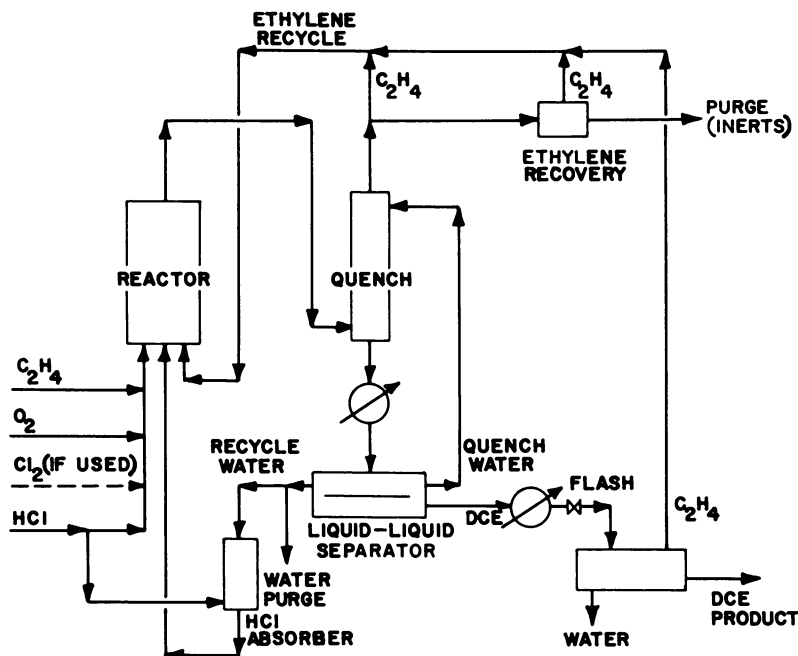


Figure 1. Commercial plant flow sheet

composition. On the basis of these tests, design levels for oxygen concentration have been set comfortably below the flammability limits, with ample margin for control variations.

Construction materials for the plant include prestressed brick linings, Hastelloys B and C, tantalum, Kynar, and Teflon. All these materials have been successfully tested under process conditions.

DCE product from the process is a quite pure, high quality material. Commercial raw product of the following typical analysis can be expected on a water- and ethylene-free basis:

	Wt. %
$C_2H_4Cl_2$ (DCE)	98.7
C_2HCl_3O (trichloroacetaldehyde)	0.5
C_2HCl_3	0.3
C_2Cl_4	0.3
Other C_2 chlorinated hydrocarbons	0.2
	100.0

Of particular importance is the fact that the product has been shown to be virtually free of hexachloroethane, a seriously troublesome compound in cracking DCE to vinyl chloride. Its level in product DCE has been found to be about 3 p.p.m.

Pilot-Plant Studies

The essential elements of the process design were established in the pilot plant shown in Figure 2. The pilot plant consisted of a mechanically agitated reactor, feed metering and product recovery systems, and extensive control and on-line analytical equipment. Provisions were also available for recycling unconverted ethylene and oxygen and for catalyst circulation from storage vessels. Regeneration or chlorination could be studied separately, at steady state, by flowing catalyst continuously into and out of the reactor or both regeneration and chlorination reactions could be carried out simultaneously without catalyst transfer. From a practical standpoint, simultaneous operations are the most interesting and have been given the greatest emphasis, but the catalyst transfer

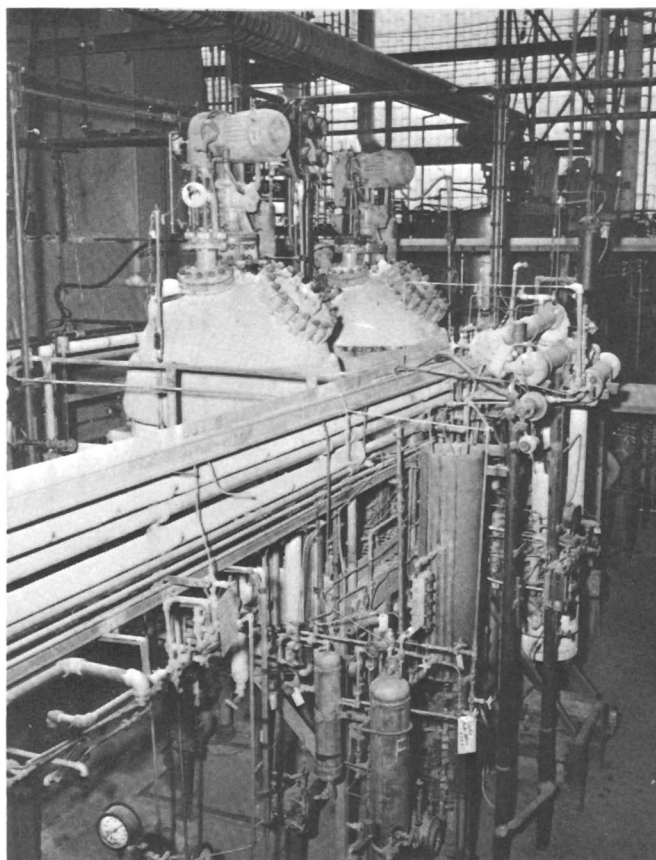


Figure 2. Pilot plant

operations were useful in delineating mass transfer limitations and chemical kinetics.

The chlorination reaction rate can be limited either by chemical kinetics or ethylene mass transfer, depending on ethylene partial pressure, agitation, catalyst composition, and temperature. If the ethylene partial pressure, and/or agitation rate are low, the transfer rate of ethylene to the catalyst solution will be too small to satisfy the kinetic capabilities of the catalyst, and the system will be mass-transfer limited. As either or both ethylene partial pressure and agitation are increased, the mass transfer rate will increase, and eventually ethylene can be supplied to the system at a rate equal to, or in excess of, the kinetic rate capabilities, and the reaction system will be limited kinetically from this point. The mass transfer and kinetic-limiting regimes have been delineated, and simultaneous feed operations were normally made under conditions where chlorination kinetics—not ethylene mass transfer—was controlling.

Catalyst regeneration will usually be oxygen-transfer limited since both the chemical reaction and hydrogen chloride mass transfer rate are fast. Where both chlorination and regeneration reactions are being carried out simultaneously, steady-state operation dictates that the rates of both be equal. If ethylene partial pressure is maintained sufficiently high to ensure that ethylene mass transfer is not limiting, the steady-state rate of DCE formation will be a function of catalyst composition and hence of catalyst regeneration rate. With total gas recycle, the regeneration rate is determined by the rates of adding HCl and oxygen to the process, and the effluent oxygen concentration will line-out at the level dictated by mass transfer considerations. Ethylene feed is then supplied on demand to maintain the pressure of the system.

The effect of trace contaminants on the reaction has been investigated carefully. All uncondensed effluent gases were recycled to the reactor, except for the amounts present in the streams taken off for analysis or flashed upon depressuring of the organic phase. Aqueous phase from the separator containing the water soluble by-products has been used as the water feed to the reactor. Hydrogen chloride containing chlorinated hydrocarbons and acetylene was used in all operations. In addition, certain possible impurities were tested for their effect on the kinetics and selectivity of the process. Paraffins, carbon monoxide, sulfide, carbon dioxide, alkali, and alkaline earth metals were found to be chemically inert. Olefins, diolefins and acetylenic compounds are chlorinated to the expected products. No deleterious effects of by-product recycle were observed even when some of the main by-products were added extraneously.

Operating conditions varied over wide ranges in these studies as shown below.

Temperature	265–365°F.
Pressure	150–275 p.s.i.g.
STY ^a	4.2 max (basis HCl/O ₂)
STY ^a	2.1 max (basis Cl ₂)
STY ^a	5.0 max (total)
C ₂ H ₄ Conv./pass	7.6–24.1%
O ₂ Conv./pass	28.8–84.1%

^a STY = Space time yield in units of gram-moles of products/hr./liter of unexpanded catalyst solution.

The chlorination rate was found to be a function of the total copper concentration, cupric/cuprous ratio, and temperature. An empirical expression relating these variables to the space-time yield has been derived. Extensive oxygen mass transfer studies have been carried out in both process and sodium sulfite solutions; these taken together make possible the scale-up and design of a commercial reactor with ample safety factor on O₂ concentration level.

Selectivity relationships have been developed which permit the prediction of product distribution at any reasonable set of process design conditions. Latest design conditions for simultaneous operation (350°F., $P_{\text{H}_2\text{O}} = 50$ p.s.i.a., $P_{\text{DCE}} = 15$ p.s.i.a., $STY_{\text{total}} = 3.0$, $P_{\text{HCl}} = 0.1$ p.s.i.a.) lead to the following predicted selectivity values:

Oxygenates	2.9% of C ₂ H ₄ converted
Ethyl chloride	0.3
Chlorinated hydrocarbons	0.4
Total by-products	3.6
DCE (by diff.)	96.4

Results of typical pilot-plant chlorinations with HCl/O₂ and HCl/O₂/Cl₂ regenerants are shown in Table I. Run C was 111 hrs. long and was performed with a single batch of catalyst that had been in use for 28 days. No change in catalyst activity occurred during this time, and build-up of impurities was not observed. Composited crude DCE made during Run C was dried and subsequently cracked to vinyl chloride. The resulting vinyl chloride was roughly purified and polymerized to vinyl chloride polymer with conventional emulsion recipes. The resulting polymer was typical for the polymerization conditions employed.

These studies have demonstrated that the homogeneously catalyzed oxychlorination of ethylene to 1,2-dichloroethane is feasible under relatively mild operating conditions without the need for catalyst circulation and that selectivities better than 96% can be achieved in sustained operations. A rational basis for reactor design has been devised, taking into account such factors as ethylene- and oxygen-mass transfer rates, chemical kinetics, water vapor pressure over the catalyst, selectivity relation-

Table I. Operating Conditions and Results

Run No.	A	B	C
Length of run, hrs.	4	8	111
Temp., °F.	365	361	335
Pressure, p.s.i.g.	225	225	225
Regenerant	Cl ₂ /HCl/O ₂	HCl/O ₂	HCl/O ₂
STY	5.0	4.2	2.1
Selectivity, %			
C ₂ H ₃ Cl	0.2	0.1	—
C ₂ H ₅ Cl	—	<0.1	0.5
<i>tert</i> -1,2-C ₂ H ₂ Cl ₂	0.1	—	0.1
1,1-C ₂ H ₄ Cl ₂	—	—	—
C-1,2-C ₂ H ₂ Cl ₂	0.1	0.1	—
1,2-C ₂ H ₄ Cl ₂	96.9	96.3	96.0
C ₂ HCl ₃	0.1	0.2	0.1
C ₂ Cl ₄	0.1	0.2	0.1
C ₂ HCl ₃ O	0.2	0.9	1.2
C ₂ H ₅ ClO	0.1	<0.1	0.6
C ₂ H ₂ Cl ₂ O	0.1	<0.1	0.4
C (unacctd. for in product water)	—	—	0.2
CO	0.1	—	—
CO ₂	2.0	2.0	0.8

ships, and flammability measurements. These have been incorporated into comprehensive process flowsheets, and detailed economics have been prepared showing that the process, while competitive in investment and utility requirements, shows a distinct economic advantage because of its high selectivity.

Economics

For a 350 MM lbs./year DCE plant, using HCl as the only chlorinating gas, DCE manufacturing cost is as follows:

Raw Materials (lbs.)	Unit Cost, cents/lb.	Units/lb. DCE	Cents/lb. DCE
Ethylene	4.0	0.298	1.19
HCl, Fresh	1.5	0.404	0.61
Recycle ^a	—	0.372	—
Oxygen	1.0	0.193	0.19
			1.99

All other operating costs (catalyst and chemicals, utilities at typical rates; fixed charges at 18%/yr. of investment; operating labor at 2 men/shift; overhead, etc. at 100% of operating labor)

$$\text{DCE Manufacturing Cost} = \frac{0.36}{2.35}$$

^a From cracking DCE in associated vinyl chloride production.

When chlorine is fed to the reactor instead of an outside supply of HCl (with HCl still being fed from associated DCE cracking), DCE manufacturing cost, for chlorine at \$55/ton, is 2.70 cents/lb. DCE. Intermediate mixes of outside HCl and chlorine would show DCE manufacturing costs between these limits of 2.35 cents and 2.70 cents/lb., depending on the relative proportions of HCl and chlorine.

Another feed combination that might be used in an over-all vinyl chloride plant would be one in which chlorine is fed to a direct ethylene chlorination unit, and HCl from DCE cracking is recycled to a Kellogg oxychlorination reactor. Approximately half the DCE requirement would come from each of these two units.

The major component of manufacturing cost is, quite obviously, raw materials. Hence, costs are quite sensitive to feed utilization and feed prices. The high selectivity of the Kellogg process is important in this respect. The effect of feed price on DCE cost is illustrated below, where costs for all HCl feed operation, with fresh HCl at 1.5 cents/lb. are compared on the basis of 3.0 as well as 4.0 cents/lb. ethylene:

	<i>Ethylene</i> 4.0 cents	<i>Ethylene</i> 3.0 cents
Manufacturing cost for DCE, cents/lb.	2.35	2.05

Similarly, a cost-free source of waste HCl would drop the manufacturing cost (with 4.0 cents ethylene) to 1.74 cents/lb. For HCl, there is a real potential for utilizing cheap waste HCl since the oxychlorination plant can be designed to accept aqueous HCl. This degree of flexibility is unique.

Acknowledgment

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Homogeneous Hydrogenation of Unsaturated Fatty Esters by $\text{Fe}(\text{CO})_5$ and Diene- $\text{Fe}(\text{CO})_3$

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The mechanism of homogeneous hydrogenation and isomerization catalyzed by $\text{Fe}(\text{CO})_5$ was studied with mixtures of unsaturated fatty esters containing a radioactive label. Although pure monoenes were readily hydrogenated and isomerized with $\text{Fe}(\text{CO})_5$, in a mixture of conjugatable 1,4-diene and monoene, diene hydrogenation was dominant. The formation of diene- $\text{Fe}(\text{CO})_3$ apparently competes with and largely inhibits monoene hydrogenation. Studies with mixtures of methyl linoleate and free or complexed conjugated dienes showed that diene- $\text{Fe}(\text{CO})_3$ complex is an essential intermediate in the catalysis by $\text{Fe}(\text{CO})_5$. Ligand exchange occurred between linoleate and diene- $\text{Fe}(\text{CO})_3$ and was accelerated by adding free $\text{Fe}(\text{CO})_5$. A direct reduction path from linoleate to monoene was an important feature of the catalysis by diene- $\text{Fe}(\text{CO})_3$ alone.

Homogeneous hydrogenation of olefins catalyzed by organometallic complexes has received much attention lately (12). Research in this area has afforded problems of significance in inorganic, organic, and biochemistry (2). These investigations may also contribute to our understanding of heterogeneous catalysis. Isolating catalytically active organometallic intermediates makes this approach more amenable to direct study than work with heterogeneous catalysts.

Among the various organometallic compounds studied at the Northern Laboratory as homogeneous catalysts for hydrogenating unsaturated fats (4, 6, 8, 9, 10), iron pentacarbonyl has been the best model. It cata-

lyzes the reactions at the double bond generally observed with most heterogeneous catalysts, such as reduction, geometric, and positional isomerization. It is selective for the hydrogenation of polyunsaturated fatty esters. Furthermore, it forms stable and isolable π -complexes with dienes and trienes. Since these complexes have been implicated as catalytic intermediates (5, 7) in homogeneous hydrogenation, they serve as suitable model systems for basic studies in catalysis.

Diene complexes formed during the homogeneous hydrogenation of methyl linoleate (*cis*-9,*cis*-12-octadecadienoate) with $\text{Fe}(\text{CO})_5$ were characterized as mixtures of isomers of conjugated methyl octadecadienoate-iron tricarbonyl (7). Triene complexes from methyl linolenate (*cis*-9,*cis*-12,*cis*-15-octadecatrienoate) proved to be mixtures of isomers containing a conjugated diene- $\text{Fe}(\text{CO})_3$ unit and a noncomplexed *cis* or *trans* olefinic bond either α,β to the π -complexed system or separated by several methylene groups (5). A recent study (20) of the ^{13}C NMR spectra of methyl octadecadienoate- $\text{Fe}(\text{CO})_3$ and butadiene- $\text{Fe}(\text{CO})_3$ supported a structure for these complexes in which bonding of Fe involves π -orbitals on all four carbon atoms of the butadiene system.

To elucidate the mechanism of homogeneous hydrogenation catalyzed by $\text{Fe}(\text{CO})_5$, kinetic studies were carried out with mixtures of unsaturated fatty esters containing a radioactive label. A ^{14}C -labeled methyl octadecadienoate- $\text{Fe}(\text{CO})_3$ complex was prepared to serve as a catalytic intermediate. Hydrogenation of methyl oleate (*cis*-9-octadecenoate) and palmitoleate (*cis*-9-hexadecenoate) and of their mixtures with methyl linoleate was also studied to determine the selectivity of this system, the function of the diene- $\text{Fe}(\text{CO})_3$ complex, and the mechanism of homogeneous isomerization. Mixtures of reaction intermediates with a ^{14}C label helped achieve unique simulation of the kinetic data with an analog computer.

Experimental

Materials. $\text{Fe}(\text{CO})_5$ was obtained from Antara Chemicals, General Aniline and Film Corp., and pure methyl oleate, linoleate, and palmitoleate were obtained from The Hormel Institute, Austin, Minn. Methyl linoleate-1- ^{14}C (Tracerlab, Inc.) was both chemically and radioactively pure by gas-liquid chromatography-radioactivity analysis after removing oxidation impurities by partitioning five times between 1-hexane and 75% aqueous methanol. The specific activity was 9.3 mc./mM. The preparation of methyl octadecadienoate- $\text{Fe}(\text{CO})_3$ has been described (6, 7). Methyl octadecadienoate-1- ^{14}C - $\text{Fe}(\text{CO})_3$ was prepared by allowing methyl linoleate-1- ^{14}C (1.03 mM, 0.399 mc.) to react with $\text{Fe}_2(\text{CO})_9$ (1.01 mM) in cyclohexane solution (48 ml.) in a 150-ml. autoclave at 180°C. for 14 hours. The final reaction solution was filtered with Celite through fine-fritted glass. It analyzed 80.2% diene- $\text{Fe}(\text{CO})_3$ by infrared (6). The conjugated methyl *trans,trans*-octadecadienoate

was prepared by decomposition of the corresponding diene-Fe(CO)₃ with FeCl₃ (7).

Hydrogenations. Hydrogenations were made on a 5–10 mM scale in cyclohexane solution (50 ml.) in a 150-ml. magnetically stirred autoclave, provided with sampling tube as described (5, 7). All runs were conducted at 180°C. and 400 p.s.i.g. H₂.

Analyses. The hydrogenations were followed by sequential analyses of the reaction mixtures before and after decomposition of diene-Fe(CO)₃ with ferric chloride. For this purpose, an aliquot was evaporated to dryness, and the free Fe(CO)₅ was removed by heating *in vacuo*. A portion of the residual sample was treated with 95% ethanol solution saturated with FeCl₃ with nitrogen bubbling. The sample in which the diene-Fe(CO)₃ was completely decomposed was then extracted with hexane. Composition was determined with a Cary-Loenco Model 70 chromatograph, provided with simultaneous mass (thermal conductivity) and radioactivity (ion chamber) detectors (17). Columns (6 ft. x ¼ in.) packed with Chromosorb W (100-120 mesh) and coated with 11% ethylene glycol succinate (EGSS-X, Applied Science) were used. Diene-Fe(CO)₃ was determined by infrared before decomposition with FeCl₃ (6). The rate curves were simulated with an analog computer (Electronic Associates EAI-TR-48) by procedures similar to those previously described (3). Position of the double bond in the reduced methyl oleate was determined by the KMnO₄-KIO₄ oxidative cleavage technique of Jones and Davison (14).

Results

Hydrogenation of Monoenes. Methyl oleate was readily hydrogenated and isomerized with Fe(CO)₅ at 180°C. and 400 p.s.i.g. hydrogen (Figure 1). Infrared analyses showed conversion of *cis*- to *trans*-monoenes (21.8% *trans* after 6 hours) and no evidence of iron tricarbonyl complex formation (no absorption in the carbonyl stretching region). Analysis of the cleavage dicarboxylic acid products from KMnO₄-KIO₄ oxidation revealed that 54% of the double bond in the unreduced monoene remained in the original 9-position. The rest of the unsaturation was distributed among the carbons between the 6- and 14-positions.

We found previously (10) that in a natural mixture of mono-, di-, and triunsaturated fatty esters the hydrogenation of monoenes with Fe(CO)₅ was minor. Therefore, competitive hydrogenation studies were carried out with an equal mixture of methyl oleate and linoleate. Diene hydrogenation in such a mixture was indeed dominant (Figure 2). At 0.1M initial concentration of Fe(CO)₅ the formation of stearate was a minor reaction; the diene-Fe(CO)₃ complex reached a maximum of 4% and remained constant. On the other hand, at 0.5M Fe(CO)₅, stearate formation became a more important reaction; diene-Fe(CO)₃ reached a maximum of 7% and decreased during the course of hydrogenation. Free conjugated dienes were minor products.

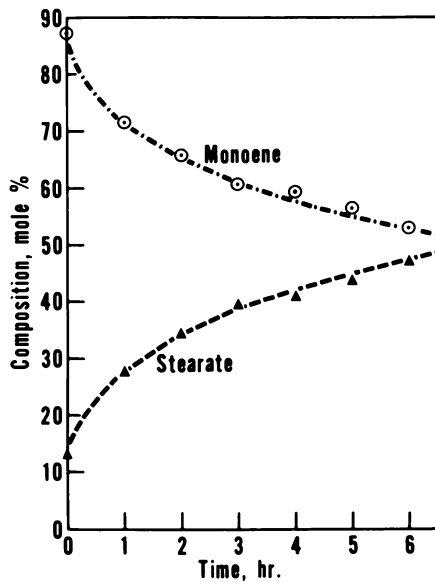


Figure 1. Rate curves for hydrogenation of methyl oleate. Run 1, 0.1M $Fe(CO)_5$

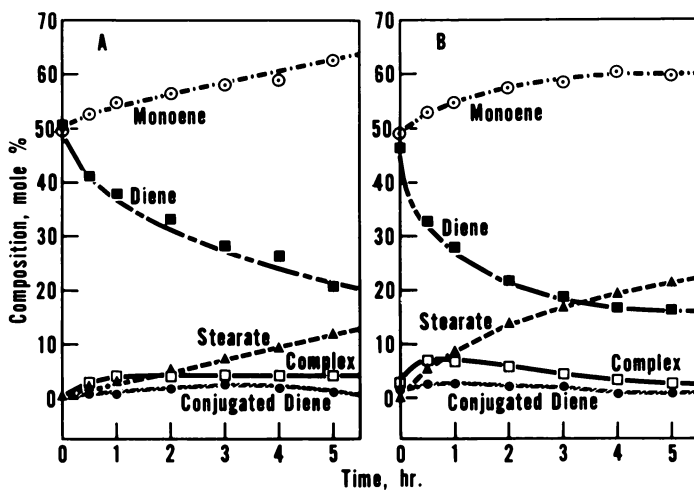


Figure 2. Rate curves for hydrogenation of a mixture of methyl oleate and linoleate: (A) Run 2, 0.1M $Fe(CO)_5$; (B) Run 3, 0.5M $Fe(CO)_5$

To distinguish between the monoenes from unreduced oleate and those formed from linoleate, a mixture of methyl palmitoleate and linoleate was hydrogenated. A control run demonstrated that the rates of oleate and palmitoleate hydrogenation in a mixture were identical. When a mixture of linoleate and palmitoleate reacted under the same conditions as Run 2 in Figure 2A, the dominance of diene hydrogenation was confirmed (Figure 3). Stearate formed at a slightly higher rate than palmitate. Since no significant amount of oleate was present initially, the formation of stearate indicates that direct reduction paths exist from either linoleate or diene- $\text{Fe}(\text{CO})_3$ to stearate. Such direct reductions would be the only way to account for the initial formation of stearate in the absence of oleate. No free conjugated diene was detected in Run 4. If conjugated diene were an intermediate in the reaction, however, then a direct path from conjugated diene to stearate would also be indicated. Since palmitoleate reacts with the same rate constant as oleate, the rate from oleate to stearate could be determined from the rate of palmitoleate to palmitate.

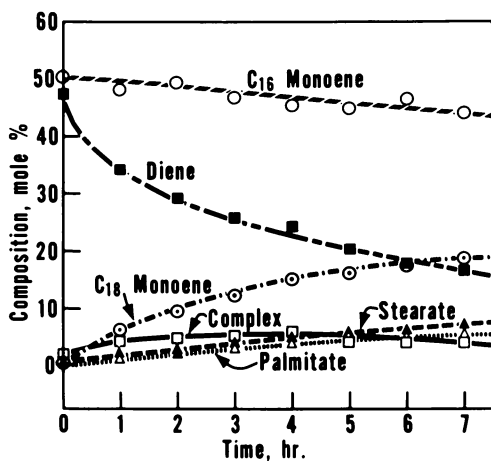


Figure 3. Rate curves for hydrogenation of a mixture of methyl palmitoleate (C_{16}) and linoleate (C_{18}). Run 4, $0.1\text{M Fe}(\text{CO})_5$

In these experiments, therefore, using a C_{16} -monoene in the presence of a C_{18} -diene permitted us to distinguish between the two types of monoenes in the reaction, to establish the presence of direct reduction paths from diene or diene- $\text{Fe}(\text{CO})_3$ to stearate, and to estimate the rate of conversion of oleate to stearate. It was not possible, however, to evaluate the relative importance of the linoleate or diene- $\text{Fe}(\text{CO})_3$ shunts to stearate without using radioactive tracers.

In a mixture of 1,4-diene and monoene the dominant path includes formation of diene- $\text{Fe}(\text{CO})_3$ complex followed by diene hydrogenation. At low concentration the catalyst becomes tied up in this diene complex, and monoene reduction is thus inhibited. In the presence of excess $\text{Fe}(\text{CO})_5$ (Figure 2B), however, diene- $\text{Fe}(\text{CO})_3$ formation is not sufficiently large to tie up all the $\text{Fe}(\text{CO})_5$, and monoene reduction becomes more important. Kinetic evidence is presented to support this pathway.

Hydrogenation of Dienes. The mechanism we previously postulated for the homogeneous hydrogenation of methyl linoleate catalyzed by $\text{Fe}(\text{CO})_5$ involved conjugated dienes and their iron tricarbonyl complexes as important intermediates (7). After these complexes were isolated, they proved to be more efficient catalysts and more active at lower temperatures than $\text{Fe}(\text{CO})_5$. Rate studies were first made with mixtures of methyl linoleate and conjugated dienes. In these mixtures the non-conjugated linoleate was reduced with $\text{Fe}(\text{CO})_5$ at approximately the same rate as the conjugated dienes. Therefore, if hydrogenation proceeds *via* conjugation, then this step is not limiting.

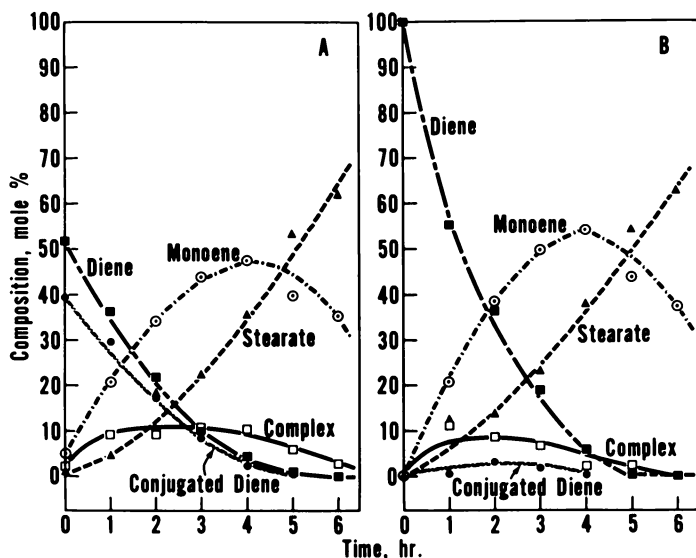


Figure 4. Rate curves for hydrogenation of a mixture of methyl linoleate-1- ^{14}C and *trans,trans*-conjugated diene. Run 5, 0.2M $\text{Fe}(\text{CO})_5$: (A) chemical data, (B) radioactivity data

The hydrogenation of a mixture of methyl linoleate-1- ^{14}C and free *trans,trans*-conjugated diene with 0.2M $\text{Fe}(\text{CO})_5$ is shown in Figure 4. Both linoleate and conjugated dienes disappeared at approximately the same rate, forming monoene, stearate, and diene- $\text{Fe}(\text{CO})_3$ complex.

This complex reached a maximum of about 10% in the early stages of reduction and then decreased. Initially the relative specific radioactivity was 1.93 for methyl linoleate and zero for conjugated diene. Relative specific radioactivity in the products at 50% reduction was about equal in the monoene (1.0), stearate (0.96), and diene- $\text{Fe}(\text{CO})_3$ (1.0), but only minor in the free conjugated diene (0.14). Although the diene- $\text{Fe}(\text{CO})_3$ complex is a significant intermediate in the reduction of linoleate, the free conjugated diene is not.

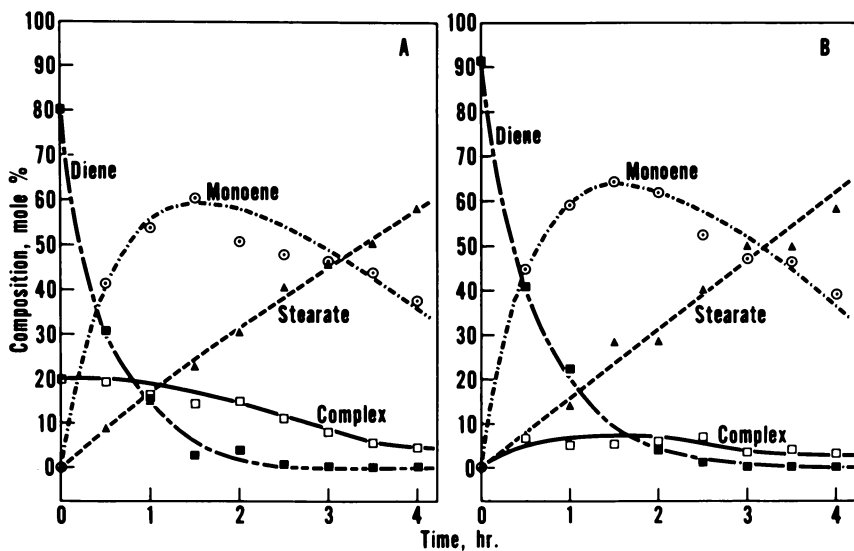


Figure 5. Rate curves for hydrogenation of a mixture of methyl linoleate-1-¹⁴C and diene- $\text{Fe}(\text{CO})_3$. Run 6, 0.2M diene- $\text{Fe}(\text{CO})_3$; (A) chemical data, (B) radioactivity data

Figure 5 shows the hydrogenation of methyl linoleate-1-¹⁴C with 0.2M diene- $\text{Fe}(\text{CO})_3$. The rapid disappearance of diene was followed by the formation of monoene and stearate. Initially, the complex concentration was constant and then slowly decreased during hydrogenation. The initial formation of stearate indicates the occurrence of direct paths from linoleate and diene- $\text{Fe}(\text{CO})_3$ to stearate without going through a monoene stage. From the amount of radioactive stearate formed, the relative magnitudes of these direct paths has been determined. No free conjugated diene was detected in this run. Relative specific activity of the products at 50% reduction decreased in the order: monoene (1.1), stearate (0.94), and diene- $\text{Fe}(\text{CO})_3$ complex (0.63). Formation of radioactive diene- $\text{Fe}(\text{CO})_3$ confirms the previous evidence that it is a catalytic

intermediate and that ligand exchange occurs between radioactive linoleate and inactive complex.

To study the ligand exchange between linoleate and diene- $\text{Fe}(\text{CO})_3$, a run complementary to the previous one was made by reversing the radioactive label. A mixture of methyl linoleate and 0.1M diene- $1\text{-}^{14}\text{C}\cdot\text{Fe}(\text{CO})_3$ was used. About 25% of the radioactivity in the initial reaction mixture resided in the uncomplexed diene because no attempt was made to purify the radioactive complex after its preparation from linoleate- $1\text{-}^{14}\text{C}$. Rates given in Figure 6 closely resemble those in Figure 5. Again, the initial formation of stearate shows that direct paths occur between linoleate and diene- $\text{Fe}(\text{CO})_3$, on one hand, and stearate on the other. At 50% reduction relative specific activity was also approximately the same for monoene (1.1) and stearate (0.95). This large amount of radioactivity transferred from the complex to the reduction products indicates that a significant exchange occurs between linoleate and diene- $\text{Fe}(\text{CO})_3$ complex.

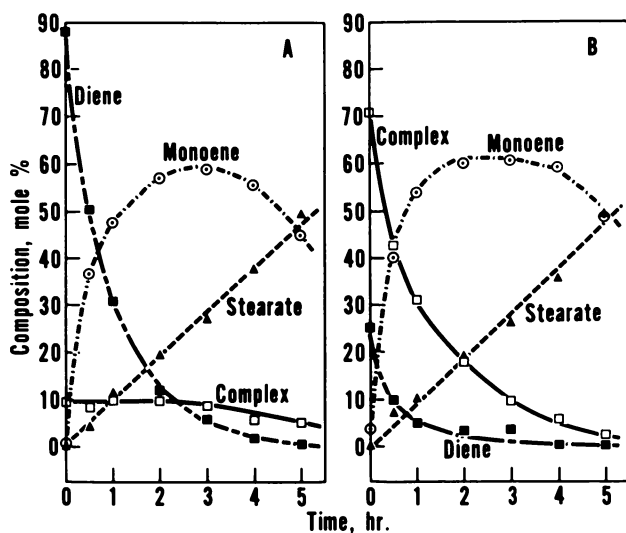


Figure 6. Rate curves for hydrogenation of a mixture of methyl linoleate and diene- $1\text{-}^{14}\text{C}\cdot\text{Fe}(\text{CO})_3$. Run 7, 0.1M diene- $\text{Fe}(\text{CO})_3$: (A) chemical data, (B) radioactivity data

We next investigated the effect of free $\text{Fe}(\text{CO})_5$ on this ligand exchange. Methyl linoleate was hydrogenated with a mixture of 0.05M diene- $1\text{-}^{14}\text{C}\cdot\text{Fe}(\text{CO})_3$ and 0.05M $\text{Fe}(\text{CO})_5$. Figure 7 shows that the

hydrogenation of methyl linoleate is more selective toward the formation of monoene and that there is a much more rapid incorporation of the radioactivity from the complex to the monoene in the presence of both diene- $\text{Fe}(\text{CO})_3$ and $\text{Fe}(\text{CO})_5$ than in the absence of free $\text{Fe}(\text{CO})_5$ (Figure 6). This evidence indicates that the ligand exchange between linoleate and diene- $\text{Fe}(\text{CO})_3$ is greatly accelerated in the presence of free $\text{Fe}(\text{CO})_5$. Therefore, monoene formation through the diene- $\text{Fe}(\text{CO})_3$ complex becomes a major path, and the direct paths from linoleate and from complex to stearate become less important.

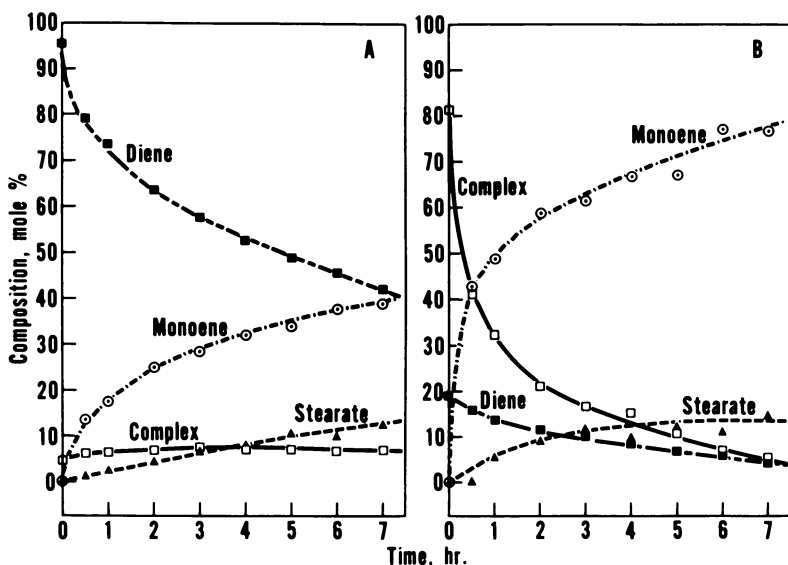
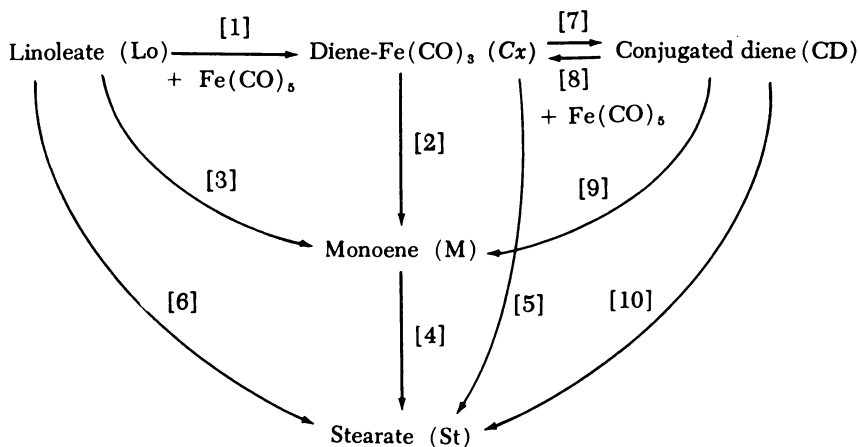


Figure 7. Rate curves for hydrogenation of a mixture of methyl linoleate, diene- $1\text{-}^{14}\text{C}\cdot\text{Fe}(\text{CO})_3$ and $\text{Fe}(\text{CO})_5$. Run 8, 0.05M diene- $\text{Fe}(\text{CO})_3$, 0.05M $\text{Fe}(\text{CO})_5$: (A) chemical data, (B) radioactivity data

Kinetics and Proposed Mechanism

The rate curves in Figures 2–7 were satisfactorily simulated by an analog computer according to Scheme I.

Better fits of the kinetic data were obtained by treating Step 1 (and Step 8) as a second-order reaction in linoleate and $\text{Fe}(\text{CO})_5$. All other reactions were treated as first order. Since the concentration of $\text{Fe}(\text{CO})_5$ could not be determined accurately under the experimental conditions used, it was estimated from the concentration of diene- $\text{Fe}(\text{CO})_3$ (Cx)



by assuming

$$(\text{Fe}(\text{CO})_5) = (C x_m - C x_t)$$

$C x_m$ = Maximum concentration of complex that can be formed (= initial concentration of $\text{Fe}(\text{CO})_5$ used)

$C x_t$ = Concentration of complex at time t .

The mathematical model is as follows.

$$d(\text{Lo})/dt = -(k_3 + k_6) (\text{Lo}) - k_1 (\text{Lo}) (C x_m - C x_t)$$

$$d(Cx)/dt = +[k_1(\text{Lo}) + k_8(\text{CD})] (C x_m - C x_t) - (k_2 + k_3 + k_7) (Cx)$$

$$d(\text{CD})/dt = -(k_9 + k_{10}) (\text{CD}) - k_8 (\text{CD}) (C x_m - C x_t) + k_7 (\text{CD})$$

$$d(\text{M})/dt = -k_4 (\text{M}) + k_3 (\text{Lo}) + k_2 (Cx) + k_9 (\text{CD})$$

$$d(\text{St})/dt = +k_4 (\text{M}) + k_3 (Cx) + k_6 (\text{Lo}) + k_{10} (\text{CD})$$

Composition curves were calculated from the concentration of individual components and plotted as molar composition *vs.* number of double bonds. Treating the 10 reactions in Scheme I by these simultaneous equations, the best rate constants were obtained from computer plots that best matched the experimental composition patterns. The accuracy of this simulation of the kinetic data is increased by using radioactively labeled intermediates, which provide two sets of kinetic curves with different initial conditions. By thus doubling the independent experimental measurements, we approach a unique solution by the analog computer. Figure 8 illustrates the results of simulation of the model

(Scheme I) on the analog computer and the degree of matching of experimental points (for Figure 5) obtained with the computer-drawn kinetic curves.

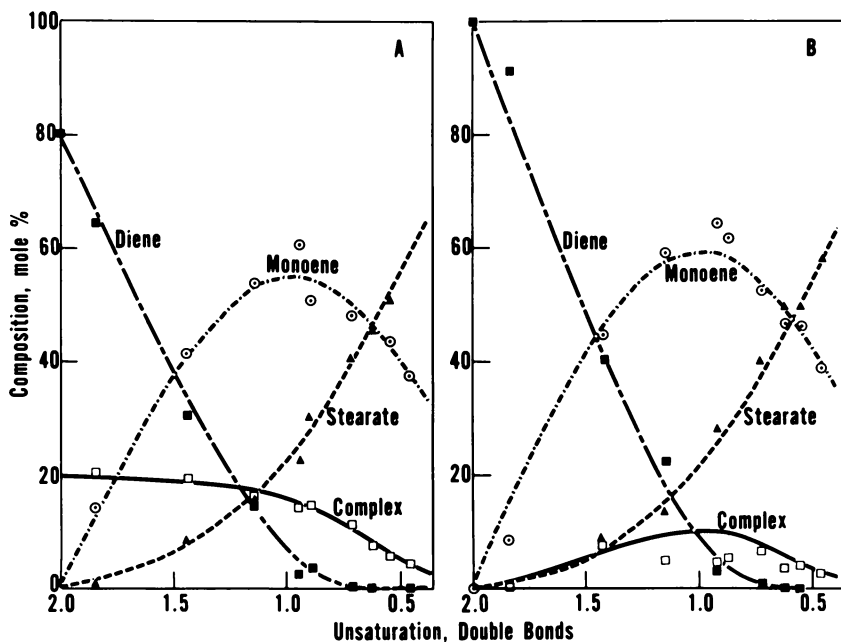


Figure 8. Analog computer simulation for data in Figure 5

Table I summarizes the relative first-order constants of the various reactions simulated with the analog computer. Each reaction step in Scheme I is calculated relative to the reduction of complex to monoene [2].

In simulating the kinetics of Runs 2 and 4, since palmitoleate and oleate have the same rate constants, the reduction of oleate to stearate [4] was taken as equal to the rate of palmitoleate to palmitate (Run 4). Because these runs did not involve radioactive intermediates, their simulation was not reliable. However, the same rate constants could be used to fit data of both Runs 2 and 4, which are complementary; this matching increased the confidence in the simulation. The kinetics on these runs show that the direct reduction paths from linoleate to monoene [3] and from conjugated diene to monoene [9] (Scheme I) are significant. Rates calculated for Run 5 (Table I) are more reliable because a radioactive label was used and because the conjugated diene was an important component in the reaction mixture. Rates of reduction [3 and 9] relative

Table I. Relative Rates of Hydrogenation

Reaction	Rate Constant	Runs 2 and 4 (Figures 2A and 3)	Run 5 (Figure 4)
		Linoleate + oleate (palm 01) + Fe(CO) ₅ (0.1M)	Linoleate-1- ¹⁴ C + conj. diene + Fe(CO) ₅ (0.2M)
Cx → M	k ₂	1.0	1.0
Lo → M	k ₃	0.21	0.61
M → St	k ₄	0.08	0.30
Cx → St	k ₅	0.21	0.20
Lo → St	k ₆	0.06	0.08
Cx → CD	k ₇	~0.6	0.16
CD → M	k ₉	~0.2	0.50
CD → St	k ₁₀	~0.06	0.08

^a See Scheme I. Steps 1 and 8 are second-order and not considered here.

to monoene formation [2] for linoleate and conjugated diene are about the same. Although the direct reduction path [3] is significant in Run 5, it becomes much more important when pure complex is used as the catalyst (Run 6) instead of Fe(CO)₅. Comparing complementary Runs 6 and 7 shows that the direct reduction paths [3, 5, and 6] are much smaller at a lower initial concentration of diene-Fe(CO)₃ complex. Furthermore, the path involving the complex as an intermediate is much more important when Fe(CO)₅ is present (Runs 5, 8) than when the complex is the only source of catalyst (Runs 6,7). Apparently Fe(CO)₅ accelerates the ligand exchange between linoleate and diene-Fe(CO)₃ complex.

Discussion

The ready hydrogenation and isomerization of methyl oleate and palmitoleate with Fe(CO)₅ confirm the results of Ogata and Misono (18) with monounsaturated aliphatic compounds. In the isomerization of monoolefins Manuel (15) suggested the occurrence of equilibria involving either π -olefin HFe(CO)₃ and σ -alkyl Fe(CO)₃ complexes, or π -olefin Fe(CO)₃ and π -allyl HFe(CO)₃ complexes. The formation of olefin-iron tetracarbonyl complexes has been reported (19). The reaction of butadiene and Fe₂(CO)₉ has been observed to lead to the formation of butadiene-Fe(CO)₄ and butadiene-[Fe(CO)₄]₂ complexes in which one or both double bonds are pi-bonded to the iron (16). A mechanism involving both monoene-Fe(CO)₄ (I) and allyl-HFe(CO)₃ complexes (II) is postulated for the isomerization of methyl oleate (Scheme II) and for its homogeneous hydrogenation.

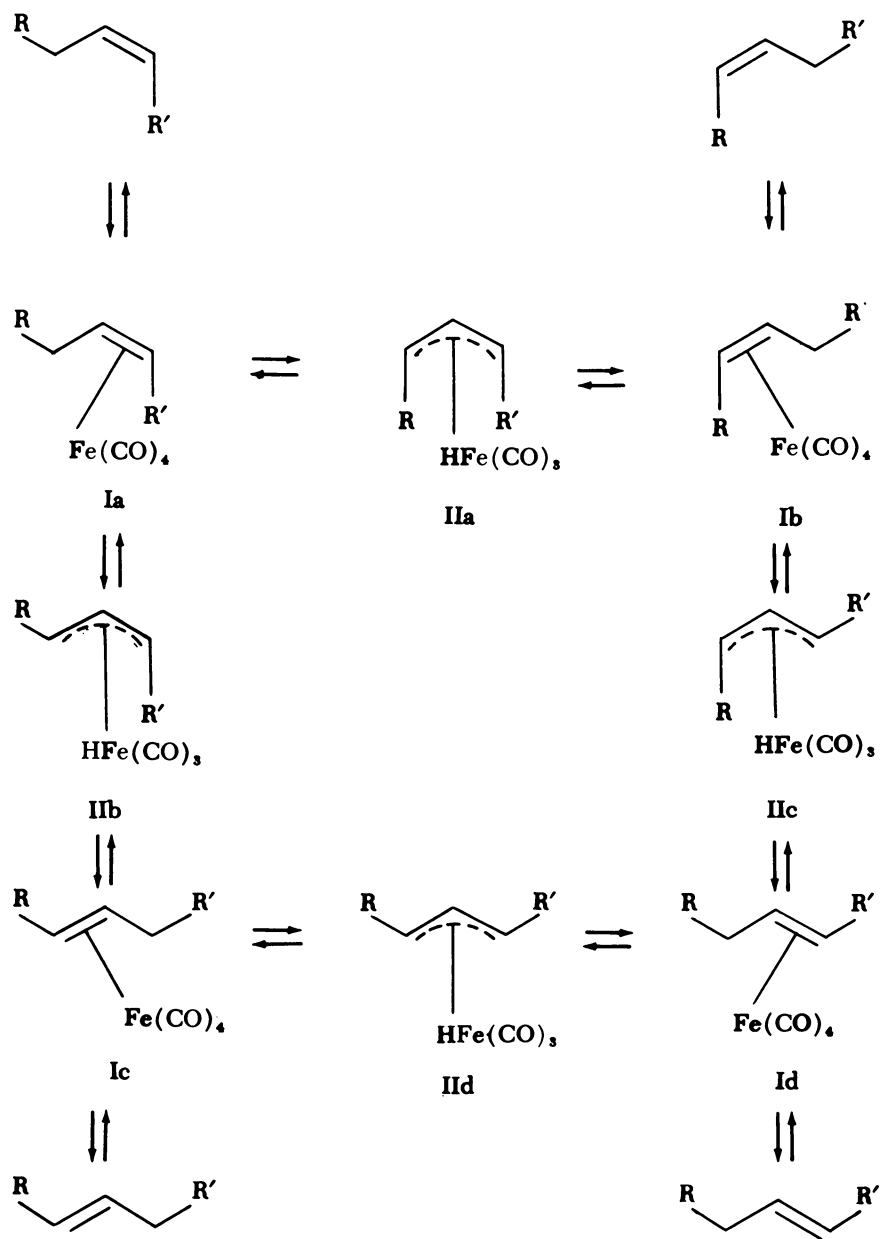
of Unsaturated Fatty Esters^a

Run 6 (Figure 5)	Run 7 (Figure 6)	Run 8 (Figure 7)
<i>Linoleate-1-¹⁴C + complex (0.2M)</i>	<i>Linoleate + complex-1-¹⁴C (0.1M)</i>	<i>Linoleate + complex-1-¹⁴C (0.05M) + Fe(CO)₅ (0.05M)</i>
1.0	1.0	1.0
2.8	0.84	0.15
0.56	0.24	0.13
0.42	0.03	0.0
0.15	0.06	0.02
—	—	—
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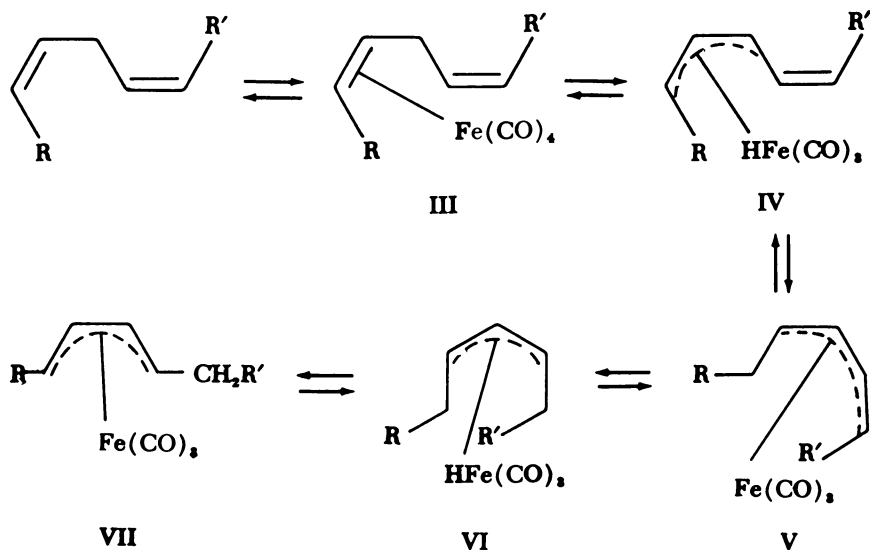
If monoolefin-Fe(CO)₄ complexes are involved in oleate hydrogenation, similar complexes may be invoked as intermediates in the formation of diene-Fe(CO)₃ complexes from linoleate (Scheme III). Iron tetracarbonyl complexes were also suggested by Pettit and Emerson (19) in the formation of conjugated diene-Fe(CO)₃ from nonconjugated dienes.

Diene-Fe(CO)₄ complexes like III and linoleate-[Fe(CO)₄]₂ (VIII) can be postulated as additional intermediates in the hydrogenation scheme for linoleate (Scheme IV). The π-complexes involving one double bond of linoleate attached to iron can undergo either direct reduction with hydrogen to form monoenes (Steps [3 and 9], Scheme I), or they can form the more stable diene-Fe(CO)₃ complexes VII (Scheme III). These intermediates can be reduced to monoene and stearate. Diene-[Fe(CO)₄]₂ complexes, in turn, would be reduced to monoene-Fe(CO)₄ complexes (I), which would either dissociate or hydrogenate to form stearate.

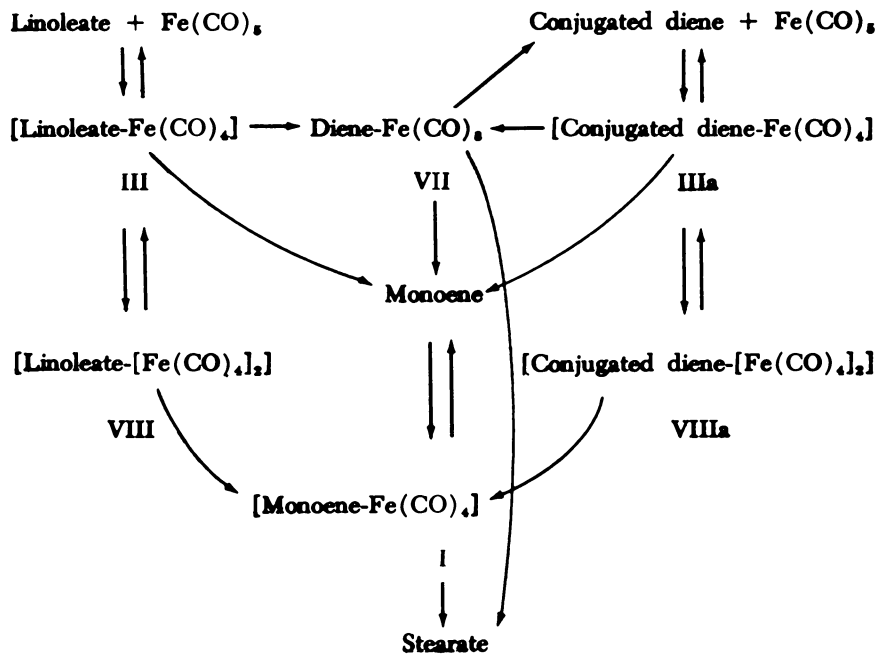
The Fe(CO)₄ intermediates of types III and VIII in Scheme IV explain the direct reduction paths evidenced in the hydrogenation of mono- and diunsaturated fatty esters. Competition between monoene and diene hydrogenation can be related to the stability of the Fe(CO)₃- and Fe(CO)₄-complexes. At a low concentration of Fe(CO)₅, the formation of Fe(CO)₃ complexes is favored because they are more stable. At a high concentration of Fe(CO)₅, formation of mono- and di-Fe(CO)₄ complexes becomes important, and selectivity for diene hydrogenation is decreased. Although the occurrence of olefin-Fe(CO)₄ complexes has precedence in the literature (19), no such species has yet been identified with either methyl oleate or linoleate.



Scheme II

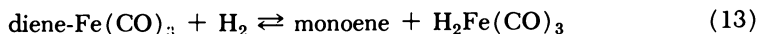


Scheme III

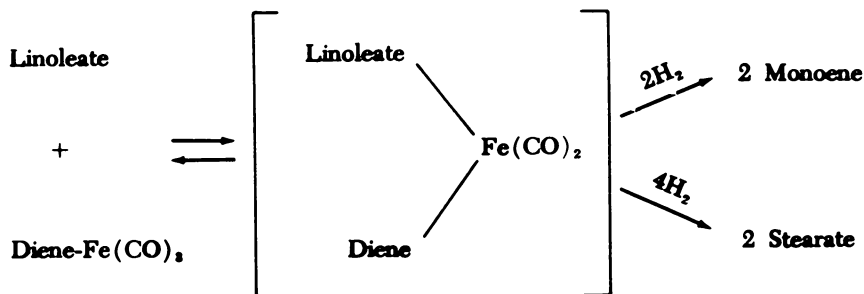


Scheme IV

Hydrogenations with diene-Fe(CO)₃ as the source of catalyst appear to involve ligand exchange with linoleate and can be rationalized according to the following reactions:



Reactions (11) and (12) provide means for ligand exchange between linoleate and diene-Fe(CO)₃, which would be accelerated in the presence of free Fe(CO)₅. Alternatively, the formation of a bisdiene-Fe(CO)₂ complex (IX) as a transient intermediate may be invoked.



IX

The mechanism for homogeneous hydrogenation of methyl linoleate by Fe(CO)₅ based on kinetic evidences and radioactive tracers involves monoene- and diene-Fe(CO)₄ and diene-Fe(CO)₃ complexes as important intermediates. Contrary to our previous postulate (7) the free conjugated diene is only a minor intermediate. Confirmatory evidence is needed for the occurrence of oleate- and linoleate-Fe(CO)₄ complexes during hydrogenation and isomerization with Fe(CO)₅. Also, the species of iron carbonyl hydrides formed during hydrogenation should be elucidated.

Pure diene-Fe(CO)₃ complexes provide suitable model systems for basic catalytic studies. Many types of organometallic intermediates have been implicated to explain the mechanism of various catalytic reactions with transition metals (1, 11, 13, 21, 22). Little direct evidence on these intermediates has been obtained, however, especially in studies with heterogeneous catalysts. Our work with iron carbonyl complexes has afforded a direct approach to studying active organometallic intermediates during the homogeneous reactions catalyzed by Fe(CO)₅.

Comparison between the soluble complexes of iron carbonyl and similar pi-adsorbed species, postulated as intermediates in heterogeneous catalysis, may be useful and may contribute to our understanding of the mechanism of catalytic hydrogenation. Bond and Wells (1) have reviewed and correlated common features between the organometallic chemistry of the transition metals of Group VIII and their catalytic chemistry in heterogeneous systems. Other workers (11, 12, 21, 22) have also suggested the probable relevance of reactions of metal-olefin complexes to the chemistry of catalytic reactions of these metals. Apparent correlations have suggested that pi-bonding is involved in both olefin adsorption and metal-olefin complexes. Therefore, the common chemistry of organometallic compounds and metal-adsorbed olefins seems to justify mechanistic implications from certain homogeneous to corresponding heterogeneous systems.

Acknowledgment

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Chelate Complexes of Iridium

Their Chemistry and Use in Catalysis

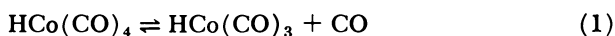
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The d^8 complexes exist mainly as four- or five-coordinate compounds. They form 1:1 adducts with donor ligands and react with RX molecules to form six-coordinate products containing R and X as separate ligands. These properties play a key role in homogeneous catalysis by such complexes. Trans-IrX(CO)(PPh₃)₂ reacts with chelating ligands containing phosphorus and sulfur donor atoms to give IrX(CO)-(chelate)₂ or IrX(chelate)₃. Small changes in the ligand cause large changes in the lability of the CO ligand. Some of the products react with hydrogen and will catalyze the hydrogenation of alkenes and alkynes. Analogous reactions with rhodium complexes yield different products and properties.

The d^8 configuration holds a special place in the field of organometallic chemistry. From an inorganic chemist's point of view it encompasses a wide range of stereochemical behavior, and coordination numbers of four, five, and six are common (17, 34, 37). By comparison, almost the whole of the chemistry involving d^5 , d^6 , and d^7 complexes is that of octahedral stereochemistry (35). In catalysis many of the more important reactions almost certainly involve complexes of the d^8 configuration. The "oxo" process for hydroformylation of olefins (2, 43), the Hoechst-Wacker oxidation of ethylene (23, 41), the hydrosilation (4, 18, 38), isomerization (3, 10, 19, 32, 42), hydrogenation (9, 13, 14, 15, 22, 49, 52) and oligomerization (8, 51) of olefins are common examples. The two observations are undoubtedly related, and from mechanistic schemes advanced for some of these catalytic reactions it is clear that the multitude of stereochemical possibilities plays a key role. The proposed initial step

in the hydroformylation reaction is loss of carbon monoxide from the catalyst as in Reaction 1:



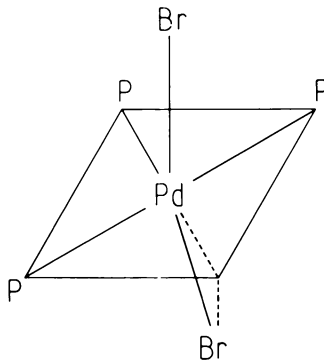
This provides a route for entry of the olefin molecule to the active site. In fact the ability of square-planar d^8 systems to take on more ligands seems to dominate much of their chemistry. The best known example of this is the reversible addition of O_2 and SO_2 to *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (44). d^8 Square planar substitution reactions, particularly for Pt(II), are thought to be associative in character with formation of five-coordinate intermediates. These intermediates probably have trigonal bipyramidal structures, particularly where they contain π -acceptor ligands (24). Examples are also known where two ligands are introduced. This usually results in formal oxidation of the metal as in the reaction between M(I) (M = Ir, Rh) and various RX molecules to give M(III) (M = Ir, Rh) complexes with R^- and X^- as ligands. Examples of RX include H_2 , (45, 47), hydrogen halides (48), alkyl and allyl halides (20), and silanes (4). A kinetic study of this type of reaction has recently been reported (6). The reaction probably occurs in Rh(I)-catalyzed olefin dimerization (8) and hydrogenation reactions (22, 52) and Rh(I)- and Pt(II)-catalyzed hydrosilation of olefins (4), where the proposed initial steps involve addition of HCl, H_2 , and R_3SiH to the catalyst, respectively.

The work described here is an attempt to determine the factors which are important in controlling stereochemistry, chemistry, and use as catalysts of d^8 complexes. These complexes are known for oxidation states 2- to 3, the range of metals covering chromium to gold (37). Table I gives the preferred coordination number, with other less common

Table I. Coordination Numbers for d^8 Complexes

2-	1-	0	1	2	3
Cr5	Mn5	Fe5	Co5	Ni4(5)(6)	
Mo5	Tc5	Ru5	Rh4,5	Pd4(5)(6)	
W5	Re5	Os5	Ir4,5	Pt4(5)(6)	Au4(5)

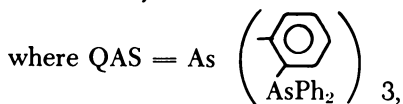
ones in parentheses, for metals in these groups. It is immediately clear that there is a change from five coordination for low oxidation states to four coordination in higher oxidation states. This has been related to the separation of the $(n-1)d$ and np orbitals of the metal ion. The smaller this difference, the easier it is to hybridize all the np orbitals to form dsp^3 hybrids which give the trigonal bipyramidal stereochemistry (36). The d - p separation increases with increasing formal charge on the metal—*i.e.*, with increasing oxidation state. For the low oxidation states, 2-, 1-, 0, the majority of the d^8 complexes are of the $[\text{M}(\text{CO})_5]^{n-}$ ($n = 2, 1, 0$)



P = 2-PHENYLISOPHOSPHINDOLINE

Figure 1. Structure of $PdBr_2(2\text{-phenylisophosphindoline})_3$

type or substituted derivatives (34). The stereochemistry is most likely trigonal bipyramidal as proved conclusively for $Fe(CO)_5$ (12). At the other extreme, four coordination with square-planar stereochemistry is common with $(PR_3)_2MX_2$ ($M = Ni, Pd, Pt$; $X = \text{halogen, pseudohalogen, hydride}$) and $(PR_3)AuX_3$ as typical examples. Where five coordination does occur for these metals, the structure can be either trigonal bipyramid or tetragonal pyramid. Thus, for monodentate ligands as in the $[Pt(SnCl_3)_5]^{3-}$ ion the arrangement is trigonal bipyramidal (11). By comparison the red isomer of $PdBr_2(2\text{-phenylisophosphindoline})_3$, shown in Figure 1, has a structure closely approximating a tetragonal pyramid (7). Complexes containing multidentate ligands behave similarly. $NiBr_2(\text{triars})$, where $\text{triars} = CH_3As[CH_2CH_2CH_2As(CH_3)_2]_2$ has a structure similar to the $Pd(II)$ (26) complex above (Figure 2). In each case the bromine atom is below the tetragonal plane, and this $M-Br$ bond is considerably shorter than the axial one. The tetradentate ligand QAS:



has the correct geometry for occupying three equatorial and one axial position of a trigonal bipyramid and complexes containing this ligand are expected to have this stereochemistry. $[PtI(QAS)]BPh_4$ is a good example where the iodine atom occupies the remaining axial position (27).

Between these extremes of largely five or largely four coordination is the cobalt, rhodium, iridium group of metals. The I^+ oxidation state is not the most stable for these metals, and only in the last five years have

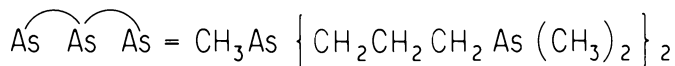
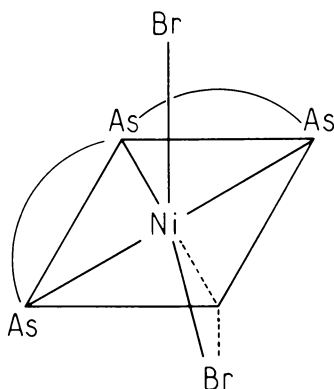


Figure 2. Structure of $\text{NiBr}_2[\text{CH}_3\text{As}\{\text{CH}_2\text{CH}_2\text{CH}_2\text{As}(\text{CH}_3)_2\}_2]$

examples of such complexes been reported. Within this group it may be expected that both four and five coordination will occur frequently, depending on both metal and ligands, and that examples of facile addition and removal of a fifth ligand will be found. In the literature there are already examples illustrating these points. Thus, with isonitriles as ligand Co(I) forms $[\text{Co}(\text{CNR})_5]^+$ probably with a trigonal bipyramidal structure (31), but Rh(I) (30) and Ir(I) (28) form $[\text{M}(\text{CNR})_4]^+$ complexes where R = *p*-tolyl. The compound *trans*-IrCl(CO)(PPh₃)₂ will add both O₂ and SO₂ reversibly (25, 44), and the preparation of IrCl(CO)₂(PPh₃)₂ has been reported (35). In addition the monohydrido, IrH(CO)(PPh₃)₃, (1) and monocarboalkoxy, Ir(CO₂R)(CO)₂(PPh₃)₂ (29), analogs of Vaska's compound are five-coordinate, as are many cationic species such as $[\text{Ir}(\text{CO})_x(\text{PPh}_3)_{5-x}]^+$ (29). This group thus appeared the most attractive for studying *d*⁸ behavior in all its facets.

More specifically Ir(I) was chosen as a model element from this group since it was expected that the complexes would be more stable, even though this may be a big disadvantage when studying catalytic processes. Hydrogenation was chosen as the reaction for study because of its wide occurrence among *d*⁸ complexes. Fe(CO)₅ has been used for hydrogenating activated double bonds, particularly for conjugated dienes and trienes (13). HCo(CO)₄ catalyzes the hydrogenation of various materials including α,β -unsaturated ketones, acrylonitrile, and aldehydes (14, 15). More recently reports of using RhCl(PPh₃)₃ (22, 52), *trans*-IrCl(CO)(PPh₃)₂ (49), and IrH(CO)(PPh₃)₃ (46) as catalysts in alkene and alkyne hydrogenation have appeared. Pt(II) with SnCl₃⁻

ligands is also active (9). It is clear that many d^8 systems catalyze hydrogenation reactions including $M(I)$, where $M = Co, Rh, Ir$, and this reaction should be a good yardstick for catalytic activity.

Ir(I) Chelate Complexes

There is rapid exchange of the ligands in $Rh(I)$ and $Ir(I)$ square planar complexes (16). This observation has been used to prepare a range of $Ir(I)$ complexes with bidentate ligands. The starting materials are *trans*- $IrX(CO)(PPh_3)_2$ where $X = \text{halogen}$. If these are treated with an excess of another phosphine, such as PPh_2Et or $PPhEt_2$, a virtually quantitative replacement of PPh_3 takes place. No change in stereochemistry occurs, and *trans* isomers are obtained. If a bidentate phosphine is used, some change in stereochemistry must occur because of the steric requirements of the ligand. The compound $IrX(CO)(\text{chelate})$ has not been isolated in any case examined. The most common behavior has been the replacement of two monodentate phosphines by two bidentate phosphines accompanied by loss of one or both of the CO and X^- ligands from the inner coordination shell. The reaction also occurs with bidentate ligands containing only one phosphorus atom but has not been observed with those containing none. In addition the nature of the phosphine in the starting material is of little importance, and both PPh_2Et and $PPhEt_2$ have been used successfully in place of PPh_3 .

Four bidentate ligands have been studied, and two types of products were obtained: $IrX(CO)(\text{chelate})_2$ and $IrX(\text{chelate})_2$. The particular product obtained for each ligand is given in Table II.

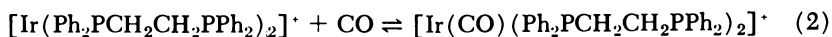
Table II. $Ir(I)$ Chelate Complexes

Ligand	$IrX(CO)(\text{chelate})_2$	$IrX(\text{chelate})_2$
$Ph_2PCH_2CH_2PPh_2$	a	a
$Ph_2PCH_2PPh_2$	a	b
$Ph_2PCH_2CH_2SPh$	b	a
$PhSCH_2CH_2SPh$	b	b

Symbols: a = isolated; b = not isolated

$Ph_2PCH_2CH_2PPh_2$. For $Ph_2PCH_2CH_2PPh_2$ two products are obtained. If the reaction is carried out in tetrahydrofuran or benzene solutions at reflux temperatures, an orange solid forms slowly. This has been identified as $[Ir(Ph_2PCH_2CH_2PPh_2)_2]X$ where $X = Cl^-, Br^-, BPh_4^-$, the latter being prepared from the halide by reaction with $NaBPh_4$ in acetone solution. The compounds have no $\nu_c \equiv o$ frequency in the infrared, have a conductivity typical of 1:1 electrolytes, show sharp peaks in the proton NMR, characteristic of phenyl and methylene protons in the ratio 5:1, and have the correct elemental analysis. At room temperature, preferably

in an atmosphere of carbon monoxide, a different yellow crystalline product is obtained. This is $[\text{Ir}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{X}$ where $\text{X} = \text{Cl}^-, \text{Br}^-, \text{ClO}_4^-$, the last compound being prepared by metathetical displacement using NaClO_4 . The complexes are again 1:1 electrolytes but now have a $\nu_{\text{C}=\text{O}}$ stretching frequency in the infrared at 1931 cm^{-1} . This is lower than in the parent $\text{IrX}(\text{CO})(\text{PR}_3)_2$ complexes ($1940\text{--}1960 \text{ cm}^{-1}$). The CO ligand in this complex is very labile. In chloroform solution the CO can be removed rapidly by passing nitrogen through the solution. This reaction can be reversed by passing CO gas into the solution when the yellow color of the CO-adduct is rapidly regenerated. In addition the electronic spectrum of the adduct contains bands typical of $[\text{Ir}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^+$ if the solution is not saturated with CO. These observations are consistent with a rapid equilibrium as in Reaction 2.



This system is an example of Ir(I) occurring in closely related forms with coordination numbers four and five.

In addition to the reaction with CO the four-coordinate complex reacts with hydrogen gas at room temperature either as a solid or in chloroform solution to give $[\text{IrH}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{X}$. This reaction is irreversible at room temperature and differs in this respect from the CO reaction. The complex is a 1:1 electrolyte and has typical infrared bands at 2060 cm^{-1} ($\nu_{\text{Ir-H}}$) and 845 cm^{-1} ($\delta_{\text{Ir-H}}$). The proton NMR spectrum suggests a *cis* arrangement of the two hydride ligands. In addition to the phenyl and methylene protons, there is a 1:1 doublet, ($J_{\text{P-H}} = 113 \text{ c.p.s.}$) of 1:3:3:1 quartets ($J_{\text{P-H}} = 16 \text{ c.p.s.}$) centered at $\tau 21.6$. The interpretation of this spectrum is that the equivalent protons are split by one *trans*-phosphorus ($J_{\text{P-H}} = 113 \text{ c.p.s.}$) and three *cis*-phosphorus atoms ($J_{\text{P-H}} = 16 \text{ c.p.s.}$). These coupling constants are similar to those found in isomers of $\text{IrH}_n\text{Cl}_{3-n}(\text{CO})(\text{PPhEt}_2)_2$ where constants of $12\text{--}16 \text{ c.p.s.}$ are found for *cis*-phosphorus and between $80\text{--}150 \text{ c.p.s.}$ for *trans*-phosphorus (5). The appearance of only one $\nu_{\text{Ir-H}}$ is unusual for a *cis*- IrH_2 grouping. Sacco has in fact shown that the cobalt analog *cis*- $[\text{CoH}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^+$ has two bands at 1940 and 1985 cm^{-1} (40). However, it is possible that with the much heavier metal atom—iridium—the separation between symmetric and asymmetric stretching frequencies, which is expected to be smaller than for cobalt, has virtually vanished. The NMR evidence is definitely against a *trans* configuration.

Other physical measurements which support the assignments for the parent ion and its CO adduct include ultraviolet, ^{31}P NMR, and x-ray structure on the CO adduct.

In the ^{31}P NMR both $[\text{Ir}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^+$ and $[\text{Ir}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^+$ show single resonances at -50 and -25 p.p.m. with respect to H_3PO_4 . This suggests an equivalence of all the phosphorus atoms for both cations. This result differs from that found in the solid state (*see later*) and probably indicates rapid equilibration in solution. The electronic spectrum of the starting materials, $[\text{Ir}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^+$ and its CO adduct are given in Table III.

Table III. Electronic Spectra of Ir(I) Complexes

Compound	Bands in the Visible Region			
<i>trans</i> -IrCl(CO)(PPh ₃) ₂	440	388	340	275sh
<i>trans</i> -IrCl(CO)(PPh ₂ Et) ₂	436	385	334	265sh
<i>trans</i> -IrCl(CO)(PPhEt ₂) ₂	434	379	332	270sh
<i>trans</i> -IrBr(CO)(PPh ₃) ₂	445	392	344	280sh
$[\text{Ir}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{Cl}$	526	443	382	318
$[\text{Ir}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{BPh}_4$	no peaks in visible region			

All four-coordinate complexes have four *d-d* bands presumably arising from transitions from the largely non-bonding d_{z^2} , d_{xy} , d_{xz} , d_{yz} orbitals to the anti-bonding $d_{x^2-y^2}$ orbital. This technique may provide a general method for distinguishing between four and five coordination for Ir(I) complexes.

The preliminary results of an x-ray structural determination of $[\text{Ir}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{Cl}$ are given in Figure 3. The structure is unusual in that it is not like any known five-coordinate d^8 complex. It can be considered as a distorted form of either a trigonal bipyramid or a tetragonal pyramid.

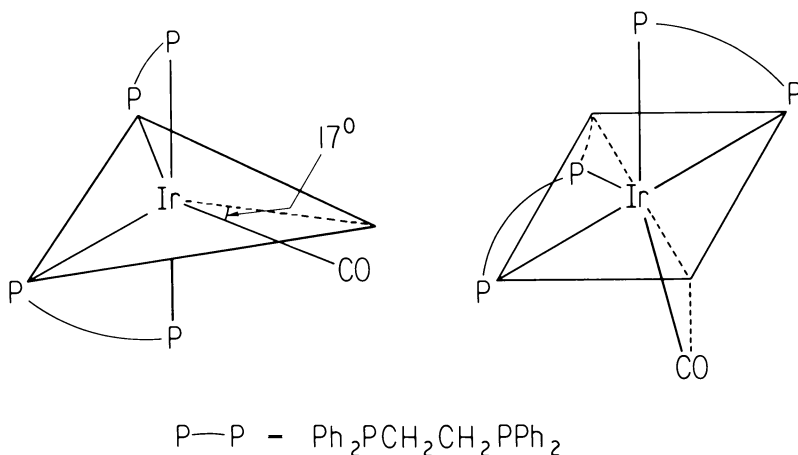


Figure 3. Structure of $[\text{Ir}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{Cl}$

In the former the unusual feature is that the CO ligand is unsymmetrically placed in the trigonal plane. Based on a distorted tetragonal pyramid the oddity is that CO and the *trans*-phosphorus are both 18–19° out of plane. This type of effect has already been mentioned for five-coordinate Pd(II) and Ni(II) complexes, but in these cases only one of the planar groups is bent out of the plane.

In this compound the nearest chlorine atom is at 9.6Å. There is, however, a hydrogen atom from one of the phenyl rings in the vicinity of the "hole" which may cause the asymmetry of CO in the trigonal structure. The full structural analysis will be published shortly. It is of course quite possible that there is a relationship between the unusual chemistry and the structure of this compound.

Ph₂PCH₂PPh₂. A different picture emerges when Ph₂PCH₂PPh₂ is used as the bidentate ligand. Reaction between this and *trans*-IrX(CO)-(PR₃)₂ at room temperature gives a CO adduct, [Ir(CO)(Ph₂PCH₂PPh₂)₂]X. The complexes with X = Br⁻, ClO₄⁻ have been characterized. The compounds are diamagnetic, 1:1 electrolytes, and have $\nu_c \approx 0$ in the infrared at 1924 cm.⁻¹. This suggests an Ir—C bond strength similar to that in the Ph₂PCH₂CH₂PPh₂ analog. Experiments at higher temperatures or passing nitrogen through a chloroform solution however have failed to yield the "parent" molecule. A red color has been observed in the higher temperature experiments but has not persisted in attempts to isolate a compound from such solutions. The CO adduct can be recovered from solutions which have had nitrogen bubbled through them. It appears then that the CO ligand is much less labile in this complex than in its Ph₂PCH₂CH₂PPh₂ analog. The reasons for this are not clear, and only an x-ray structure, which is in progress at the moment, may give some clues. Possibilities include a lower stability of the parent compound or a different stereochemistry caused by the smaller "span" of the Ph₂PCH₂PPh₂ ligand. What is clear is that a relatively small change in ligand has caused a large change in the stability of the complex.

Ph₂PCH₂CH₂SPh. Another effect is observed when Ph₂PCH₂CH₂SPh is used as the bidentate ligand. In the room-temperature reaction the isolated product is IrX(Ph₂PCH₂CH₂SPh)₂ where X = Br⁻. The small conductivity of a nitrobenzene solution suggests only partial ionization of the bromide, and the color and solubility characteristics are not like those of the ionic compounds [Ir(Ph₂PCH₂CH₂PPh₂)₂]X. It has proved impossible to prepare the CO adduct by reaction with CO, again suggesting that the parent may be a five-coordinate neutral molecule. In addition there is no reaction with H₂ at atmospheric pressure.

In summary it can be said that by slight variations in the chelate ligand we can vary the relative stabilities of IrX(chelate)₂ and

$\text{IrX}(\text{CO})(\text{chelate})_2$ from the former's being most stable, through an equilibrium system to the latter's being most stable.

Rh(I) Analogs. Some comparison with similar Rh(I) chemistry can be made. *trans*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ reacts with QAS at room temperature to give a CO adduct $[\text{Rh}(\text{CO})(\text{QAS})]\text{Cl}$ (33). If this reaction is carried out in boiling chlorobenzene, $\text{Rh}(\text{QAS})\text{Cl}$ is formed, but this compound is a nonelectrolyte and differs from $[\text{M}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{Cl}$ where $\text{M} = \text{Rh}$ and Ir , which are both 1:1 electrolytes. No report is made of the possibility of interconversion of $[\text{Rh}(\text{CO})\text{QAS}]\text{Cl}$ and $\text{Rh}(\text{QAS})\text{Cl}$ using methods mentioned earlier. $[\text{Rh}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{Cl}$ is the product of reaction of *trans*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ even in the presence of CO gas. Preliminary experiments with $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ show that the product contains only one chelate ligand per Rh atom. Thus, for both bidentate phosphines rhodium behaves differently from iridium. This difference is also found in reactions with H_2 when $[\text{Rh}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{X}$ does not give an adduct.

Hydrogenation Reactions

Some of the compounds which have been described were tested for activity as hydrogenation catalysts in homogeneous liquid phase experiments. Under the correct conditions activity is observed. These conditions are more vigorous than required for other Ir(I) complexes such as *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (49) and $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ (46) and for $\text{RhCl}(\text{PPh}_3)_3$ (22, 52). None of the systems involving Ir(I) and bidentate ligands shows appreciable activity at atmospheric pressure in refluxing mixtures of oct-1-ene and toluene. By comparison $[\text{Rh}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{Cl}$ shows small activity under these conditions. However, when the temperature and pressure are increased, typically to 150°–175°C. and 1200–1400 p.s.i.g. of H_2 both alk-1-yne and alk-1-ene can be hydrogenated.

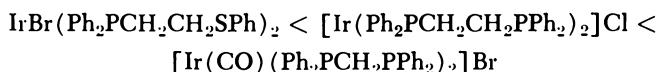
Table IV. Hydrogenation Experiments

Catalyst, mg.	Temp., °C.	C_6 Fraction, %			C_8 Fraction, %	
		hexane	hexene	hexyne	octane	octene
$[\text{Ir}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{Cl}$ (1.0)	175	16	36	48	20	80
$[\text{Ir}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2]\text{Cl}$ (1.0)	150	29	39	32	36	64
$\text{IrBr}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SPh})_2$ (0.5)	175	2	38	60	5	95

A standard experiment was done using glass-lined autoclaves containing a solution of hex-1-yne (10% by weight) and oct-1-ene (10% by weight). The catalyst was dissolved in a suitable solvent and added

to the substrate. The vessel was pressurized to 1200 p.s.i.g. with H_2 at $25^\circ C$. and then heated quickly to 150° or $175^\circ C$. The vessel was then agitated for one hour, followed by rapid cooling. The products were analyzed for hexane, hexene, octane, and unreacted starting material. The results are given in Table IV.

The turnover on catalyst is high, and 10^3 to 10^4 moles of substrate are hydrogenated per mole of catalyst. In all cases the hex-1-yne is hydrogenated faster than the oct-1-ene. The order of increasing activity is:



The results may be explained by assuming that the more stable the hydrogen adduct, the smaller the activity. Thus, $[Ir(Ph_2PCH_2CH_2PPh_2)_2]X$ adds H_2 irreversibly and is inactive under ambient conditions. The H_2 adducts of $RhCl(PPh_3)_3$ and $[Rh(Ph_2PCH_2CH_2PPh_2)_2]Cl$ have not been isolated as pure materials although for the former NMR peaks characteristics of Rh-H have been observed (52). Similarly the addition of H_2 to *trans*- $IrCl(CO)(PPh_3)_2$ is reversible (45). These three complexes are all catalysts for hydrogenations at atmospheric pressure.

Vaska has reported a comparative study of *trans*- $IrCl(CO)(PPh_3)_2$ and $IrH(CO)(PPh_3)_3$ as hydrogenation catalysts and shown that the latter is the more active (46). He ascribes this to the greater instability of the hydrogen adduct of $IrH(CO)(PPh_3)_3$ which is a seven-coordinate species compared with the relatively stable six coordination expected from the former. If, as suggested by chemical evidence, the CO ligand is difficult to remove, then the dihydride adduct of $[Ir(CO)(Ph_2PCH_2PPh_2)_2]X$ will be seven coordinate, and this catalyst will be more active than $[Ir(Ph_2PCH_2CH_2PPh_2)_2]X$, as is found. Finally, the activity observed for the latter at high, but not low temperatures is probably caused by the more ready removal of hydrogen under the more vigorous conditions.

Summary

This discussion has centered around the reaction of the hydrogen molecule, and little has been said concerning the alkyne or alkene. The detailed mechanism of catalysis by d^8 complexes is not fully understood. The question as to whether H_2 or substrate is coordinated first or even that both of them need to be coordinated simultaneously is still unanswered. Wilkinson has certainly shown that $RhCl(PPh_3)_3$ will react with H_2 to give Rh-H species which react subsequently with olefin to give the corresponding paraffin. From this study it is possible to rationalize the results by assuming that activity in catalysis is related to

the stability of the dihydride adducts of the catalyst. Nevertheless, many questions are still unanswered, and we are continuing our work to get further correlation between structure, chemical behavior, and catalytic activity of d^8 complexes, and a fuller insight into the detailed mechanism of the hydrogenation reaction. Some of the compounds mentioned have been reported independently in three recent papers (21, 39, 50).

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Catalytic Hydrogenation and Hydrogenolysis by Pentacyanocobaltate(II)

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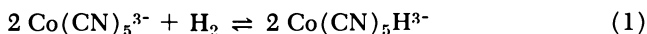
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Radical intermediates are indicated both in the hydrogenolysis of organic halides and in the hydrogenation of certain activated carbon-carbon double bonds catalyzed by $\text{Co}(\text{CN})_5^{3-}$. In both cases, formation of the reduced substrate occurs by hydrogen transfer from $\text{Co}(\text{CN})_5\text{H}^{3-}$ to the radical. In the absence of excess $\text{Co}(\text{CN})_5\text{H}^{3-}$ the radicals either disproportionate or form stable organocobalt complexes by reaction with $\text{Co}(\text{CN})_5^{3-}$. Addition of $\text{Co}(\text{CN})_5\text{H}^{3-}$ to other activated carbon-carbon double bonds results in the formation of stable organocobalt complexes, via a non-radical mechanism. Evidence is presented for the formation of N-amidocobalt complexes, $\text{RCONHC}(\text{CN})_5^{3-}$, from certain α -halo and α,β -unsaturated nitriles. The relationship of structure to the stability and catalytic activity of organocobalt complexes is discussed.

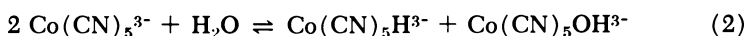
The pentacyanocobaltate(II) anion is a d^7 complex, one electron short of the electron configuration of krypton. Its solutions are paramagnetic with a moment corresponding to one unpaired electron. In a formal sense, the loss of an electron to give cobalt(III) allows a sixth ligand, with its pair of electrons, to coordinate with the metal, which thereby attains the inert configuration.

The high reactivity of this complex toward molecular hydrogen is basic to its function as a catalyst in the hydrogenation of various organic compounds (19, 20, 21). While some doubt remains concerning the detailed mechanism of this reaction (9, 10, 16), the net result is a reversible homolytic process in which hydrogen may be considered to be reduced to hydride, and cobalt(II) to be oxidized to cobalt(III) (Reaction 1). The reactive hydrido complex (the name used for $\text{Co}(\text{CN})_5\text{H}^{3-}$ through-

out this paper), thus formed, functions as an intermediate in homogeneous hydrogenation reactions, transferring the hydrogen to various organic substrates.

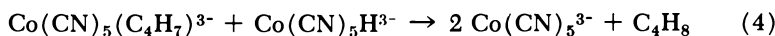
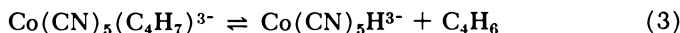


The hydrido complex may also arise from sources other than molecular hydrogen. The homolytic cleavage of water by pentacyanocobaltate (II) (9, 16) (Reaction 2) permits various substrates to be reduced stoichiometrically in the absence of molecular hydrogen (20).



Since this reaction is reversible (20, 24), hydrogenation systems which have become "poisoned" (hydrogen-active cobaltous species entirely converted to inactive cobaltic species) may be reactivated autocatalytically in the presence of molecular hydrogen (20, 22).

Organic groups may also provide hydrogen in forming the hydrido complex. Thus, the disproportionation of a butenylcobalt complex yielding an equimolar mixture of butenes and butadiene (21, 22) appears to involve the intermediate formation of hydrido complex (Reactions 3 and 4).



This paper evaluates the role of the hydrido complex in various carbon-carbon double bond hydrogenations and carbon-halogen bond hydrogenolyses, and the relationship between the two reaction types. Evidence for "free" radicals, as well as organocobalt complexes ("metal-complexed" radicals), as intermediates will be presented. The relationship of organocobalt complex stability to catalytic hydrogenation will also be discussed.

Experimental

The apparatus and procedures employed in the formation and reactions of $\text{K}_3\text{Co}(\text{CN})_5$ and $\text{K}_3\text{Co}(\text{CN})_5\text{H}$ solutions have been described (20, 22).

Alkyl Iodides with $\text{K}_3\text{Co}(\text{CN})_5$. $(\text{CH}_3)_2\text{CHI}$. Aqueous solutions of CoCl_2 (25 ml., 0.16M) and KCN (25 ml., 0.88M) were placed in the reaction flask and addition funnel, respectively. The system was successively evacuated and filled several times with nitrogen (Matheson, prepurified, 1 atm.). Following injection of the appropriate amount of isopropyl iodide into the flask, the cyanide solution was added with vigorous stirring. After 20 minutes, gas evolution was measured, and a gas sample was taken for vapor-phase chromatography (VPC) of propylene and propane. The results are indicated in Figure 1. The results of

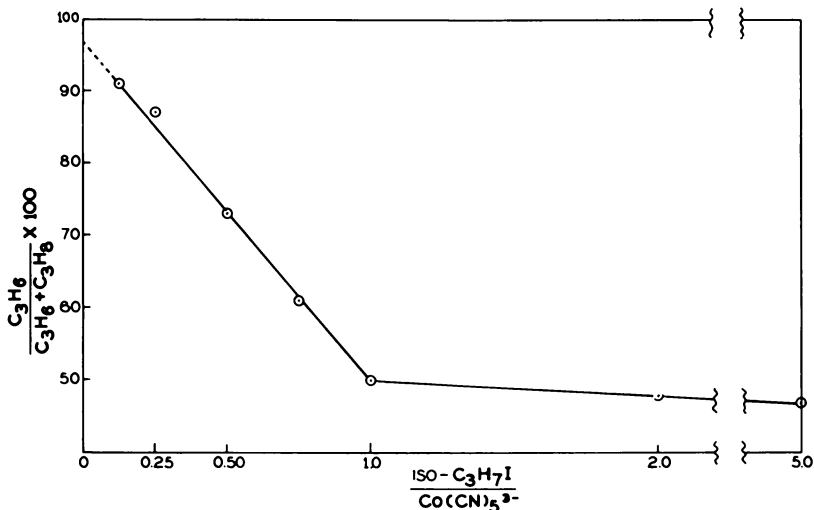


Figure 1. Relative percents of propylene formed at various ratios of isopropyl iodide to pentacyanocobaltate(II) (0.08M)

reactions carried out in the presence of acrylonitrile, injected before cyanide addition, are shown in Figures 2 and 3.

Reactions in the presence of the additives listed in Table I were carried out as shown in the following examples.

BUTADIENE. 100 ml. of 0.30M CoCl₂ and 100 ml. of 1.54M KCN in an atmosphere of butadiene were employed. Injection of isopropyl iodide was followed by cyanide addition with vigorous stirring. The solution turned red. On completion of gas evolution, a gas sample was taken for analysis. It showed the presence of 19.2% propane, 33.9% propylene, 1.00% 1-butene, 1.81% *trans*-2-butene, 0.14% *cis*-2-butene; the remainder was butadiene. The mass spectrum showed no C₇ product.

METHYL METHACRYLATE. Isopropyl iodide (0.03 mole) and methyl methacrylate (0.14 mole) were injected into 100 ml. of 0.30M CoCl₂ solution, and 100 ml. of 1.54M KCN were added with stirring under a nitrogen atmosphere. At the completion of the slow gas evolution, the solution was brown-red. The gas contained 4.72% propane and 27.1% propylene. Separation of an ether extract of the reaction mixture by preparative VPC followed by mass spectral analysis identified the components as unreacted methyl methacrylate, methyl isobutyrate, isopropyl adducts (parent masses 142 and 144) and isopropyl adduct dimers (parent masses 282, 282, and 284).

METHACRYLONITRILE. A similar reaction in which methacrylonitrile (0.13 mole) was present instead of methyl methacrylate yielded gas containing 0.22% propane and 28.73% propylene. The upper layer which formed on adding the aqueous solution to 1 liter acetone was decanted. Adding ethanol to the oily bottom layer precipitated a solid which was collected on a sintered glass filter, washed with ethanol and ether, and air dried. The infrared spectrum of the reddish solid exhibited cyanide

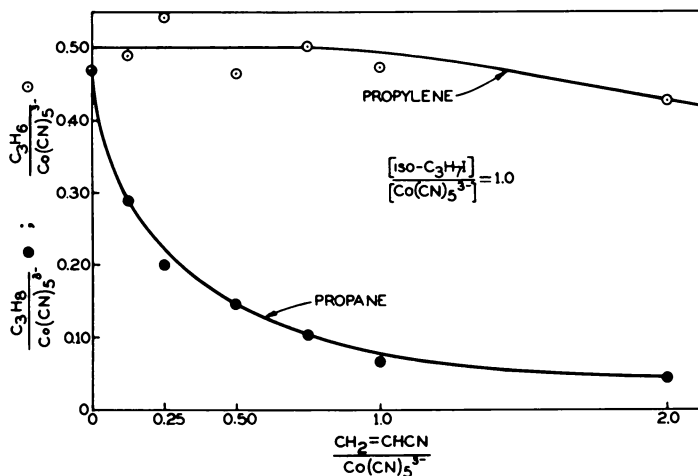


Figure 2. The effect of acrylonitrile on propylene and propane yields from isopropyl iodide and pentacyanocobaltate(II) (0.08M)

absorption bands at 2191, 2125, 2102, and 2084 cm^{-1} , indicating the presence of 1-cyanoisopropyl (2191, 2102 cm^{-1}), iodo (2125 cm^{-1}) and isopropyl (2084 cm^{-1}) complexes (cf. 22). Pyrolysis yielded propylene and propane (7.5:1), as well as methacrylonitrile, isobutyronitrile, and butyronitrile. The solid isolated from a similar reaction carried out in the absence of methacrylonitrile displayed cyanide absorption bands at 2125 and 2084 cm^{-1} . Protonation followed by alkali treatment (23) yielded isobutyronitrile, indicating the presence of $\text{K}_3\text{Co}(\text{CN})_5\text{CH}(\text{CH}_3)_2$ in the solid product.

$(\text{CH}_3)_3\text{CCH}_2\text{I}$. An aqueous solution of $\text{K}_3\text{Co}(\text{CN})_5$ (200 ml., 0.25M cobalt, 0.15M KOH, $\text{CN}/\text{Co} = 6$) was prepared in a nitrogen atmosphere. Neopentyl iodide (0.03 mole), prepared (59) from neopentyl chloride, was injected immediately before cyanide addition with vigorous stirring. After 4 hours, the tan solid reaction product was isolated as described above. The proton magnetic resonance (PMR) spectrum of a solution in deuterium oxide indicated the presence of the neopentyl group. The infrared spectrum exhibited CH stretch bands at 2967, 2915, and 2890 cm^{-1} , a CH deformation doublet at 1385 and 1359 cm^{-1} , and CN stretch bands at 2125 and 2084 cm^{-1} . Acidification followed by alkali treatment yielded neopentyl cyanide (MS).

$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{CH}_2\text{I}$. Neophyl iodide, prepared (59) from neophyl chloride (58) reacted with $\text{K}_3\text{Co}(\text{CN})_5$ in the same way, except that 12 ml. of benzene were added to disperse the halide, and reaction time was 20 hours. The infrared spectrum of the light brown solid product isolated exhibited CN stretch bands at 2125 and 2089 cm^{-1} . Acidification followed by alkali treatment yielded neophyl cyanide (infrared and PMR analysis).

Alkyl Iodides with $\text{K}_3\text{Co}(\text{CN})_5\text{H}$. An aqueous solution of $\text{K}_3\text{Co}(\text{CN})_5$ (200 ml., 0.15M cobalt, 0.15M KOH, $\text{CN}/\text{Co} = 5.1$) was prepared in a

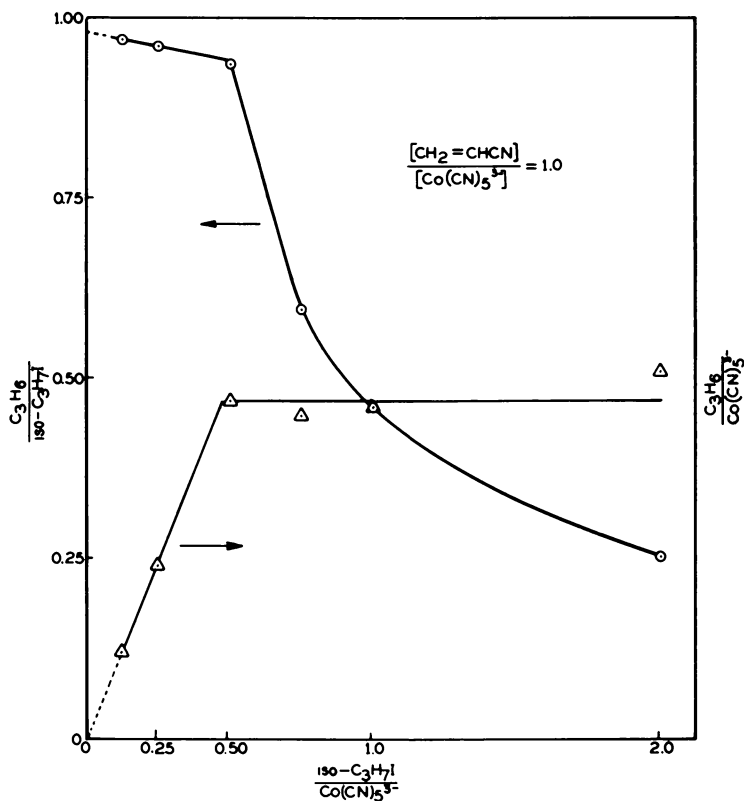


Figure 3. Amounts of propylene formed at various ratios of isopropyl iodide to pentacyanocobaltate(II) (0.08M) in the presence of acrylonitrile

Table I. Effect of Additives on Relative Amounts of Propylene and Propane Formed from Equimolar Quantities of Isopropyl Iodide and Pentacyanocobaltate (II)

Additive	Additive/ $\text{Co}(\text{CN})_5^{3-}$	Relative Amts.	
		C_3H_6	C_3H_8
	—	50	50
α -Methylstyrene	3.9	54	46
Sodium Methacrylate	5.3	65	35
Butadiene	(Atmosphere)	64	36
Methyl Methacrylate	4.7	85	15
Acrylonitrile	4.0	96	4
Methacrylonitrile	4.4	99	1
α -Phenylacrylonitrile	3.3	100	(Trace)

hydrogen atmosphere, approximately 300 ml. hydrogen being absorbed. A total of 0.024 mole methyl iodide was injected in three 0.008-mole increments. Each addition resulted in the evolution of approximately 80 ml. gas, and the reaction mixture turned red. On continued stirring, an equivalent amount of gas was absorbed, and the reaction mixture returned to its original green color. Analysis of the gas indicated a 30% yield of methane (no ethane or ethylene was formed). The remaining methyl group was present as the methylcobalt complex (22). Similar reductions of ethyl, propyl, isopropyl, and *tert*-butyl iodides gave nearly quantitative yields of hydrocarbon, consisting of the corresponding alkanes (70–90%) and alkenes (10–30%).

1-Bromo-2,2-diphenylcyclopropane Carboxylic Acid (53). A solution of 8 grams (0.025 mole) of the subject acid, $[\alpha] +103^\circ$ (pure isomer reported $+112^\circ$), in 100 ml. aqueous KOH (0.3M) was added to a 0.15M solution of $K_3Co(CN)_5H$ containing KOH (0.075M) in three portions over a period of 40 minutes. A total of 518 ml. hydrogen was absorbed. The reaction mixture was acidified (under the hood!) with dilute hydrochloric acid, extracted with ether, and the ether extract was dried over anhydrous magnesium sulfate. Evaporation left crystalline 2,2-diphenylcyclopropane carboxylic acid, $[\alpha] 0^\circ$ (pure isomer reported $+212^\circ$) (54). A repeat run employing 0.016 mole of the α -bromo acid, $[\alpha] -58^\circ$, resulted in the absorption of 340 ml. hydrogen and yielded 0.0124 mole acid, $[\alpha] +1^\circ$.

A solution of 4.76 grams of 2,2-diphenylcyclopropane carboxylic acid, $[\alpha] -128^\circ$, in 40 ml. 0.75M KOH was added to a 0.15M solution of $K_3Co(CN)_5H$ in four portions over a period of 30 minutes. After an additional reaction time of 45 minutes, 90% of the acid, $[\alpha] -115^\circ$, was recovered. Optically active 1-bromo- and 1-iodo-1-methyl-2,2-diphenylcyclopropanes (55) could not be reduced.

Methylallyl Chlorides with $K_3Co(CN)_5$. An aqueous solution of $K_3Co(CN)_5$ (200 ml., 0.15M cobalt, 0.35M KOH) was prepared in a nitrogen atmosphere. Addition of γ -methylallyl chloride (0.06 mole) (Aldrich, b.p. $84^\circ C.$, $n_D^{25} = 1.4311$) resulted in the evolution of 219 ml. gas, a sample of which was taken for analysis. Similar reactions of this substrate and of α -methylallyl chloride (Columbia, b.p. $65^\circ C.$, $n_D^{25} = 1.4123$) carried out at cyanide to cobalt ratios of 5.1 and 7.0 resulted in the formation of butenes, whose isomer distributions are listed in Tables II and III under "deficient CoH."

Methylallyl Chlorides with $K_3Co(CN)_5H$. An aqueous solution of $K_3Co(CN)_5$ (200 ml., 0.15M cobalt, 0.15M KOH) was prepared in a hydrogen atmosphere, 300 ml. hydrogen being absorbed. A total of 0.0144 mole γ -methylallyl chloride was injected in 0.004-mole increments. Each addition resulted in the rapid evolution of approximately 50 ml. gas, followed by a slow absorption of about 40 ml. gas. A gas sample was taken for analysis. Similar reductions of this substrate and of α -methylallyl chloride carried out at cyanide to cobalt ratios of 5.1 and 7.0 resulted in the formation of the isomeric butenes listed in Tables II and III under "excess CoH."

Dienes with $K_3Co(CN)_5$. An aqueous solution of $K_3Co(CN)_5$ (200 ml., 0.15M cobalt) was prepared in a butadiene atmosphere. The solution was stirred until absorption of butadiene was complete, when a gas

Table II. Effect of Hydrido Complex Concentration on Products of the Reduction of Butadiene and Butenyl Chlorides at a Cyanide to Cobalt Ratio of 5.1







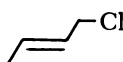






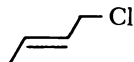
Substrate	Excess CoH	Defic. CoH				
	X		6	14	80	—
		X	2	15	83	—
	X		3	54	43	—
		X	2	17	81	112
	X		1	43	56	—
		X	2	16	82	114

Table III. Effect of Hydrido Complex Concentration on Products of the Reduction of Butadiene and Butenyl Chlorides at a Cyanide to Cobalt Ratio of 7.0




Substrate	Excess CoH	Defic. CoH				
	X		2	92	6	—
		X	4	89	7	—
	X		2	90	8	—
		X	2	90	8	86
	X		1	88	11	—
		X	3	87	10	89

sample was taken. The isomeric butenes formed at cyanide to cobalt ratios of 5.1 and 7.0 are listed in Tables II and III under "deficient CoH." The reductions of isoprene and 1,3-pentadiene, reported in Tables IV and V, respectively, were carried out in a similar manner except that a nitrogen atmosphere was employed, 0.05 mole substrate was injected, the reaction mixture was stirred for several hours, and liquid reaction products were analyzed by VPC.

Dienes with $K_3Co(CN)_5H$. An aqueous solution of $K_3Co(CN)_5$ (200 ml., 0.15M cobalt) was prepared in a hydrogen atmosphere, 260 ml. hydrogen being absorbed. A total of 35 ml. gaseous butadiene was injected in 5-ml. increments with a gas syringe. The isomeric butenes formed at cyanide to cobalt ratios of 5.1 and 7.0 are listed in Tables II and III under "excess CoH."

Reductions of norbornadiene were carried out at cyanide to cobalt ratios of 5.1 and 7.0 in a similar manner except that 0.02 mole substrate

Table IV. Effect of Cyanide Concentration on Products of the Hydrogenation of Isoprene

CN/Co			
5	21	1	78
7	91	6	3

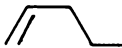
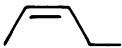
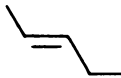
was injected in two increments. The reaction mixtures were extracted with ether, yielding liquids containing norbornene and nortricyclene (1:13) (VPC). The infrared spectrum of the latter component showed a characteristic absorption band at 802 cm^{-1} (38).

α -Halonitriles with $\text{K}_3\text{Co}(\text{CN})_5$. An aqueous solution of $\text{K}_3\text{Co}(\text{CN})_5$ (200 ml., 0.15M cobalt, 0.15M KOH, CN/Co = 5.1) was prepared in a nitrogen atmosphere. Twenty minutes after 0.03 mole 2-bromopropionitrile was injected, the red reaction mixture was filtered into 1 liter of acetone. The aqueous upper layer was decanted, and ethanol was added to the oily lower layer. The light pink solid which precipitated was removed by filtration, washed with ethanol and ether, and finally dried in air. It exhibited cyanide absorption bands at 2200, 2125, and 2100 cm^{-1} ; its PMR spectrum corresponded with that of the acrylonitrile- $\text{K}_3\text{Co}(\text{CN})_5\text{H}$ adduct (22).

The results obtained with other α -halonitriles are indicated in Table VII. With the exception of chlorodiphenylacetonitrile, PMR spectra of the resulting complexes indicated attachment of the cobalt atom alpha to the nitrile group. In the case of chlorodiphenylacetonitrile (in 25 ml. benzene), the benzene layer was separated from the yellow-aqueous layer after 1 hour reaction time. Adding ethanol to the benzene solution yielded tetraphenylsuccinonitrile, m.p. $203\text{--}4^\circ\text{C}$. (acetic acid) (205°C . reported) (49). The aqueous layer was worked up in the usual manner to obtain a white solid, exhibiting a single cyanide absorption band at 2130 cm^{-1} and a carbonyl absorption at 1575 cm^{-1} . The PMR spectrum showed aromatic and aliphatic protons in the ratio 10:1.

A solution of the complex in water was heated to boiling and cooled. The crystals which formed were collected by filtration, washed with water, and dried. The product was identified as diphenylacetamide by infrared spectroscopy and melting point (171°C .). A complex formed by the reaction of *N*-bromodiphenylacetamide (m.p. $148\text{--}50^\circ\text{C}$., prepared

Table V. Effect of Cyanide Concentration on Products of the Hydrogenation of 1,3-Pentadiene

CN/Co			
5	2	0	98
7	21	12	67

from the amide and KOB_r) with K₃Co(CN)₅ gave the same result on heating its aqueous solution.

α-Halonitriles with K₃Co(CN)₅H. Various α-halonitriles were added in small increments to aqueous solutions of K₃Co(CN)₅H containing excess KOH in a hydrogen atmosphere with the following results (0.03 mole cobalt present):

Substrate	Total Amt. Added, Moles	Total H ₂ Absorbed, Moles
CH ₂ ClCN	0.032	0.006
CH ₃ CHBrCN	0.057	0.035
(CH ₃) ₂ ClCN	0.061	0.044
C ₆ H ₅ CHBrCN	0.040	0.017

Isobutyronitrile was recovered from the reaction with α-iodoisobutyronitrile. Complexes isolated from the reaction mixtures were identical (infrared) to those obtained on reaction of the substrates with K₃Co(CN)₅.

α,β-Unsaturated Nitriles with K₃Co(CN)₅H. EXCESS NITRILE. Aqueous solutions of CoCl₂ (100 ml., 0.30M) and KCN (100 ml., 1.54M) were placed in the reaction flask and addition funnel, respectively. After purging the system with hydrogen, excess acrylonitrile (0.06 mole) was injected followed by addition of the cyanide solution with good stirring. A total of 306 ml. hydrogen was absorbed. The adduct formed was isolated in the usual manner. Its properties have been reported previously (22). A similar run with methacrylonitrile resulted in the absorption of 320 ml. hydrogen. The complex isolated exhibited cyanide absorption bands at 2190 and 2100 cm.⁻¹; its PMR spectrum indicated the presence of the (CH₃)₂C grouping.

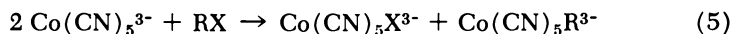
α-Phenylacrylonitrile (34) addition in a similar manner resulted in absorption of 280 ml. hydrogen. The adduct formed exhibited only a single cyanide absorption at 2130 cm.⁻¹, as well as a band at 1575 cm.⁻¹. α-Phenylpropionamide, m.p. 93-4°C., was formed on heating an aqueous solution of the complex. It was identified further by conversion to the anilide, m.p. 134-5°C., *via* the acid and acid chloride. Addition of α-ethoxyacrylonitrile (39) in a similar manner resulted in the absorption of 292 ml. hydrogen and formation of an adduct exhibiting a single cyanide absorption band at 2130 cm.⁻¹, as well as a band at 1600 cm.⁻¹. Its PMR spectrum indicated the C₂H₅OCHCH₃ grouping. Acidification of an aqueous solution of the complex, followed by neutralization and ether extraction, yielded α-ethoxypropionamide, m.p. 66-7.5°C. (hexane) (61-3°C. reported) (30).

EXCESS K₃Co(CN)₅H. α-Phenylacrylonitrile (0.045 mole) added to a solution of K₃Co(CN)₅H in a hydrogen atmosphere in 0.0075-mole increments, resulted in the absorption of 418 ml. hydrogen. Extraction of the reaction mixture yielded α-phenylpropionitrile, b.p. 56-8°C./0.55 mm. A similar run with α-ethoxyacrylonitrile (0.03 mole) resulted in the absorption of 235 ml. hydrogen and the formation of α-ethoxypropionitrile, b.p. 123°C., *n*_D²⁸ = 1.3850, parent mass at 99. Hydrolysis of the latter nitrile yielded α-ethoxypropionamide, m.p. 62-4°C. (hexane), mixed m.p. with the amide obtained from the amidocobalt complex, 64-6°C. The incremental addition of phenylcyanomethylenequinone oxime (8)

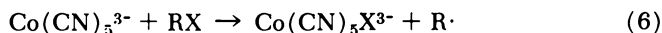
(0.03 mole in aqueous KOH) to $K_3Co(CN)_5H$ in a hydrogen atmosphere resulted in the absorption of 950 ml. hydrogen. The complex isolated from a portion of the reaction mixture exhibited a single cyanide absorption band at 2130 cm.^{-1} ; additional bands were observed at 1580 and 1515 cm.^{-1} . The bulk of the reaction mixture was acidified and heated to reflux. After cooling and making the solution basic, a solid (m.p. $80\text{--}4^\circ\text{C.}$) primary amide (infrared) was obtained. Hydrolysis with alcoholic KOH yielded *p*-aminodiphenylacetic acid, m.p. $174\text{--}7^\circ\text{C.}$ (benzene-petroleum ether) [$175\text{--}7^\circ\text{C.}$ reported (6)].

Results and Discussion

Alkyl Halides. REACTION WITH $Co(CN)_5^{3-}$. Many σ -bonded organopentacyanocobaltate(III) complexes have been prepared recently by the reaction of organic halides with pentacyanocobaltate(II) (13, 14, 21, 22) (Reaction 5). The second-order kinetics observed for this reaction (14)



supports the proposed stepwise mechanism (22) involving generation of a radical in the rate-determining step (Reaction 6), followed by reaction of the radical with pentacyanocobaltate(II) (Reaction 7). A radical intermediate is consistent with the observed dependence of the rate



constant on variation of the organic halide (14) and the formation of dimers from resonance-stabilized organic groups (22). Trapping experiments (Reaction 8) give more conclusive evidence for the formation of radicals (22).

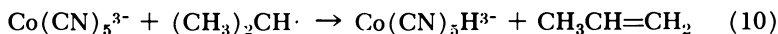
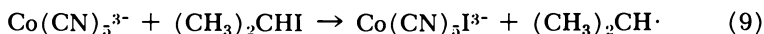


Primary alkyl iodides formed stable organocobalt complexes in good yield, accompanied by minor quantities of the corresponding alkane and alkene. Isopropyl and *tert*-butyl iodides yielded mainly mixtures of alkenes and alkanes.

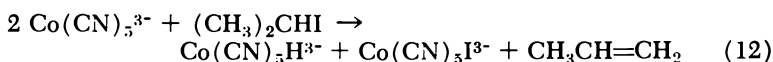
ISOPROPYL IODIDE. *General Considerations.* The reaction with isopropyl iodide afforded the opportunity of investigating the fate of an intermediate which was not trapped as a stable organocobalt complex. The results obtained when various quantities of this halide reacted with a given quantity of pentacyanocobaltate(II) are shown in Figure 1. Up to a halide to cobalt ratio of 1.0, yields of total gases based on halide were practically quantitative; at ratios greater than 1.0, yields of gas based on cobalt were nearly quantitative. Essentially equimolar quantities of propylene and propane were formed at halide to cobalt ratios of 1.0 or more; the relative quantity of propylene formed gradually increased as

the ratio was lowered, approaching nearly 100% on extrapolating to zero ratio.

These observations may be interpreted as being derived from a pentacyanocobaltate(II)-catalyzed disproportionation of an isopropyl radical intermediate (Radical Mechanism I) (Reactions 9-11).

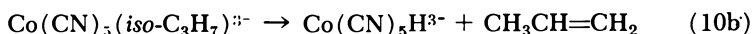


An alternate concerted-elimination mechanism (II) in which radical formation is absent may also be projected (Reactions 12-13).



A combination mechanism (III) in which propylene is formed from the radical (Reactions 9-10), but propane is formed by hydride-halide exchange (Reaction 13) is also possible.

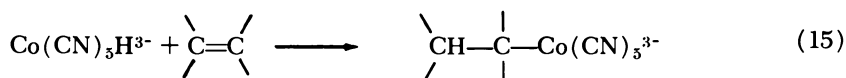
Furthermore, formation of an unstable isopropylcobalt complex intermediate in the dehydrogenation step (Reaction 10) cannot be ruled out since evidence for the formation of small quantities of such a complex has been obtained in these reactions (acid-base treatment (23) yields isobutyronitrile). This type of disproportionation resembles that



observed with a butenylcobalt complex (Reactions 3-4) and the organocobalt complex formed by addition of hydrido complex to methyl methacrylate (24).

If Mechanism I is valid, it should be possible to change the course of the reaction by adding reagents which interact with either of the two reactive intermediates indicated—*i.e.*, the isopropyl radical or the hydrido complex.

The addition of hydrido complex-scavenging reagents would be expected either to reduce the reagent (19, 20) (Reaction 14) or to form a stable organocobalt complex (22) (Reaction 15), depending on the re-



agent used. At the same time, reducible additives should act as "hydrogen sinks," lowering the amount of propane formed relative to propylene. Additives forming stable organocobalt complexes would, in addition, be expected to change the stoichiometry of the reaction since part of the pentacyanocobaltate(II) would become unavailable for further reaction with halide.

Adding radical-trapping reagents should have no peculiar effect on the relative proportions of propylene and propane formed. However, the yield of C₃ hydrocarbons would be expected to drop as isopropyl adducts of the reagent appear in their place (Reaction 8).

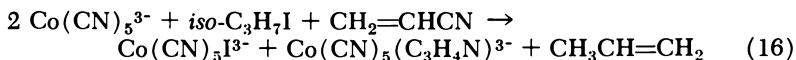
The effects discussed unfortunately are not mutually exclusive since the reagents used as hydrido complex scavengers also trap radicals. Nevertheless, the results obtained by using these additives help to establish the isopropyl radical and hydrido complex as intermediates in the reaction.

Hydrido Complex Intermediate. The influence of various additives on the relative proportions of propylene and propane formed in the reaction of isopropyl iodide with pentacyanocobaltate(II) is shown in Table I. The relative amounts of propane formed in the presence of the additives were lowered in all cases. While the amounts of additive used were not identical (nor were all the additives soluble in water), hydrido complex-scavenging efficiency and stability of the hydrido complex adduct may be roughly compared. Additives which were reduced (these include the first four shown in the table, of which only butadiene and methyl methacrylate yielded isolable though unstable adducts) had the smallest effect, while those forming stable adducts (the acrylonitriles) had the largest effect. Thus, butenes were formed from butadiene (the 6% found accounted for the 14% relative decrease in propane formation observed, butene formation requiring two moles of hydrido complex, propane formation requiring one), and isobutyrate was formed from methacrylate salt and ester. Infrared spectra of the complexes isolated from the reactions containing acrylonitriles were practically identical with those of the corresponding hydrido complex acrylonitrile adducts.

The influence of an additive, which forms a stable organocobalt complex, on the stoichiometry of the reaction was investigated by performing the reaction in the presence of various quantities of acrylonitrile (Figure 2). Up to a nitrile to cobalt ratio of 1.0, the yield of propylene remained constant as that of propane gradually dropped, presumably because of hydrido complex scavenging. At ratios greater than 1.0, the slight drop in both propylene and propane may reflect isopropyl radical trapping.

The results obtained on reaction of various quantities of halide with a given quantity of pentacyanocobaltate(II) and acrylonitrile (fixed ratio 1:1) are more instructive (Figure 3). Up to a halide to cobalt ratio of 0.5, yields of propylene based on halide were practically quantitative.

Above a ratio of 0.5, the yield of propylene dropped rapidly. Yields based on cobalt were approximately 50% at ratios of 0.5 and higher. This behavior approaches that expected for stable organocobalt complex formation in accordance with the following over-all equation:



Small quantities of propane formed are a measure of the hydrido complex not scavenged and account rather well for the deviation from expected behavior.

Radical Intermediate. Small quantities of isopropylacrylonitrile adducts have been isolated from reactions carried out in the presence of excess acrylonitrile (22). Similar adducts were isolated from the reaction in which methyl methacrylate was an additive (Table I). Their structures, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{CH}_3)\text{COOCH}_3$ and $(\text{CH}_3)_2\text{CHCH}=\text{C}(\text{CH}_3)\text{COOCH}_3$, were established by mass spectroscopy. In addition, three adducts with molecular weights approximately twice those of the structures shown (282, 282, 284) were found. These observations strongly support an isopropyl radical intermediate (Mechanism I or III).

NEOPENTYL AND NEOPHYL IODIDES. The halides mentioned above formed the corresponding organocobalt complexes on reaction with pentacyanocobaltate(II). While neopentyl radical is stable to rearrangement, the neophyl radical undergoes aryl migration (56) as follows:



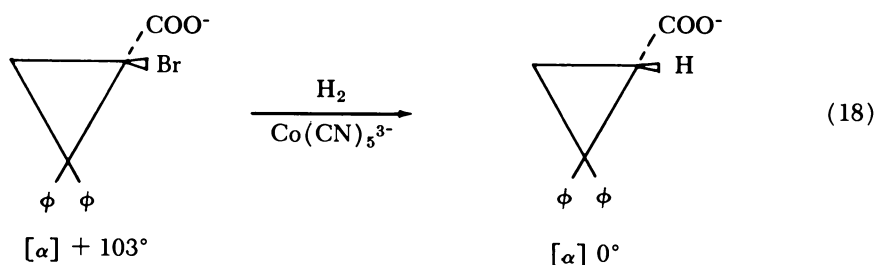
Hence, the rate of rearrangement of the neophyl radical, if such is indeed produced, is considerably slower than its reaction with pentacyanocobaltate(II). Similarly, neophyl magnesium chloride may be prepared in the usual manner (58), although the Grignard reaction is considered to involve a radical intermediate (36, 52, 62).

REACTION WITH $\text{Co}(\text{CN})_5\text{H}^{3-}$. *General Considerations.* Except for methyl iodide, primary, secondary, and tertiary alkyl iodides formed the corresponding alkanes, accompanied by minor quantities of alkenes, in good yield when added to well-stirred solutions of hydrido complex in a hydrogen atmosphere. Only about 35% of methyl iodide was converted to methane, the remainder forming the stable methylcobalt complex. This apparent preferential competition by pentacyanocobaltate(II) for the methyl radical has been used to prepare the methylcobalt complex (22).

The reaction of organic halides with hydrido complex is less readily analyzed than the reaction with pentacyanocobaltate(II) since the two complex species are in equilibrium in a hydrogen atmosphere (Reaction 1). The question of whether alkanes are formed *via* hydride reduction of a radical (Reaction 11, Mechanism I) or *via* hydride-halide exchange (Reaction 13, Mechanism III) must be determined indirectly.

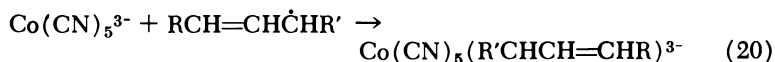
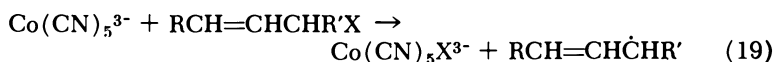
The formation of organocobalt complexes as intermediates can be ruled out for the primary iodides at least since such complexes are stable to cleavage by hydrido complex (22).

Racemization. Optically active 1-bromo-1-methyl-2,2-diphenylcyclopropane, 1-iodo-1-methyl-2,2-diphenylcyclopropane, and 1-bromo-2,2-diphenylcyclopropane carboxylic acid were prepared to study the mechanism of alkane formation by hydrido complex. While the first two substrates could not be reduced, the α -bromo acid absorbed 87 mole % of hydrogen, being converted into optically inactive acid (Reaction 18). A sample of the optically active acid retained its configuration under reaction conditions, indicating that a symmetrical intermediate was formed at some stage of the reduction.



Since racemization is consistent with a cyclopropyl radical intermediate (52), it is supporting evidence for formation of the reduced acid *via* hydrido complex reduction of a radical (Mechanism I). Configuration retention has been observed previously in the catalytic hydrogenolysis of an optically active α -chloro acid by palladium (35). The small percentage of retention observed in the Grignard reaction of 1-bromo-1-methyl-2,2-diphenylcyclopropane has been ascribed to the fact that this is a surface reaction (52). The intermediate formation of carbon to metal-bonded species in heterogeneous hydrogenolyses characterized by configuration retention has been discussed (15).

Allylic Systems. ALLYLIC HALIDES. Allylic halides also undergo homolytic carbon-halogen cleavage by pentacyanocobaltate(II) to form equimolar quantities of halo- and allylcobalt complexes (21, 22, 23). It is assumed that this reaction involves generation of the allylic radical (Reaction 19), which then reacts with pentacyanocobaltate(II) (Reaction 20).



Unlike their saturated counterparts, allylcobalt complexes are readily cleaved by hydrido complex or acids to yield mono-olefins.

While the parent allylcobalt complex ($R = R' = H$) was stable in an aqueous alkaline solution, the butenylcobalt complex ($R = CH_3$, $R' = H$) gradually evolved an approximately equimolar mixture of butenes and butadiene, suggesting a disproportionation involving the intermediate formation of hydrido complex (Reactions 3 and 4) (20, 22). Since apparently the same butenylcobalt complex is formed by adding hydrido complex to butadiene, the reduction of allylic halides is discussed with the intimately related hydrogenation of dienes later in the text.

CONJUGATED DIENES. General Observations. The catalytic hydrogenation of conjugated dienes by pentacyanocobaltate(II) is completely selective, yielding only monoolefin, which cannot be reduced further (19, 20, 21). Lack of reduction of 2,5-dimethyl-2,4-hexadiene indicates that dienes in which the *s-cis* conformation is sterically hindered might not be catalytically hydrogenated (21). However, reduction of 3-methylene cyclohexene, a diene with a fixed *s-trans* conformation, disproves this and indicates that other steric factors are probably involved (24).

Butadiene. Using butadiene as the model substrate, it has been found that the catalytic hydrogenation of dienes occurs in three steps: (1) reversible addition of hydrido complex to butadiene to form a butenylcobalt complex (Reaction 3); (2) cleavage of the butenylcobalt complex by hydrido complex to form butenes and pentacyanocobaltate(II) (Reaction 4); and (3) hydrogen absorption by pentacyanocobaltate(II) to reform hydrido complex (Reaction 1) (20, 21). The butenylcobalt complex has the same properties as the complex obtained *via* reaction of γ -methylallyl bromide with pentacyanocobaltate(II) (21, 22).

STERESELECTIVITIES. Since butenes were obtained by reducing allylic butenyl chlorides as well as butadiene, stereoselectivities of these substrates were studied.

Table II indicates the isomer distribution of the butene product obtained at a cyanide to cobalt ratio of 5.1 under two reaction conditions. The upper set of figures for each substrate refers to the product distribution obtained in the presence of excess hydrido complex. The lower set of figures refers to results obtained with pentacyanocobaltate(II) in an inert atmosphere. Under such conditions, hydrido complex is formed *via* cleavage of water (Reaction 2).

The following observations may be made. With butadiene, butene isomer distributions were nearly identical (except for *cis/trans* ratios) for the two reaction conditions. With the butenyl chlorides, the major butene isomers formed in the presence of excess hydrido complex reflect the structures of the respective substrates, 1-butene being formed from 3-chlorobutene-1, and *trans*-2-butene being formed from 1-chlorobutene-2.

With deficient hydrido complex, the chlorides gave the same product distribution as that obtained from butadiene. The formation of approximately equimolar quantities of butadiene under the latter reaction conditions indicates the intermediate formation of butenyl complexes, which decompose, forming equimolar quantities of butenes and butadiene. Thus, except for halide reduction by excess hydrido complex, it seems the reactions take place *via* a common butenylcobalt complex.

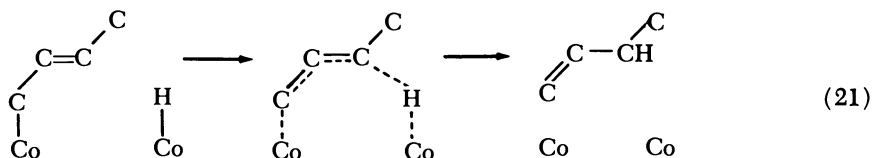
Table III shows the butene isomer distributions obtained when the same reactions were carried out in the presence of excess cyanide.

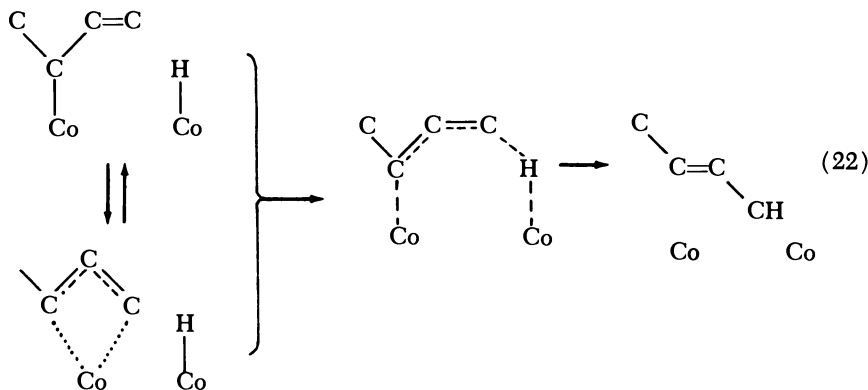
Nearly identical results were obtained for all substrates under both reaction conditions. The formation of approximately equimolar quantities of butadiene and butenes again indicates the intermediate formation of butenylcobalt complexes. While the predominant product at a cyanide to cobalt ratio of 5.1 was *trans*-2-butene, at a ratio of 7, the formation of 1-butene is favored.

Since the butenylcobalt complex was too unstable, the PMR spectrum of the allylcobalt complex was studied (21, 22) to obtain information on the structure of the organocobalt intermediates in these stereoselective reductions (20). This investigation indicated that σ -bonded allylic complexes are in equilibrium with π -allylic complexes and cyanide ion, thus providing a rationale for the stereoselectivities observed in the reduction of butadiene and butenyl chlorides.

Presumably, in the presence of excess cyanide ion only σ -bonded butenylcobalt complexes are present. These may equilibrate rapidly *via* intimate-ion or radical-pair transitions. The primary *trans*- σ -complex would be expected to be the most stable species and thus would be enriched in such an equilibrium. At low cyanide concentrations, the various σ -bonded species may be in equilibrium with two π -allylic isomers. Of these, the *syn* isomer is expected to be the most stable by analogy with the corresponding cobalt tricarbonyls.

These assumptions lead to the major products actually observed if the product-forming step involves γ -attack by hydrido complex on the allylic group. At a high cyanide concentration, such an attack would produce 1-butene (Reaction 21), while at low cyanide concentration, *trans*-2-butene would be formed (Reaction 22).








Work with other dienes, such as isoprene and pentadiene-1,3, indicates that coordination control of stereoselectivity by cyanide ion is rather general (Tables IV and V). On the other hand, the reduction of the homoconjugated norbornadiene results in the same distribution of products (7% norbornene, 93% nortricyclene) at both high and low cyanide concentrations. Presumably, a π -homoallylic complex (21) is not involved in this case.

BUTENYL RADICALS. Walling and Thaler have shown that the "free" butenyl radicals formed in chlorinating butenes by *tert*-butyl hypochlorite are configurationally stable (57); *cis*-2-butene yielded no *trans*-2-butenyl chloride, and *trans*-2-butene yielded no *cis*-2-butenyl chloride. Thus, hydrogen transfer from hydrido complex to butenyl radicals may account for the partial retention of structure observed in the reduction of butenyl chlorides (Table II). Menapace and Kuivila likewise postulate the formation of such radicals as intermediates in the reduction of the isomeric chlorides with triphenyltin hydride (26).

Castro and Kray have reduced the isomeric butenyl chlorides, using chromous sulfate (5). Again, allylic radicals were proposed as intermediates in the reaction. However, unlike the tin hydride reductions, 1-butene was obtained almost exclusively from each of the isomeric chlorides. The process has been described as occurring within a chromium complex. The preponderant formation of 1-butene from butenyl metal complexes has also been noted by others (12, 23, 46).

Kochi's study of the copper salt-catalyzed oxidation of butenes by peresters (17) is interesting because the role of a ligand in controlling stereoselectivity was clearly demonstrated. This reaction, which involves the oxidation of allylic radicals by cupric ion, results in the formation of high yields of allylic ester in which the double bond is terminal, and it is described as occurring within a metal complex. When phenanthroline

Table VI. Products of Homogeneous and Heterogeneous Hydrogenations of Butadiene

Various Catalysts			
Homogeneous (CN/Co = 5)	2	15	83
Equilibrium (25°C.)	22	3	75
Heterogeneous ^a			
Pd on BaSO ₄	19	6	75
Pd black	11	49	40
Pt black	10	72	18
Homogeneous (CN/Co = 7)	2	92	6

^a Young *et al.* (61).

was present in the reaction mixture, this stereoselectivity was lost, presumably because of the inability of the fully coordinated copper to π -complex the allylic group.

The oxidation of butenes by mercuric acetate (40), involving a butenylmercury intermediate, exhibits a high degree of stereoselectivity. Apparently such stereoselectivities are a unique feature of reactions involving allylmetal intermediates.

Turning our attention to heterogeneous catalysis, it is interesting to compare our results for the hydrogenation of butadiene with those obtained in interrupted hydrogenations over metal surfaces. Table VI (61) shows that a platinum black catalyst favors 1-butene formation, while palladium on barium sulfate yields a butene isomer distribution which corresponds closely to that of the equilibrium composition. Distributions from the pentacyanocobaltate(II) catalyst system lie in extreme positions, illustrating the high degree of stereoselectivity of the homogeneous system.

For hydrogenations over metals which show little stereoselectivity (and where isomerization was not a factor), Meyer and Burwell suggested the intermediate formation of π -allylic species (27). Rooney and Webb inferred that stereoselective hydrogenations resulted from the reaction of a σ -bonded species (42). While our results with the pentacyanocobaltate(II) system indicate that either π - or σ -bonded allylic species may lead to a high degree of stereoselectivity, in general, they support the above observations.

The stereospecific polymerization of butadiene catalyzed by transition metal salts is also controlled by the nature of the ligand (3, 4, 29, 41, 60) and may involve intermediates similar to those discussed.

Nitriles. α -HALONITRILES. Considering the results obtained with alkyl iodides, it was assumed that the reaction of α -halonitriles with pentacyanocobaltate(II) would result in halogen abstraction to form a resonance-stabilized radical. The fate of the radical would be expected to depend on the structure of the particular nitrile used. The products obtained from six α -halonitriles [α -chloroacetonitrile previously reported (22)] are shown in Table VII.

Table VII. Products of the Reaction of α -Halonitriles with Pentacyanocobaltate(II)

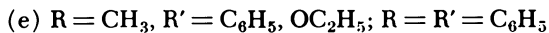
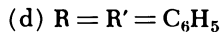
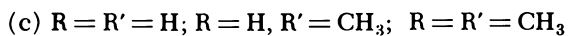
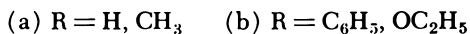
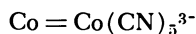
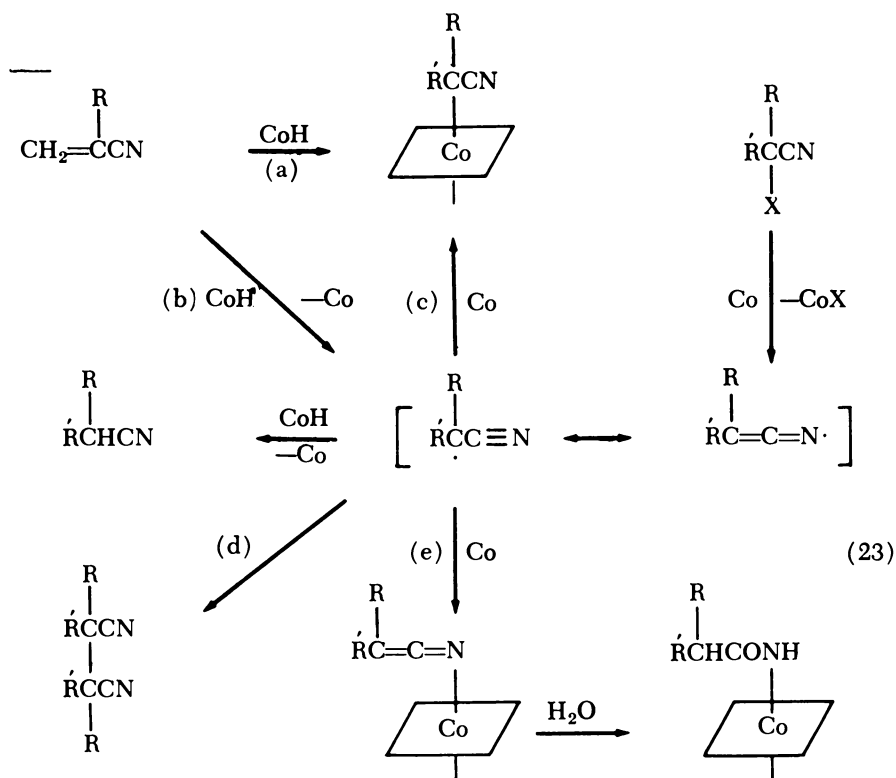
$$RR'CXCN + Co(CN)_5^{3-} \rightarrow \text{Products}$$

R	R'	X	$\left[\begin{array}{c} RR'CCN \\ \\ Co(CN)_5 \end{array} \right]^{3-}$	$\left[\begin{array}{c} RR'CHCONH \\ \\ (CN)_5Co \end{array} \right]^{3-}$	$\begin{array}{c} RR'CCN \\ \\ RR'CCN \end{array}$
H	H	Cl	+	-	-
H	CH ₃	Br	+	-	-
CH ₃	CH ₃	Cl	+	-	-
CH ₃	CH ₃	I	+	-	-
H	C ₆ H ₅	Br	+	-	-
C ₆ H ₅	C ₆ H ₅	Cl	-	+	+

Except for chlorodiphenylacetonitrile, 1-cyanoalkylcobalt complexes were isolated in each case and identified by infrared [CN stretches at approximately 2210, 2125, and 2105 cm.⁻¹ (22)] and PMR spectra. While the structures of acidified complexes have not been investigated, the original complexes were recovered from acidified solutions after they were made basic. Analogous 1-cyanoalkyliron complexes are reported to be reversibly protonated by strong acids (1). α -Pyridylpentacyanocobaltate(III) has also been reported to be stable to acid (14), in contrast to the organopentacyanocobaltates previously described (13, 23).

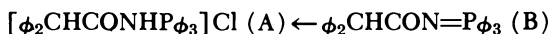
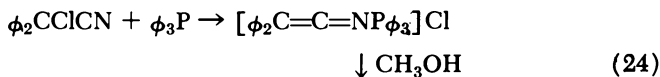
Chlorodiphenylacetonitrile formed tetraphenylsuccinonitrile as well as a different type of complex. The infrared spectrum of the latter contained no nitrile absorption band (2210 cm.⁻¹) but exhibited a cyanide stretch at 2130 cm.⁻¹, characteristic of inorganic pentacyanocobaltate(III) complexes (14, 22), and a carbonyl band at 1575 cm.⁻¹. Its PMR spectrum indicated the presence of the (C₆H₅)₂CH group. Diphenylacetamide precipitated on heating an aqueous solution of the complex. Apparently the resonance-stabilized radical initially formed in the reaction of this α -halonitrile with pentacyanocobaltate(II) may either dimerize or combine with pentacyanocobaltate(II) to form an *N*-keteniminocobalt complex. The latter is unstable in water, being converted to an *N*-amidocobalt complex, which may be further hydrolyzed to the free amide (Reaction 23, paths d and e). Presumably the radical cannot add penta-

cyanocobaltate(II) at the α -carbon owing to resonance stabilization [cf. trityl radical, (22)] and steric hindrance.

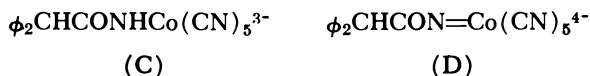


While a polar mechanism has been suggested for the formation of ketenimines by attack of triphenylphosphine or triethyl phosphite on the nitrogen of chlorodiphenylacetonitrile (36), ketenimines form from 1-cyanoalkyl radicals as well (32, 50).

The acylphosphinimine(B) isolated from the triphenylphosphine reaction exhibited a carbonyl band at 1575 cm^{-1} , while the amidophosphonium salt(A) derived from it did not (Reaction 24).



Therefore the complex isolated from the reaction with pentacyanocobaltate(II) (band at 1575 cm^{-1}) may be an acyliminocobalt(D), rather than an amidocobalt(C) complex.



PMR spectra cannot indicate the presence of amide hydrogen because of rapid exchange of the proton with deuterium oxide solvent. We have found that nitrogen-cobalt bonded complexes with infrared absorptions at 1575 cm^{-1} may be formed when *N*-bromo primary amides react with pentacyanocobaltate(II). Comparison with the spectrum of a complex formed from an *N*-bromo secondary amide, in which no acidic hydrogen would be present, should help resolve this problem.

Hydrogenolyses of the α -halonitriles listed in Table VII, carried out in the presence of excess hydrido complex, led to varying yields of the corresponding reduced nitriles.

α,β -UNSATURATED NITRILES. The products obtained by adding hydrido complex to four α,β -unsaturated nitriles are shown in Table VIII. Acrylonitrile [previously reported (22)] and methacrylonitrile formed stable 1-cyanoalkylcobalt complexes identical to those obtained by reaction of the corresponding α -halonitriles with pentacyanocobaltate(II) (*see* Table VII). However, these unsaturated nitriles were not reduced to the corresponding saturated nitriles by treatment with excess hydrido complex. Since reduction of the α -halonitriles is believed to occur with the intermediate formation of radicals (*cf.* above text), it is inferred that such radicals are not formed when the hydrido complex is added to those acrylonitriles forming stable 1-cyanoalkylcobalt complexes (Reaction 23, path a).

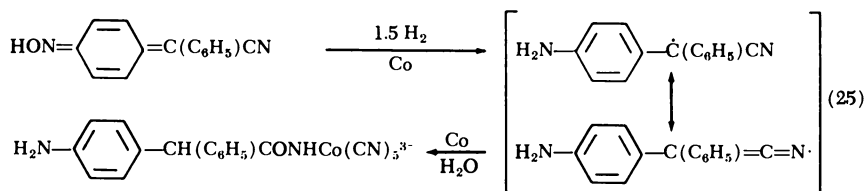
Table VIII. Products of the Reaction of α,β -Unsaturated Nitriles with Hydrido Complex

$$\text{CH}_2=\text{CRCN} + \text{Co}(\text{CN})_5\text{H}^{3-} \rightarrow \text{Products}$$

R	$\left[\begin{array}{c} \text{CH}_3\text{CRCN} \\ \\ \text{Co}(\text{CN})_5 \end{array} \right]^{3-}$	$\left[\begin{array}{c} \text{CH}_3\text{CHRCONH} \\ \\ (\text{CN})_5\text{Co} \end{array} \right]^{3-}$	CH_3CHRCN
H	+	-	-
CH_3	+	-	-
C_6H_5	-	+	+
$\text{C}_2\text{H}_5\text{O}$	-	+	+

On the other hand, adding hydrido complex to excess α -phenyl or α -ethoxy acrylonitriles resulted in the formation of *N*-amidocobalt complexes, identified in the same way as the complex obtained from chlorodiphenylacetoneitrile. Since these acrylonitriles were catalytically hydrogenated to the corresponding saturated nitriles in the presence of excess hydrido complex, it is inferred that both the hydrogenation and *N*-amidocobalt complex formation occur *via* a common radical intermediate (Reaction 23, paths b and e).

Reduction of phenylcyanomethylenequinone oxime also resulted in the formation of an *N*-amidocobalt complex, presumably in the following manner:



The radical intermediate shown has also been proposed as an intermediate in the heterogeneous reduction of this substrate by Raney nickel catalyst (7).

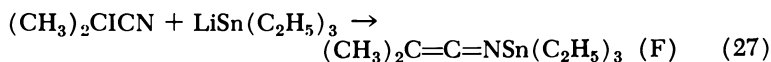
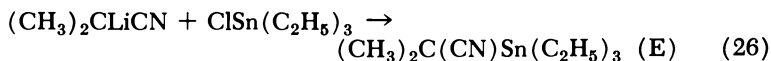
It appears that the type of complex formed is determined by the structural features of the substrate. Thus, α -halonitriles, which apparently all react *via* a radical mechanism, may yield either 1-cyanoalkylcobalt or *N*-amidocobalt complexes; acrylonitriles may react *via* a polar mechanism to form 1-cyanoalkylcobalt complexes or *via* a radical mechanism to form *N*-amidocobalt complexes.

OTHER NITRILE COMPLEXES. While similar additions of iron (I) and rhodium (II) hydrides to acrylonitrile to form 1-cyanoethylmetal complexes have been reported, 2-cyanoethylmetal complexes also form in certain cases (43, 51). Organotin hydrides may add to acrylonitrile in either direction, depending on the conditions of the reaction (25). Formation of the 2-cyanoalkyltin adduct apparently involves a radical mechanism, whereas a polar mechanism is operative in forming the 1-cyanoalkyl adduct. A four-center transition state was not considered probable in the latter case.

Hydrostannation of highly polarized α,β -unsaturated nitriles leads to the formation of *N*-stannylketenimines (31, 33) in what is considered to be a polar 1,4-addition. Thus, polar mechanisms are ascribed to reactions leading to either 1-cyanoalkyl or ketenimine adducts.

Of considerable interest is the report (32) that both 1-cyanoisopropyl triethylstannane(E) and triethylstannyl dimethylketenimine(F) may be

prepared from isobutyronitrile derivatives.



The products are not interconvertible and could not have formed *via* a common intermediate. Obviously formation of a ketenimine derivative does not necessarily depend on the cyanoalkylmetal derivatives being unstable.

Organocobalt Complex Stability and Catalytic Hydrogenation. We have shown that radical species may be intermediates in catalytic hydrogenations as well as hydrogenolyses. Simandi and Nagy first proposed a radical intermediate in the pentacyanocobaltate-catalyzed hydrogenation of a double bond (45). Their kinetic results indicated that an organocobalt complex played no essential role in hydrogenating cinnamic acid. On the other hand, we ascribe the stereoselectivities observed in the reduction of allylic halides and conjugated dienes to the formation of organocobalt complex intermediates. Thus, the structure of the substrate may determine the manner in which hydridocomplex adds to a double bond, as well as whether organocobalt complexes form from organic halide derived radicals.

In addition to the work described here, experiments with styrenes and α,β -unsaturated acids, esters and ketones, as well as related halides (24), suggest certain generalizations concerning the effect of structure on organocobalt complex stability and catalysis. Table IX lists several organocobalt complexes, whose preparations, either by reaction of the halide with pentacyanocobaltate(II) or by addition of hydrido complex to the corresponding unsaturated substrate, have been attempted. In many cases, both methods were used.

Table IX. Attempted Preparations of Organopentacyanocobaltates*

Complex Type	$\text{RCo}(\text{CN})_5^{3-}$					
	1°R		2°R		3°R	
Benzyl	$\text{C}_6\text{H}_5\text{CH}_2$	(++)	$\text{C}_6\text{H}_5\text{CHCH}_3$	(-)	$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2$	(-)
Alkyl	CH_3CH_2	(++)	CH_3CHCH_3	(+)	$(\text{CH}_3)_3\text{C}$	(-)
Allyl	$\text{CH}_2=\text{CHCH}_2$	(++)	$\text{CH}_2=\text{CHCHCH}_3$	(+)	$\text{CH}_2=\text{CHC}(\text{CH}_3)_2$	(-)
Ketone	RCOCH_2	(++)	RCOCHCH_3	(++)	$\text{RCOC}(\text{CH}_3)_2$	(-)
Ester	ROOCC_2	(++)	ROOCCCH_3	(++)	$\text{ROOCC}(\text{CH}_3)_2$	(+)
Nitrile	NCCH_2	(++)	NCCHCH_3	(++)	$\text{NCC}(\text{CH}_3)_2$	(++)

* Symbols: (++) , stable complexes isolated; (+) , unstable complexes isolated; (-) , complexes which could not be isolated. The α -methylallyl complex shown is inferred; only the γ -isomer was isolated.

All of the primary organocobalt complexes (necessarily formed from the corresponding halides) were stable to spontaneous decomposition. Only those secondary complexes which were α -substituted by a carbonyl or nitrile group were stable, while only the nitrile derivative in the tertiary series was stable. Therefore, it appears that electropositive α -substituents destabilize these organocobalt complexes, while electronegative groups stabilize them. Although an organocobalt complex could not be isolated by adding hydrido complex to styrene or by reaction of α -bromoethylbenzene with pentacyanocobaltate(II), unstable complexes have been isolated from *p*-cyanostyrene and 2-vinylpyridine. Thus, electronegative groups again increase the stability of organocobalt complexes. The destabilizing effect of α -phenyl- and α -ethoxy substituents has been discussed in connection with the reduction of acrylonitriles.

Unsaturated substrates forming stable organocobalt complexes on adding hydrido complex could not be catalytically hydrogenated (the catalyst may be considered "poisoned"). Organic halides, which formed the same stable organocobalt complexes on reacting with pentacyanocobaltate(II), underwent catalytic hydrogenolysis in the presence of excess hydridocomplex. It is implied that a polar mechanism is involved in the addition of hydrido complex to these unsaturated substrates, while a radical mechanism is involved in the reduction of the halides.

While all the primary organocobalt complexes are seen to be stable, the allyl complex constitutes a special case. It was the only one which was readily reduced by hydrido complex, although a small amount of reduction was also observed with the ketone complex. Since protons readily release the organic groups from both types of complex (23), the hydrido complex may be operating as a hydrogen atom or hydride source, the allyl group providing the more effective electron pathway for hydrogen attack.

The unstable complexes which could be isolated underwent spontaneous disproportionation. The reduction of substrates leading to the formation of such complexes may involve radical intermediates.

Deuteration studies are presently being carried out in the hope that the results will clarify the role of unstable organocobalt complexes and/or radical species in catalytic hydrogenation. This work will allow a comparison to be made with a parallel study of heterogeneous hydrogenation by Smith and Roth (47, 48). The chemistry of organopentacyanocobaltates finds many parallels in the reactions of analogous organocobalt carbonyls, cobalamins and cobaloximes (44).

A review of reactions catalyzed by pentacyanocobaltate(II) has been published recently (18). The hydrido complex $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ has been isolated by Banks and Pratt (2). Misono and co-workers (28) have shown that the 1-cyanoethyl complex, rather than the 2-cyanoethyl isomer

previously reported (43), is formed by the addition of a hydridocobaloxime to acrylonitrile.

Acknowledgment

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Homogeneous Catalysis of Polymerization

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Polymerization reactions are initiated by "catalysts." Most classical polymerizations are homogeneous, and although heterogeneous catalysis has provided striking advances in stereospecific polymerization, much of the newer research is concerned with homogeneous catalysts. Reactions of interest include homogeneous polymerization of vinyl compounds by free-radical, anionic, and cationic catalysts, and polycondensation reactions. Both the catalyst and reaction conditions may influence the polymer structure. If the monomer has two polymerizable or potentially polymerizable groups, either or both may participate in the polymerization, depending on the catalyst; the dienes, acrolein, and acrylamide are examples of this type of monomer. Isomerization may also occur in homogeneous polymerization—e.g., by rearrangement of intermediate carbonium ions. Recognition of this fact has led to renewed interest in polymerizing branched olefins and other vinyl compounds.

Homogeneous catalysis is of major importance in polymer chemistry and technology—e.g., in producing vinyl polymers, polydienes, and polycondensation polymers. It permits precise control of all reactants, usually eliminates the necessity of removing catalyst residues from the product, and allows the use of relatively simple apparatus. On the other hand, polymerizations in homogeneous media, especially bulk polymerizations of vinyl monomers, are sometimes so vigorous that proper heat removal may not be effected on a large scale. This drawback has limited some of the possible industrial applications (34).

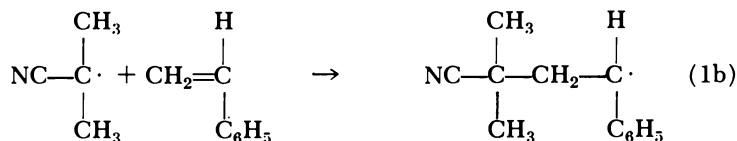
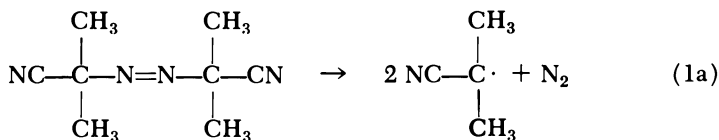
Homogeneous catalysis encompasses the use of various types of catalysts, polymerization media, and monomers. Consequently, it is not possible to describe *the* mechanism of homogeneous catalysis. This article

presents, instead, a survey of polymerization reactions that are homogeneous in nature, with particular emphasis on those of actual or potential industrial significance. For additional information, the reader is referred to more comprehensive treatments (23, 27).

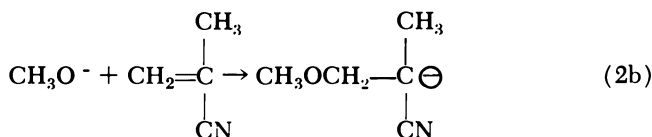
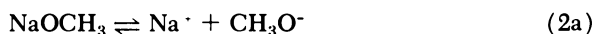
Definitions and Scope

Catalysts. The term "catalyst," as used by polymer chemists, describes essentially one or a combination of substances capable of inducing polymerization. Although many polymerization catalysts do fit the conventional concept of a catalyst—*e.g.*, the acid used in polyesterification—other so-called catalysts act simply as initiators for a chain reaction producing polymer. In that case, the catalyst, or a portion thereof, is normally incorporated as an integral part of the polymer—namely as an end group. Analysis of these end groups has been a powerful tool in characterizing polymers (5) and in studying polymerization mechanisms (*see, e.g.*, Refs. 28, 29). End groups are also important if the polymer is to be used for subsequent reaction (as in polyurethan formation). In a sense, even such substances as chain-transfer agents (regulators) may be considered catalysts since they do initiate polymerization of the monomer. The distinction here is that the chain-transfer agent is not capable by itself of producing polymer in the absence of another initiating substance. For example, dodecyl mercaptan cannot induce polymerization of a vinyl monomer unless a substance like a peroxydisulfate has started the process. Crosslinking agents—*e.g.*, for epoxy resins—are also referred to as catalysts in the industry.

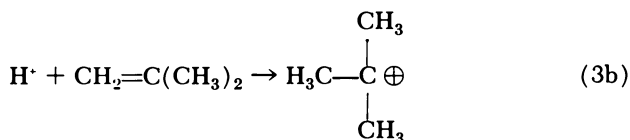
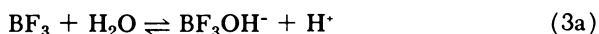
In many cases, the catalyst is not able to initiate polymerization without a prior activation step. Azo or peroxy catalysts must be heated to effect dissociation. This is illustrated in Reaction 1 for 2,2'-azobisisobutyronitrile. Decomposition produces free radicals (Reaction 1a) that are then capable of reacting with monomer (in this case styrene) in the polymerization-initiation step (Reaction 1b):



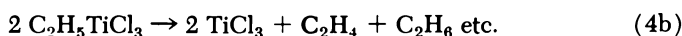
Similarly, anionic catalysts must dissociate before reaction; this is illustrated in Reactions 2a and 2b for sodium methoxide and methacrylonitrile.



A reaction with a cocatalyst is necessary in cationic polymerization, as well as in coordinate polymerizations with many complex metallic catalysts. In cationic polymerization, the reaction involves traces of water and generates hydrogen ion, the actual initiator. This is shown in Reaction 3 for boron trifluoride and isobutylene.



Reaction of titanium tetrachloride with triethylaluminum (the cocatalyst) results in reduction of the transition metal. This is shown in Equation 4 (30):



Activation with water or oxygen or by heating is also necessary with some complex catalysts. These reactions are not always well defined.

Homogeneous Polymerizations. One may distinguish between at least three situations relating to homogeneity or heterogeneity in polymerization:

(1) The reaction mixture is homogeneous throughout the entire polymerization—*i.e.*, the catalyst, monomer, polymer, and solvent (if used) form a single phase. This is the subject discussed here. Bulk polymerization and solution polymerization are examples of reactions that are usually homogeneous.

(2) The mixture is homogeneous at first, but the polymer eventually precipitates because of limited solubility in the medium. Although the catalysis itself may be considered to be (at least in the beginning) homogeneous, many complications arise—*e.g.*, in the termination process. Precipitative polymerization and crosslinking are examples of this type.

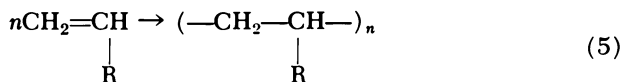
(3) The reaction mixture is heterogeneous during the entire polymerization because of insolubility of any of the components. Heterogeneous polymerization has been practiced for many years as suspension

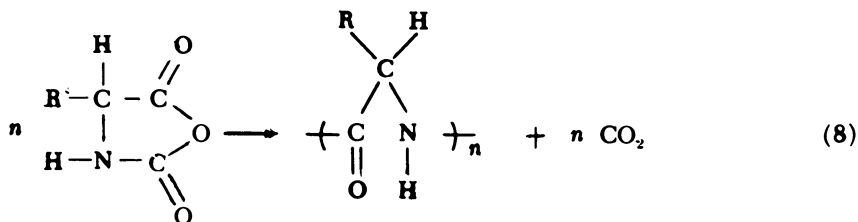
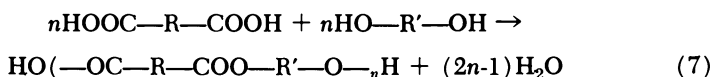
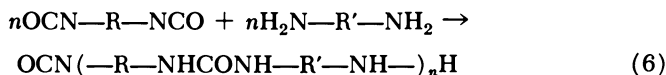
polymerization and as emulsion polymerization, wherein the monomer and polymer are insoluble in the medium, but the catalyst is usually soluble. A recent development of great interest has been polycondensation by interfacial polymerization using two immiscible solvents. Each of two complementary monomers is soluble in only one of the solvents, and polymerization proceeds at or near the interface (26). Heterogeneous polymerization with insoluble catalysts became one of the most exciting frontiers of science with the discovery of coordinate polymerization by Karl Ziegler and Giulio Natta in the 1950's. The tremendously fruitful studies that followed in many laboratories led to the development and exploitation of numerous important industrial processes, including the production of high-density polyethylene, isotactic polypropylene, and stereoregulated elastomers (30, 31).

Heterogeneous catalysis is still a major, and perhaps the major, field of polymer investigation, as attested by the flood of publications, including patents, emanating from all parts of the world. However, in recent years, homogeneous polymerization has received new attention. It was found that, surprisingly, stereospecific polymerization may also be carried out in homogeneous medium and frequently offers many advantages over heterogeneous systems. Certainly, investigations of the mechanism of Ziegler-Natta catalysis have been greatly aided by studies in homogeneous media (*see e.g.*, Refs. 28, 29, 30). Many significant new developments have also taken place in anionic and cationic polymerization, including the study of "living" polymers (32, 40) and of isomerization polymerization (11, 16). Another subject of considerable interest has been the selective polymerization of monomers with two or more reactive sites. Ingenious methods, utilizing all knowledge of polymer synthesis, have been brought to bear on these problems with great success. Highlights of these various topics will be reviewed here.

Polymerization Reactions

The traditional way to classify polymerization reactions has been by stoichiometry—*i.e.*, whether or not the molecular weight of the polymer produced is an exact multiple of the molecular weight of the monomer (exclusive of end groups). If so, the reaction has been termed an addition polymerization; if weight was lost during polymerization, it was named condensation polymerization. Vinyl polymerization (Reaction 5) and polyurea formation (Reaction 6) are examples of the former, whereas polyesterification (Reaction 7) and formation of poly(α -amino acids) from *N*-carboxyanhydrides (Reaction 8) are examples of the latter.





When dealing with catalysis it is best, however, to classify polymerization reactions according to the mechanism of chain propagation (2). One may distinguish in this way between chain-reaction polymerization and step-reaction (stepwise) polymerization. The essential features of these classes are shown in Table I (15). The differences between the two types of polymerization are also evident from equations of rate (R_p) and average degree of polymerization (\overline{DP}). For a free-radical polymerization of vinyl compounds (an example of a chain reaction), R_p and \overline{DP} are functions of monomer and catalyst concentration (Equations 9 and 10):

$$R_p \propto [\text{M}][\text{C}]^{1/2} \quad (9)$$

$$\overline{DP} \propto [\text{M}]/[\text{C}]^{1/2} \quad (10)$$

On the other hand, for polyesterification (an example of a stepwise reaction), the rate and degree of polymerization depend on the number of functional groups in the system, regardless of whether they are on the monomer, the high polymer, or any species intermediate in molecular weight (Equations 11, 12, and 13):

$$\text{Catalyzed} \quad R_p \propto [\text{H}^+][\text{COOH}][\text{OH}] \quad (11)$$

$$\text{Self-catalyzed} \quad R_p \propto [\text{COOH}]^2[\text{OH}] \quad (12)$$

$$\overline{DP} = \frac{1}{1-p} \quad (13)$$

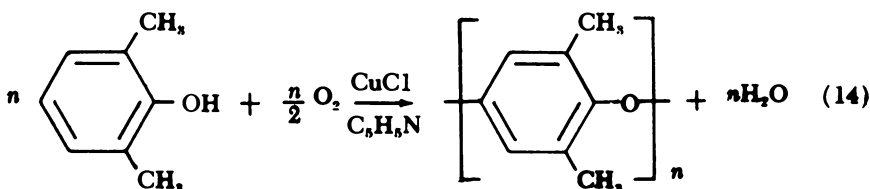
where p is the fraction of functional groups that has reacted (15).

Chain-reaction polymerization may be induced by various catalysts. For example, vinyl polymerization (Reaction 5) occurs with free-radical, anionic, or cationic catalysts, as well as with coordinate catalysts (which may be of the anionic or the cationic type) (30, 31). Poly(α -amino acid) formation (Reaction 8) may be carried out with basic catalysts.

Table I. Characteristics of Polymerization Reactions (15)

	<i>Chain Reaction</i>	<i>Step Reaction</i>
High molecular-weight material	Formed in earliest stages	Formed only at high conversions
Propagation	Every step involves a monomer unit	Steps involve all molecular sizes
Monomer concentration	Monomer is most plentiful single size until the end	Decreases rapidly in early stages
Polymer-polymer reactions	none	After early stages, almost entire reaction is between polymer molecules

Catalysts are also required in many stepwise polymerizations. For example, reaction of polycarboxylic acids and polyols (Reaction 7) is catalyzed by acids; ester interchange, by metal compounds such as titanium alkoxides. On the other hand, polyurea synthesis (Reaction 6) generally does not require a catalyst. Metallic compounds are also useful in oxidative polymerization of phenols to give poly(phenylene oxides), illustrated in Reaction 14.



Examples of some polymers that may be prepared by homogeneous catalysis are given in Table II, together with typical catalysts and the probable nature of each reaction. A further discussion of homogeneous catalysis of polymerization is given by Halpern (14) and Tsutsui *et al.* (42).

Selective Polymerization

An important aspect of polymerization is the ability to obtain different products from the same monomer by proper choice of catalyst and reaction conditions. These products may differ in stereochemical configuration or in the nature of the repeating unit. For example, it has been possible to polymerize selectively one or all of the functional groups of polyfunctional monomers. A subject of particular fascination has been

Table II. Some Important Homogeneous Polymerizations (23, 27)

<i>Polymer Formed</i>	<i>Typical Catalysts</i>	<i>Probable Reaction Type^a</i>
Polyacrylamide	$K_2S_2O_8$ - $NaHSO_3$	C-F
Polymethacrylonitrile	$NaOCH_3$	C-A
Poly(methyl methacrylate)	$(C_6H_5CO)_2O_2$	C-F
Poly(vinyl acetate)	$(CH_3)_3COOH$	C-F
Polystyrene	none (heat); $(C_5H_5CO)_2O_2$	C-F
Polyisobutylene	BF_3	C-Cat
Polyethylene	$VOCl_3$ - $(C_6H_5)_4Sn$ - $AlBr_3$	C-Coor
Ethylene-propylene-dicyclopentadiene terpolymer	$V(AcAc)_3$ - Et_2AlCl^b	C-Coor
Polymethylene ^c	BF_3	C-Cat
<i>cis</i> -1,4-Polybutadiene	$CoCl_2$ - Et_2AlCl	C-Coor
<i>cis</i> -1,4-Polyisoprene	C_4H_9Li	C-Coor
Poly(oxypropylene) glycol	$NaOH$	M-A
Poly(oxytetramethylene) glycol	PF_5	C-Cat
Polyoxymethylene	$(C_6H_5)_3P$; $(C_4H_9)_3N$	C-A
Dextran ^d	Enzyme from <i>Leuconostoc mesenteroides</i>	C
Alkyd resin	$(CH_3COO)_2Ca$; lead compounds	S
Epoxy resin	$(C_2H_5)_3N$; carboxylic anhydride; BF_3 - CH_3NH_2	S
Melamine-formaldehyde	Base or acid	S
Phenol-formaldehyde	Base or acid	S
Polyester	Acid; $Ti(OR)_4$	S
Nylon-6 ^e	Na	M-A
Polycarbonate	C_5H_5N	S
Polyurethan	triethylenediamine	S
Poly(phenylene oxide)	$CuCl$ -pyridine	S

^a C= chain reaction, S= step reaction, M= mixed (has features of C and S); A= anionic, Cat= cationic, Coor= coordinate, F= free radical

^b AcAc= Acetylacetonate

^c From diazomethane

^d From sucrose

^e From ϵ -caprolactam

preparing polymers with different repeating units from monomers that are usually considered to be monofunctional. These subjects will be discussed in turn.

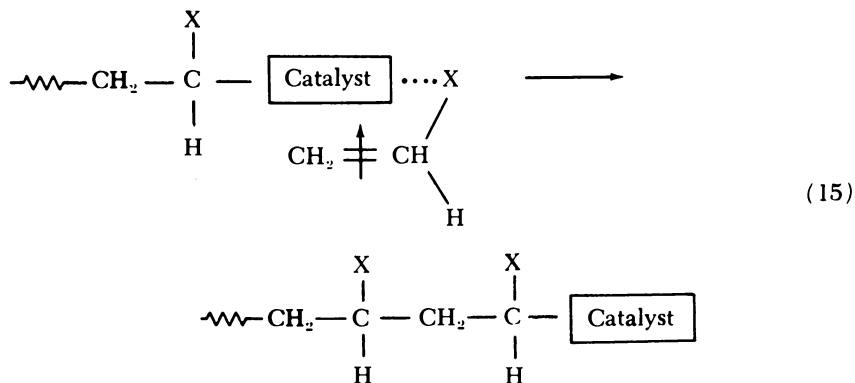
Stereospecific Polymerization. It was found quite early in the development of Ziegler-Natta catalysts that stereospecific polymerization usually requires the presence of a crystalline catalyst surface—*i.e.*, heterogeneous catalysis. Most recently, this has been confirmed in the careful examination of catalyst surfaces by Rodriguez, van Looy, and Gabant (35). It must be remembered, however, that this work dealt largely with α -olefins.

Table III. Homogeneous Stereospecific Polymerizations (23, 30, 31)

Monomer	Typical Catalyst ^a	Configuration
	<i>Cationic</i>	
Alkyl vinyl ether	EtAlCl ₂	isotactic
Alkyl <i>cis</i> -β-chlorovinyl ether	EtAlCl ₂	<i>erythro</i> -diisotactic
Alkyl <i>trans</i> -β-chlorovinyl ether	EtAlCl ₂	<i>threo</i> -diisotactic
<i>o</i> -Methoxystyrene	EtAlCl ₂	isotactic
	<i>Anionic</i>	
Vinylpyridine	EtMgBr	isotactic
Acrylonitrile	Cr(AcAc) ₃ -Et ₂ Zn	syndiotactic
Acrylates	Mg amides; RMgX	isotactic
Methyl methacrylate	9-Fluorenyllithium—THF	syndiotactic
Aliphatic aldehydes	Et ₃ Al	isotactic
Propylene	V(AcAc) ₃ -R ₂ AlCl (-78°C.)	syndiotactic

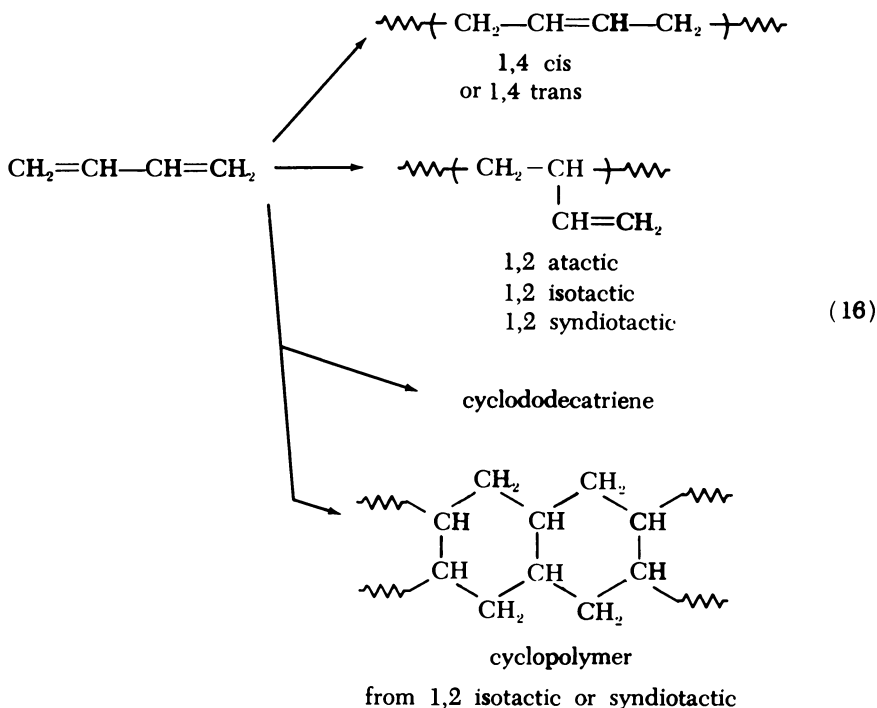
^a AcAc = acetylacetonate; THF = tetrahydrofuran

Natta subsequently recognized that stereospecific polymerization of vinyl monomers is possible in homogeneous media, provided that the monomer has at least two sites capable of coordinating with the catalyst. The orientation in space of the reacting monomer molecule is thereby controlled during the critical propagation step (31). Monomers of this type are the dienes or the vinyl monomers having substituents characterized by the presence of free electrons—*e.g.*, ether, amine, carbonyl, carboxyl, or nitrile groups. In this connection, it may be recalled that one of the first authentic preparations of isotactic polymers involved alkyl vinyl ethers (37, 38). Table III lists some of the vinyl monomers polymerized stereospecifically by homogeneous catalysts. The polymerization process has been represented (in a rather simplified way) in Reaction 15 (18):



Propylene also gives stereoregular polymers by homogeneous catalysis but only at low temperatures (Table III). The related polymerization of ethylene is described by Tsutsui *et al.* (42).

Dienes. The dienes present a particularly challenging case since both stereoisomerism and geometric isomerism can be observed in the products (the dienes are not only polyfunctional but also permit different tacticities). For butadiene, the following possibilities exist: *trans*-1,4; *cis*-1,4; atactic 1,2; isotactic 1,2; syndiotactic 1,2; cyclic oligomers; and cyclic high polymers (Reaction 16).



For 2-substituted butadienes, a distinction must also be made between 1,2 and 3,4 polymerization. For 1-substituted butadienes, 11 possible crystalline high polymers may be expected, including two diisotactic (*erythro* and *threo*) 3,4 isomers, but excluding any possible cyclopolymer; only three of these polymers have been characterized (30, 31).

Table IV lists some diene polymers prepared by homogeneous catalysis. The cobalt catalyst for butadiene and the lithium catalyst for butadiene and isoprene are believed to be used commercially in the United States to prepare the so-called "stereoelestomers" (32, 36).

The extraordinary behavior of cobalt in coordinate catalysis is also evident from Figure 1. Nickel and cobalt acetylacetonate in the presence

Table IV. Polymerization of Dienes with Homogeneous Catalysts

Monomer	Catalyst ^a	Product	Ref.
Butadiene	VCl ₃ · 3THF-R ₂ AlCl	99% trans-1,4	31
Butadiene	Co compounds-R ₂ AlCl	98% cis-1,4	31
Butadiene	MoO ₂ (AcAc) ₃ -R ₃ Al	92-96% 1,2-syndiotactic	31
Butadiene	Cr(AcAc) ₃ -R ₃ Al (high Al:Cr)	97-99% 1,2-isotactic	31
Butadiene	BuLi	9% 1,2; 45% 3,4; 46% trans-1,4	32
Butadiene	EtAlCl ₂ -CH ₃ OH	cyclopolymer	20, 21
Butadiene	bis-π-allylnickel	oligomers	3
Isoprene	(V(AcAc) ₃ or Ti(OR) ₄)-R ₃ Al	95% 3,4	31
Isoprene	EtAlCl ₂	cyclopolymer	20, 21
Isoprene	BuLi	93% cis-1,4	32

^a AcAc = acetylacetone; THF = tetrahydrofuran

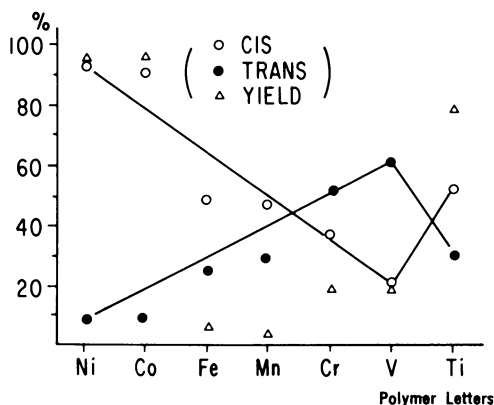
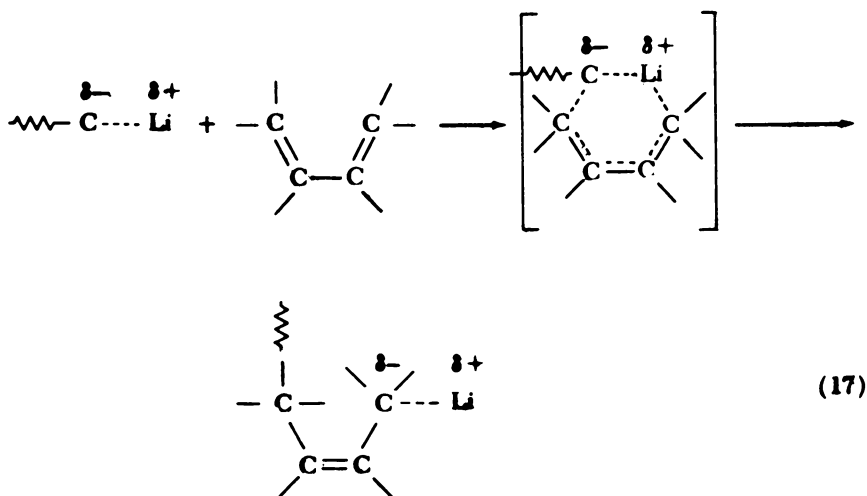


Figure 1. Effect of transition metal on the microstructure and yield of polybutadiene. Initial concentrations: $M(\text{acac})_3$, 10^{-3}M ; Et_2Al , $6 \times 10^{-3}\text{M}$; AlCl_3 , $3 \times 10^{-3}\text{M}$; butadiene, ca. 2M (25).

of Et_3Al and AlCl_3 (1:6:3 molar ratio) gave the highest yield of polymer and the highest *cis*-1,4 content in polymerizing butadiene (25). A possible mechanism involving binding of the diene to a $[\text{CoX}]^+$ ion has been proposed (10).

Lithium catalysts exhibit particularly high stereospecificity with isoprene. There is some disagreement in the literature regarding the mechanism of polymerization. The medium must be inert for maximum stereospecificity—*i.e.*, it should be incapable of coordinating with the catalyst. Association of the catalyst is important in the kinetic scheme, but present thinking is that the butyllithium monomer alone initiates polymerization of isoprene and that propagation likewise involves only a

nonassociated species, (butadiene)_nLi (8, 32). A six-membered cyclic transition state has been suggested (32) (Reaction 17).



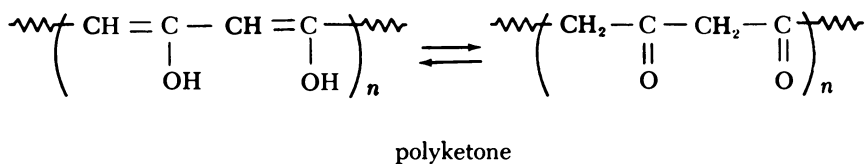
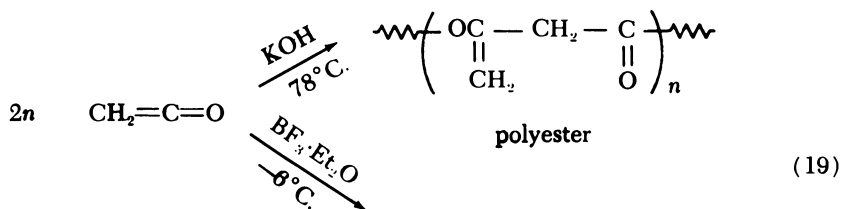
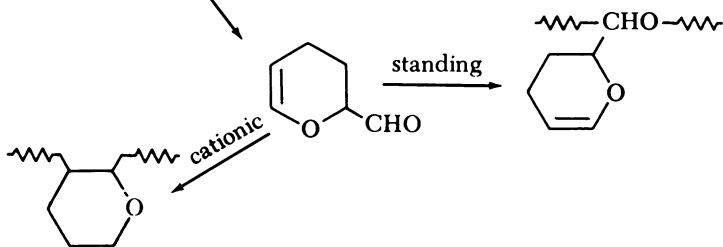
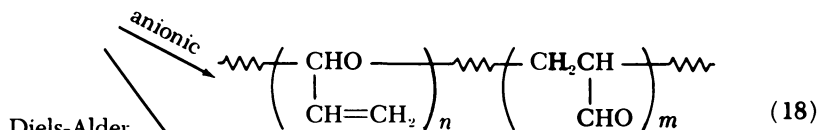
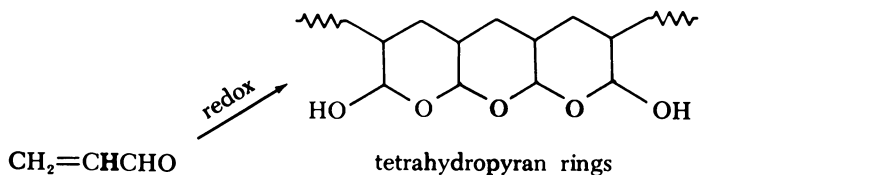
The polymers are "living"—*i.e.*, they are capable of propagating as long as monomer is present, and no termination occurs in the absence of impurities (40). Block copolymers of butadiene and styrene that are thermoplastic in nature may be prepared by lithium catalysis. Apparently, the butadiene polymerizes first without much participation of styrene; styrene then reacts after butadiene has been consumed (8, 22).

Acrolein. The polymerization of acrolein—another bifunctional monomer—has been studied recently in several laboratories, particularly by Schulz in Germany and by the Shell group in the United States (39). This monomer is potentially available in large quantities and at low cost.

Depending on the catalyst chosen, polymers with different structures may be obtained, either involving the double bond, the carbonyl group, or both. These results are summarized in Reaction 18 (39).

Numerous other acrolein polymers have been prepared whose structures have not been elucidated. Acrolein polymers are highly reactive and may be converted to various derivatives. Of these, the bisulfite adduct of the polymer prepared by free-radical initiation has been used as an emulsifying agent, as a crosslinking agent for proteins and for cellulose, and to produce water-insoluble adducts, in the form of films or sheets, with poly(vinyl alcohol) (39).

Ketene. This potentially inexpensive monomer likewise acts as a difunctional monomer. It produces either a polyester or a polyketone, depending on the catalyst used (33) (Reaction 19).

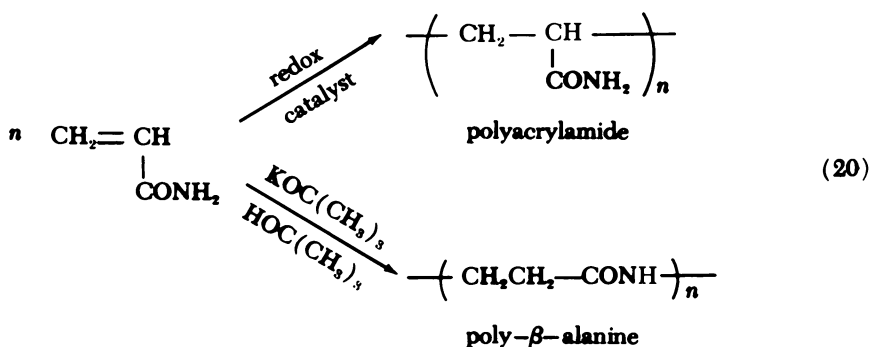


Other ketenes react similarly. The possible utility of these polymers has not received much attention.

Dialdehydes. The polymerization of dialdehydes, like suberaldehyde, may involve either one or both aldehyde groups. Thus, aluminum isopropoxide catalysis gives a linear polyester (by the classical Tishchenko reaction), sodium hydroxide a partially crosslinked aldol condensate, and boron trifluoride a polyacetal involving only one carbonyl group (19). Malealdehyde (which has a carbon-carbon double bond in addition to two aldehyde groups) gives a cyclopolymer with triethylaluminum, a

linear (vicinal) polyaldehyde with 2,2'-azobisisobutyronitrile (3,4 addition), and a polyether with aldehyde groups (apparently conjugated and unconjugated—*i.e.*, resulting from 1,2 and 1,4 addition, respectively) with pyridine (1). These examples illustrate how the polymerization of dialdehydes may be directed to produce a variety of products.

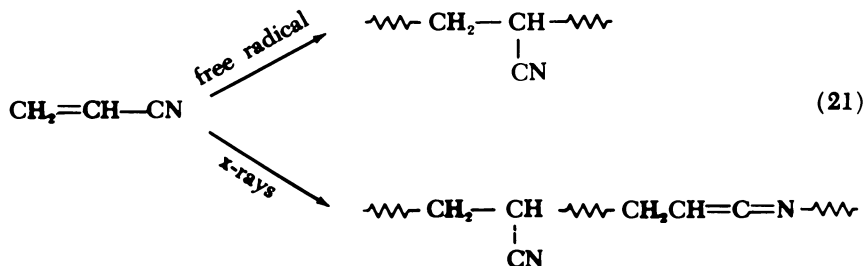
Acrylamide. The dienes, acrolein, ketene, and the dialdehydes represent monomers that are obviously polyfunctional. Acrylamide, on the other hand, was not thought until recently to be capable of any polymerization reactions other than at the vinyl group (*e.g.*, with free-radical catalysts). Breslow and Matlack demonstrated, however, that under anhydrous conditions and in the presence of strong bases the product obtained is poly- β -alanine (nylon-3) (6). These structures are shown in Reaction 20.



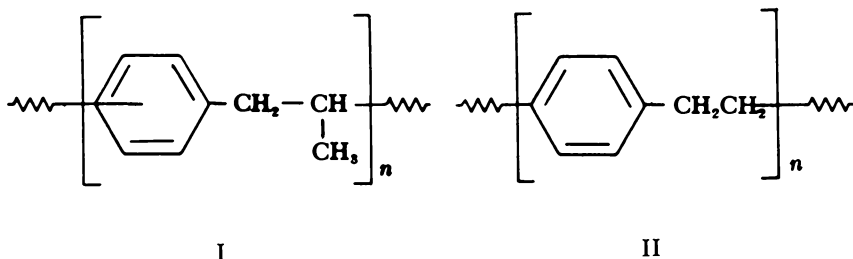
Other monomers, such as methacrylamide and ethylenesulfonamide, react similarly. Useful catalysts include potassium *tert*-butoxide, sodium methoxide, and phenylmagnesium bromide. Recent evidence suggests that both vinyl polymerization and polyamide formation may occur simultaneously. The mechanism has been the subject of some controversy, particularly with regard to the nature of the end groups and whether a chain reaction or step reaction is involved. The original literature or a recent review (12) may be consulted for details.

Acrylonitrile. Acrylonitrile is usually considered to be monofunctional in polymerization—*i.e.*, it reacts normally with free-radical and anionic catalysts. It has been reported, however, that irradiation with x-rays at -78°C . results in partial formation of keteneimine groups (7), as shown in Reaction 21.

Unsaturated Aromatic Compounds. Although they do not ordinarily do so in free-radical polymerization, aromatic compounds with allyl or vinyl side chains should be capable, under certain conditions, of undergoing reaction not only in the side chains but also at the ring. This has



been confirmed, for example, in the case of allylbenzene. Using aluminum bromide at -30°C ., Davidson demonstrated that the product obtained is (I)—*i.e.*, the result of both isomerization and alkylation of the ring (9).



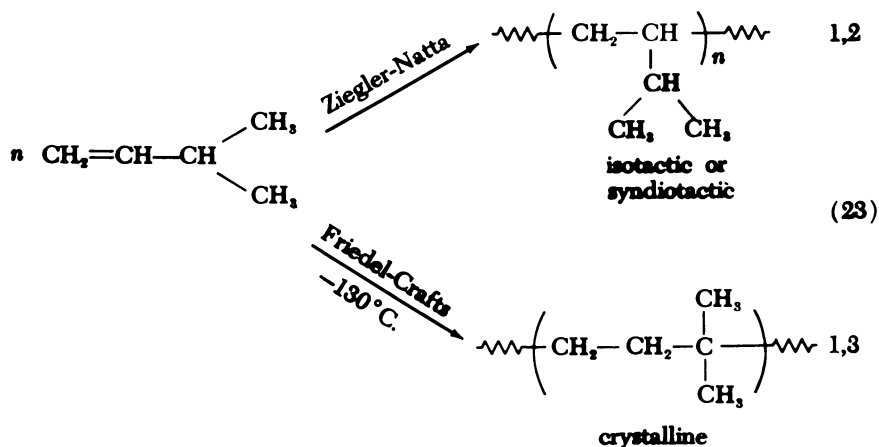
Topchiev has reported obtaining a 1,6 polymerization with styrene, resulting in a polymer with structure II. Catalysts used included $\text{AlCl}_3\text{-VOCl}_3$ (41). It has been suggested that the product is not II, but rather a crosslinked self-alkylation product brought about by Friedel-Crafts reaction (12).

Olefins. A problem that has fascinated polymer chemists has been obtaining polyethylene by polymerizing propylene (Reaction 22).

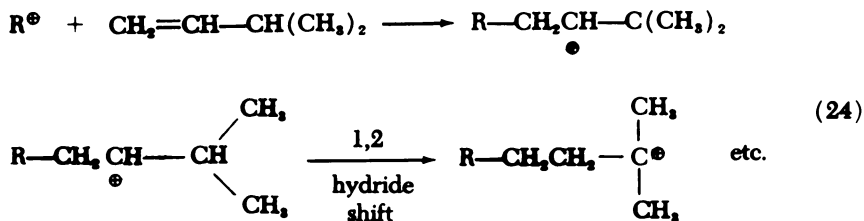


This reaction has indeed been reported in a German monograph on polyethylene published in 1961 (13) which, unfortunately, referred only to secondary sources that could not be verified. More recently, workers from the Toyo Rayon Co. reported obtaining polyethylene (identified by melting point and infrared spectrum) from the polymerization of propylene, using a catalyst consisting of vanadium (IV) chloride, iron (III) acetylacetonate, and triethylaluminum (43). Some of the ethylene units must have originated from the triethylaluminum, by analogy with the behavior of similar Ziegler-Natta catalysts (28, 29). Unfortunately, propylene input was not measured, and no analysis was given for monomer ethylene content. Publication of further details and verification in other laboratories would be of great interest.

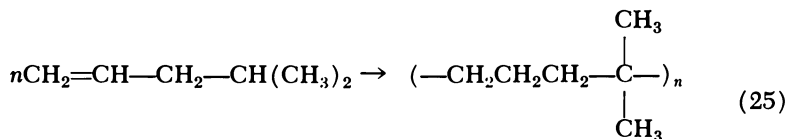
On the other hand, rearrangements are well-documented in the polymerization of branched olefins thanks to the elegant studies of Kennedy and co-workers (16, 17). They are known as isomerization polymerizations and occur with cationic catalysts at low temperatures—*i.e.*, under conditions where a given carbonium ion has sufficient lifetime, before reacting with a molecule of monomer, to rearrange to an energetically favored position. The repeating unit of the polymer has, therefore, a structure different from that of the monomer (*i.e.*, isomerization has taken place during polymerization). This is illustrated in Reaction 23 for 3-methyl-1-butene.



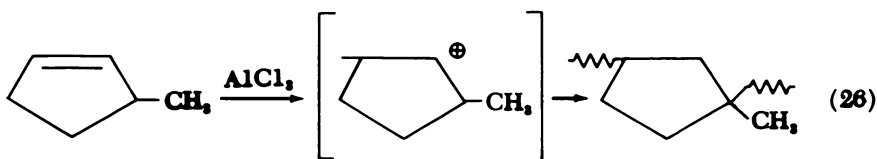
If the temperature of polymerization is above -130°C ., an elastomeric mixture of normal and rearranged units is found. The mechanism of propagation may be formulated as in Reaction 24.



Isomerization from the secondary to the more stable tertiary carbonium ion precedes reaction with the next molecule of monomer. A 1,3 polymerization has therefore occurred. Similarly, 4-methyl-1-pentene gives a 1,4 polymer (probably involving two successive 1,2 hydride shifts) that has a structure corresponding to an ethylene-isobutylene copolymer (Reaction 25).



Unsaturated cyclic hydrocarbons, like β -pinene or 1,1-dimethylcyclopropane also react, but with ring opening (16). On the other hand, 3-methylcyclopentene polymerizes with isomerization but without ring opening (4). This is shown in Reaction 26.



Isomerization polymerization promises to make available entirely new types of polymers from readily available raw materials in many cases. This potential justifies its active investigation at present.

Conclusion

Although homogeneous polymerization encompasses a vast area and no single unifying principle is apparent, intensive study is shedding new light on various aspects of the subject. As our understanding of polymerization catalysis increases, it will be possible to prepare not only new products by using hitherto intractable monomers but also to obtain novel products from conventional monomers.

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π -Allylnickel Compounds as Homogeneous Catalysts

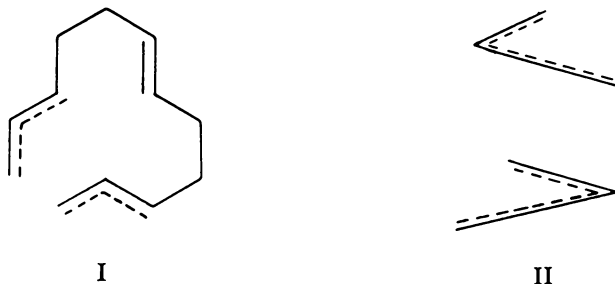
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New methods for preparing π -allylnickel halides and bis(π -allyl)nickel and its homologues are described. π -Allylnickel alkoxides, acetylacetonates, amides, and alkyls were also made. The chemical properties of these compounds are described and compared with those of π -allylnickel halides. π -Allylnickel halides combined with aluminum halides are homogeneous catalysts for dimerizing ethylene and propylene. When these catalyst systems are modified by adding phosphines, dimerization of propylene can be directed, depending on the phosphine used, to give predominantly either 2-methylpentenes or 2,3-dimethylbutenes. These are the precursors of isoprene and 2,3-dimethylbutadiene, respectively. This process is in pilot-plant scale operation.

Recent articles of this series (18) reported investigations of the synthesis of cyclododecatriene from butadiene (6) using a nickel catalyst. These investigations culminated in isolating a crystalline intermediate of this cyclization reaction (19). Strong support for the proposed structure of the intermediate, I was obtained by synthesizing bis(π -allyl)nickel II (20). Subsequently, several π -allyl compounds of many transition metals were synthesized (21).

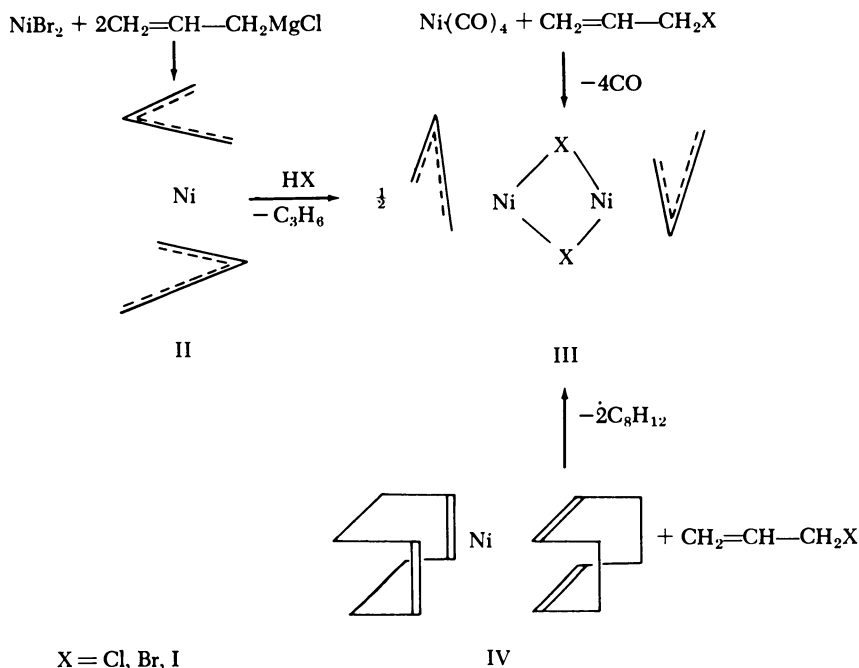
This article describes further progress in the chemistry of π -allylnickel compounds. First, preparative methods for π -allylnickel halides, alkoxides, amides, and alkyls are described. Next, some chemical properties of these compounds—*e.g.*, a recently observed disproportionation reaction—are discussed. Then, the use of π -allylnickel halides as homogeneous catalysts is discussed. Whereas bis(π -allyl)nickel is a catalyst for butadiene cyclootrimerization, π -allylnickel halides combined with Lewis acids, such



as aluminum halides, are highly active catalysts for dimerizing ethylene and propylene and polymerizing butadiene (24, 25). The propylene dimerization, especially the possibility to direct it at will towards 2-methylpentenes or towards 2,3-dimethylbutenes by adding specific phosphines, is discussed in some detail. Finally, propylene dimerization on a pilot-plant scale and some technical aspects of propylene dimers are outlined.

Synthesis of π -Allylnickel Halides and of Related Compounds

Halogen bridged, dimeric π -allylnickel halides, III, were first described by Fischer and Bürger, who prepared them in low yields by the reaction of nickel tetracarbonyl with allylic halides (9, 10).



In our laboratory, they were first prepared from bis(π -allyl)nickel, II. Thus, treating bis(π -allyl)nickel or a bis(π -allyl)nickel-type compound with 1 mole of an anhydrous hydrogen halide at -80° to 0° in ether, for example, yields the corresponding π -allylnickel halide and an olefin nearly quantitatively (22). [The term bis(π -allyl)nickel-type compound is used here to designate compounds with substituted allyl groups such as bis(π -methallyl)nickel, bis(π -crotyl)nickel, etc., and also the intermediate of cyclododecatriene synthesis (I).] Although quite simple, this method is not "economical" since one of the two allyl groups introduced as its Grignard reagent in preparing bis(π -allyl)nickel is lost in the cleavage reaction as propylene.

The common preparative method for π -allylnickel halides is at the moment the reaction of nickel(0) olefin complexes like bis(cycloocta-1,5-diene)nickel, (IV), with allylic halides (23). The olefin complex, IV, can be prepared easily by reducing nickel(II) salts (like nickel acetylacetonate) with aluminum organic compounds in the presence of cycloocta-1,5-diene (5). π -Allylnickel halides and substituted π -allylnickel halides prepared according to this method are listed in Table I.

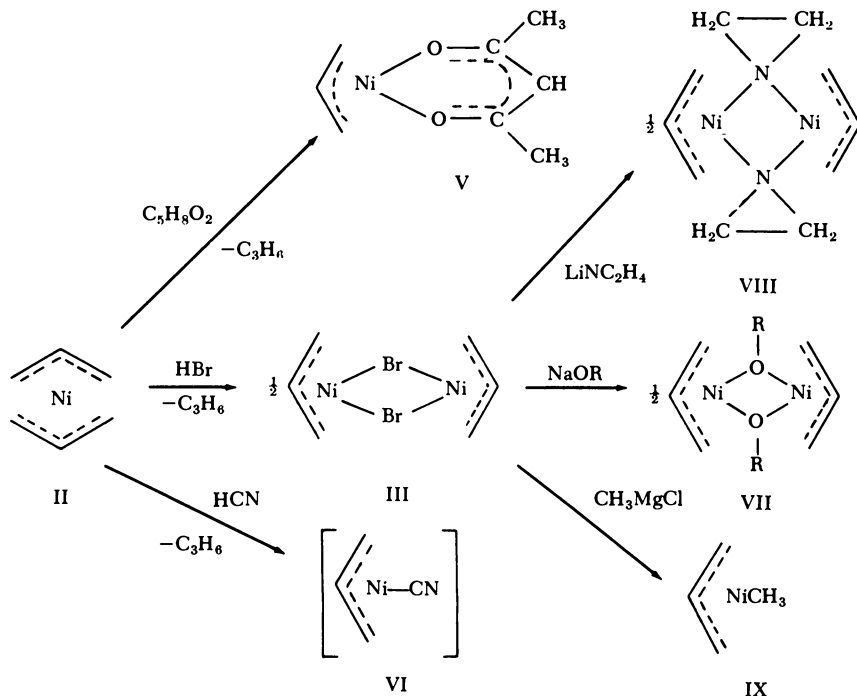
Table I. π -Allylnickel Halides Prepared from Bis(cycloocta-1,5-diene)nickel(0)

π -Allylnickel chloride
π -Allylnickel bromide
π -Allylnickel iodide
π -Cinnamylnickel chloride
1-Benzyl- π -allylnickel chloride
Triphenyl- π -cyclopropenylnickel bromide
1,3-Dimethyl- π -cyclobutenylnickel bromide
π -Cyclopentenylnickel chloride
π -Cyclohexenylnickel chloride
π -Cycloheptenylnickel chloride
π -Cyclooctenylnickel chloride

By using bis(cycloocta-1,5-diene)nickel in place of nickel tetracarbonyl as a starting material for preparing π -allylnickel halides, the reaction of the π -allylnickel halide with the displaced carbon monoxide (11) is avoided. Since olefins like cycloocta-1,5-diene do not react with π -allylnickel halides, yields of π -allylnickel halides are accordingly high. We have demonstrated recently that Fischer's method can give high yields of π -allyl-nickel halides if carbon monoxide is continuously removed during reaction (17).

In connection with the investigation of π -allylnickel halides, we synthesized some compounds of the type π -allylnickel X, where X⁻ is the anion of a proton acid. Two preparative methods have been used: (a)

partial cleavage of bis(π -allyl)nickel with the corresponding proton acid, as already described for the hydrogen halides, and (b) treatment of a π -allylnickel halide with an alkali metal salt. Thus, treating bis(π -allyl)nickel with 1 mole of acetylacetonate or hydrocyanic acid yields the volatile monomeric π -allylnickel acetylacetonate, V, (2) or the polymeric insoluble π -allylnickel cyanide, VI, (15, 16), respectively.



Although, in principle, it is possible to displace one allyl group from bis(π -allyl)nickel with any proton acid of greater acidity than propylene; in fact, reaction with proton acids like water or alcohols is slow. In such cases, π -allylnickel X-type compounds, can be prepared, for example, by treating π -allylnickel bromide with the alkali salt of the corresponding acid. In this way, π -allylnickel alkoxides, VII (with $R \equiv -CH_3$, $-C_2H_5$ and $-C_6H_5$), (3), π -allylnickel amides (2), the π -allylnickel aziridide, VIII, and π -allylnickel diphenylamide, were prepared.

The first alkyl derivative, the π -allylmethylnickel, IX, was prepared by treating π -allylnickel bromide with methyl magnesium chloride at $-100^\circ C$. (3, 4). π -Allylmethylnickel, the first transition metal compound having a π -allyl and a σ -alkyl group as ligands, is a violet crystalline compound stable only below $-80^\circ C$.

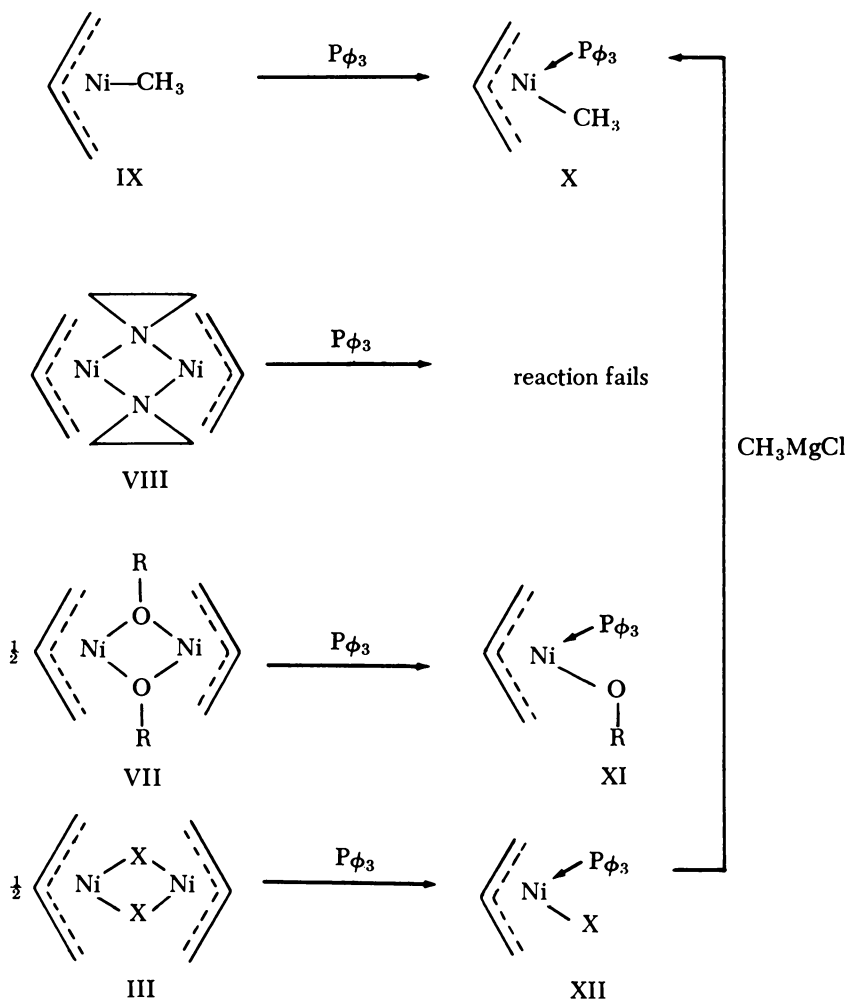
Properties of π -Allylnickel X-Type Compounds

Among the four previously mentioned X groups, only the methyl does not possess a free electron pair. Association of monomeric π -allylmethylnickel, with methyl as the bridging group, requires formation of electron-deficient bonds as found in the case of dimeric trimethylaluminum or tetrameric methyl lithium. [The possibility that allyl acts as the bridging group can be excluded on the basis of the $^1\text{H-NMR}$ spectrum.] Although the molecular weight of π -allylmethylnickel in solution has not yet been measured because of its low stability, it seems to exist in monomeric form as judged by its volatility in high vacuum even at -80°C .

π -Allylmethylnickel is typical of transition metal compounds in which the metal has an incompletely filled electron shell. It has at most 14 electrons in the valence shell. According to Chatt (7), the instability of transition metal alkyls is caused by the small energy difference between the highest occupied and the lowest unoccupied d orbitals. Thus electrons can be promoted easily to the next higher unoccupied orbital, leading to destabilization of the metal-to-carbon bonds and to decomposition of the compound. This concept may be used to explain the low stability of π -allylmethylnickel since nonbonding d electrons or vacant d orbital must be present in this compound.

The presence of nonbonding d electrons may also explain the high magnetic shielding of the methyl protons found in the $^1\text{H-NMR}$ spectrum of π -allylmethylnickel. The signal of the methyl protons is at 12.1 p.p.m. (TMS = 10.0 p.p.m.), which is surprisingly high to be explained on the basis of the polarity of Ni-CH₃ bond alone. The correlation between the low thermal stability and the high shielding of the methyl protons is further demonstrated by the fact that both effects disappear in the triphenylphosphine adduct (X) of π -allylmethylnickel. This complexation presumably lowers the energies of the d electrons. The 1:1 phosphine or phosphite adducts of π -allylmethylnickel obtained in the two ways shown are stable at ordinary temperature, and the signal of the methyl group is shifted to lower field strength (9.7 p.p.m. in triphenylphosphine adduct). The stability of phosphine adducts of π -allylmethylnickel shows that the low thermal stability of π -allylmethylnickel is not caused by an intrinsic weakness of the Ni-CH₃ bond but rather by the electron configuration of the complex. Work on the other π -allylnickel alkyls and aryls is in progress.

The thermal stability of π -allylnickel amides, alkoxides, and halides is considerably higher than that of π -allylmethylnickel. With the exception of some π -allylnickel alkoxides, these compounds are stable at ordinary temperatures. The reason for the increased stability may be, aside from the greater polarity of the bond between nickel and the nonmetal, the



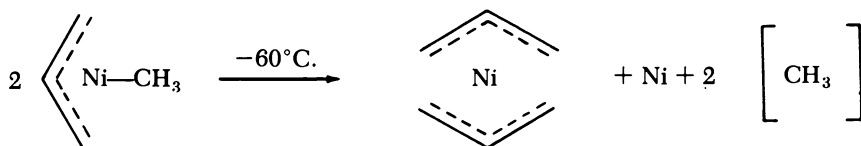
X = Cl, Br, I

$\phi = C_6H_5$

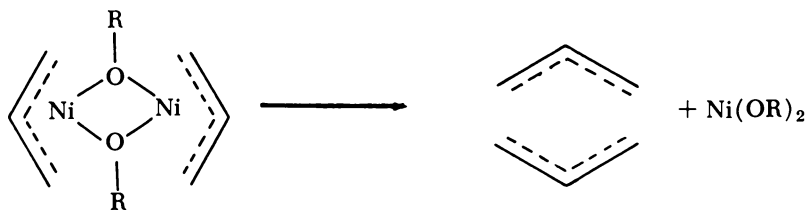
possibility of filling the vacant nickel orbital by the free electron pairs from nitrogen, oxygen, and halogen. The donation of electron pairs can be intramolecular, as for monomeric aminoboranes (13), or intermolecular, as for dimeric dialkylaluminum amides (8). The mentioned π -allylnickel X compounds are of the intermolecular donation type since they exist in solution and in the gas phase as dimers. The strength of association in the series π -allylnickel amides, alkoxides, halides should decrease

in that order, which agrees with the observation that the dimeric π -allyl-nickel halides and alkoxides can be cleaved under mild conditions with triphenylphosphine to give the monomeric 1:1 adducts, XI and XII, whereas π -allylnickel aziridide does not react under comparable conditions.

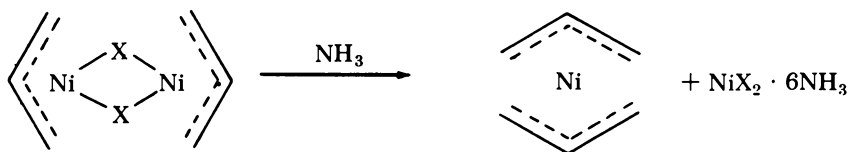
A new reaction observed with π -allylnickel methyl, alkoxides and halides is disproportionation. π -Allylnickel methyl decomposes spontaneously in solution even at -60°C . to bis(π -allyl)nickel, elemental nickel, and presumably transient methyl radicals. The reaction proceeds quantitatively accordingly to the reaction shown below since after removal of elemental nickel by filtration, exactly half of the nickel is found in the filtrate in the form of bis(π -allyl)nickel.



IX



VII



III

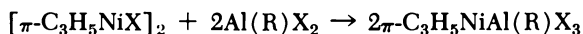
π -Allylnickel alkoxides, VII, disproportionate even in the solid form. The temperature at which the disproportionation reaction proceeds depends on the nature of R; π -allylnickel methoxide is unstable at 0°C ., ethoxide at 25°C ., and phenoxide at about 65°C . If the reaction is performed in a high vacuum system, bis(π -allyl)nickel sublimes, while nickel dialkoxides are obtained in pure form as nonvolatile residues. This reaction thus is useful as a synthetic method for preparing nickel dialkoxides.

π -Allylnickel halides are more stable, and thermal disproportionation is not observed even at higher temperatures. Recently, we found that π -allylnickel halides can be disproportionated easily by treating them in solution with excess gaseous ammonia (2). Bis(π -allyl)nickel and ammonia adducts of nickel dihalides are obtained in quantitative yields and can be separated easily. In fact, the disproportionation reaction represents at the moment the easiest way to synthesize bis(π -allyl)nickel type compounds since as mentioned, all types of π -allylnickel halides can be prepared easily. The advantage of the new method lies in the fact that bis(π -allyl)nickel type compounds can be prepared without prior preparation of organometallic allyl compounds, such as Grignard compounds, which are sometimes difficult to prepare. The disproportionation of π -allylnickel halides has an analog in the chemistry of alkylmercuric halides, some of which disproportionate under the influence of ammonia (12).

Ethylene and Propylene Dimerization with π -Allylnickel Halide Catalysts

In considering dimeric π -allylnickel halides as homogeneous catalysts it should be remembered that solutions of π -allylnickel halides in toluene, for example, show only poor catalytic activity toward olefins like ethylene or propylene. Under forcing conditions of temperature and pressure a slow oligomerization of these olefins to a mixture of dimers, trimers, etc., is observed.

While investigating the catalytic properties of π -allylchromium compounds, it was observed (14) that the catalytic activity of bis(π -allyl)chromium iodides toward olefins increases upon adding alkylaluminum halides. Using this experience, we added ethylaluminum dichloride to the red solution of π -allylnickel chloride in toluene and observed an immediate separation of a red oily liquid from the solution (24, 25). Subsequent investigations showed the red liquid to be the complex π -allylnickel ethylaluminum trichloride (XIII, R=C₂H₅, X = Cl) containing appreciable amounts of the solvent. It is sparingly soluble in toluene owing to its polar character. Complexes of this type are formed quite generally between π -allylnickel halides and aluminum halides or alkyl halides:



III

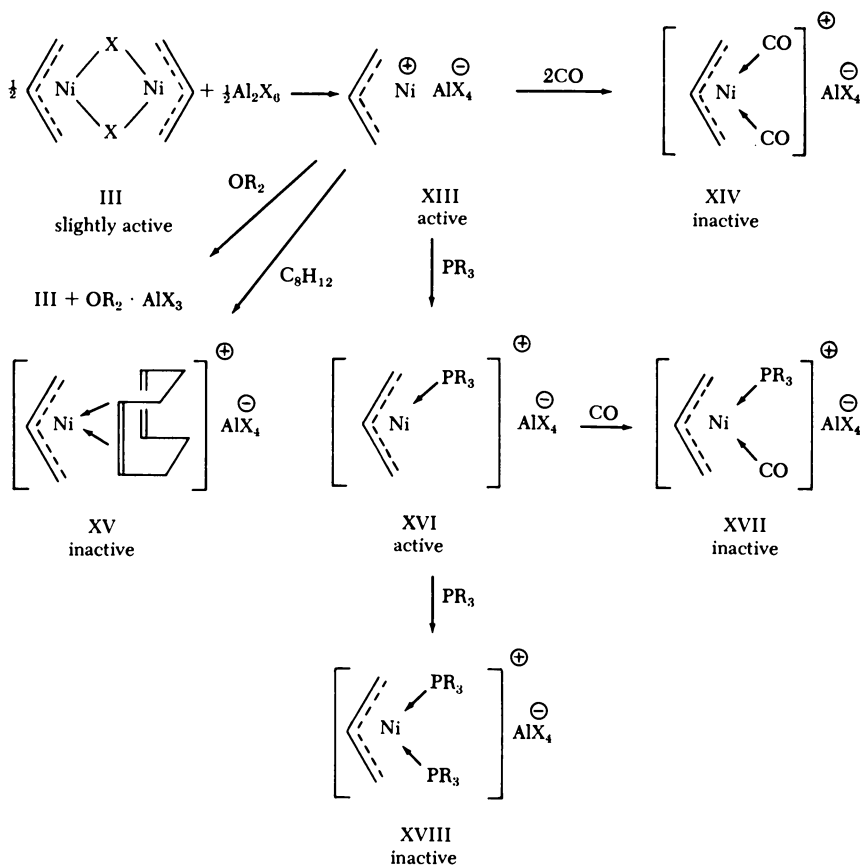
XIII

X = Cl, Br, I

R = alkyl, X

Even as a toluene emulsion, these complexes show catalytic activity towards ethylene and propylene which is several orders higher than that of π -allylnickel halides. Paralleling the increase in catalytic activity, the selectivity of this catalyst is also increased—*i.e.*, the products are mainly ethylene or propylene dimers. The most active catalytic systems for dimerizing ethylene and propylene are obtained by replacing toluene with halogenated hydrocarbons such as chlorobenzene since in these more polar solvents, the complexes XIII are soluble.

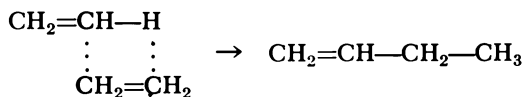
Some experiments designed to obtain information about the nature of the catalytically active species have been carried out (15, 16). Complex formation between π -allylnickel halides and aluminum halides can be followed by the shift of the π -allyl protons in the $^1\text{H-NMR}$ spectrum. By adding n electron donors, such as ethers or amines, the catalytically active complexes, XIII, are decomposed.



The transfer of halide from π -allylnickel halide to aluminum to give a haloaluminum anion results in a strong decrease in the electron density and formation of free coordination positions on nickel. The presence and number of free coordination positions can be demonstrated by reaction with carbon monoxide. The catalytically active complex, XIII, reacts at -40°C . with 2 moles of carbon monoxide to give the inactive XIV which can be isolated. In XIII, there are accordingly two free coordination positions. During catalysis, these positions are presumably occupied by olefins in the form of π -complexes. A stable olefin π -complex, π -allylnickel (π -cycloocta-1,5-diene) aluminum tetrabromide, XV, can actually be isolated by adding cycloocta-1,5-diene to a solution of the active complex, XIII.

By adding 1 mole of an organic phosphine per mole nickel in XIII, the catalytic activity is further increased. This phosphine-modified complex, XVI, reacts at -40°C . with only 1 mole of carbon monoxide to yield an inactive complex XVII. In the phosphine-modified complex XVI, there is accordingly one free coordination position. Catalytic activity disappears also on adding a second mole of a phosphine (XVIII).

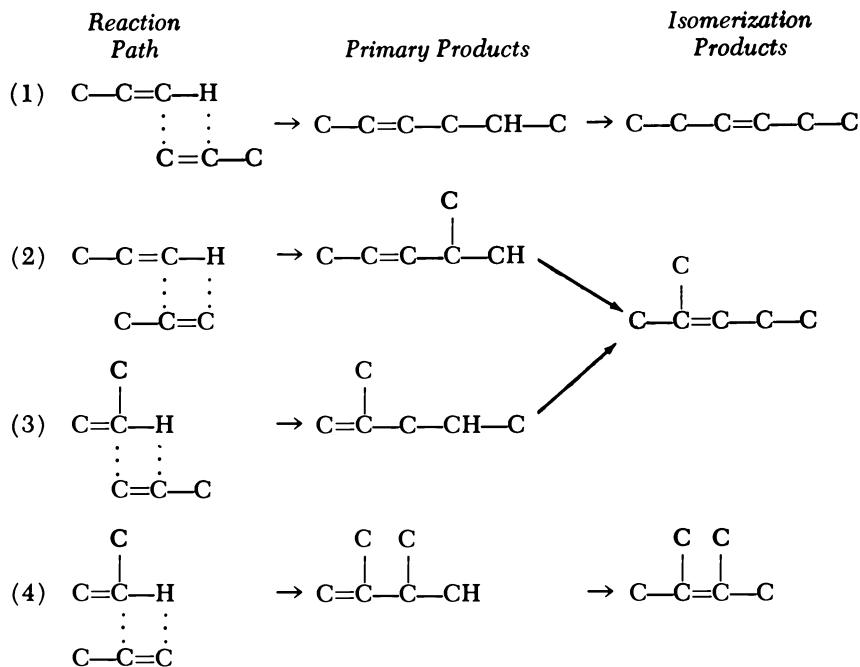
Of prime importance for utilizing the new catalyst was the observation that the products of propylene dimerization with phosphine-modified catalyst system, XVI, are strongly influenced by the nature of the phosphine PR_3 (24, 25). To understand the phosphine effect, it is necessary to examine the dimerization of ethylene and of propylene in some detail. The dimerization of ethylene formally involves the addition of the C-H bond of one olefin molecule across the double bond of a second one:



The ethylene dimerization product should be accordingly 1-butene, but actually a mixture of 1-butene and *cis*- and *trans*-2-butene is obtained. This is because the dimerization catalyst is also an isomerization catalyst. Thus, if 1-butene is brought in contact with the catalyst, it is rapidly isomerized to 2-butene. Upon longer action of the catalyst on 2-butene, it is dimerized to a mixture of octenes, but this reaction is quite slow.

For propylene dimerization, four products can be written (Table II) if only vinylic C—H bonds are considered. In Paths 1 and 2 the C—H bond of the terminal carbon atom is "added" giving rise to two products. If the addition proceeds in the manner of metal hydrides, the product is 2-hexene (Path 1); for acidic-type addition (Markovnikov rule), the product is 4-methyl-2-pentene (Path 2). In Paths 3 and 4, the C—H bond of the middle carbon atom is "added," giving rise to 2-methyl-1-pentene (hydridic-type addition) and to 2,3-dimethyl-1-butene (acidic-

Table II. Propylene Dimerization

Table III. Influence of Phosphines PR_3 on

<i>Reaction Path</i>	<i>Products, %</i>	<i>$\text{R}=\text{C}_6\text{H}_5$</i>	<i>No Phosphine</i>
1	Σn -hexenes	21,6	21,3
2 and 3	$\Sigma 2$ -methylpentenes	73,9	73,2
4	$\Sigma 2,3$ -dimethylbutenes	4,5	5,5
	Σ isomerization products	58,1	29,5
	σ^*	+0,60	—

type addition). Gas chromatographic analysis revealed all of these olefins as products of propylene dimerization. In addition, olefins are found which are obviously isomerization products—namely, 3-hexene, 2-methyl-2-pentene, and 2,3-dimethyl-2-butene.

The influence of the phosphine PR_3 in the phosphine-modified catalyst, XVI, on the distribution of the isomeric C_6 olefins is shown in Table III.

Using the catalysts containing the phosphines PR_3 in the sequence $\text{R} = \text{phenyl, methyl, ethyl, } n\text{-butyl, cyclohexyl, and isopropyl}$, there is a steady increase in the yield of 2,3-dimethylbutenes, from 4 to 68%

and a steady decrease in the yields of *n*-hexenes, from 21 to 2%. In other words, in this sequence of phosphines, the propylene dimerization proceeds more and more by Path 4 (with the C—H bond of the middle carbon atom being added), and less and less by Path 1 (with the C—H bond of the terminal carbon atom being added). This order of the phosphines is roughly comparable with the order of the basicities of phosphines, but it parallels better the σ° values of the organic groups R in the Taft equation (15, 16) (shown in the last row of Table III).

The total extent of isomerization during the dimerization reaction is shown in the fourth row, where the sums of isomerized C₆ olefins are given. The most efficient isomerization catalyst is accordingly the catalyst containing trimethylphosphine (75.8% isomerization products). With tri(isopropyl)phosphine as a catalyst component, little isomerization is observed (3.7%). In this case, 96% of the dimers are primary reaction products.

Table IV contains the distribution of the C₆ isomers using tri(isopropyl) phosphine as a catalyst component (neglecting isomerization). From the distribution of the products it follows that 13% of terminal (sum of *n*-hexenes and 4-methylpentene-2) and 84% of middle (sum of 2-methylpentene-1 and 2,3-dimethylbutene-1) C—H bonds reacted. Similarly, the direction of addition was roughly 80% of the acidic and 20% of the hydridic type. The direction of addition remains roughly in the

Propylene Dimerization at -20°C . and 1 atm.

CH ₃	C ₂ H ₅	<i>n</i> -C ₄ H ₉	<i>c</i> -C ₆ H ₁₁	<i>i</i> -C ₃ H ₇
9,9	9,2	7,1	3,3	1,8
80,3	69,7	69,6	37,9	30,3
9,8	21,1	23,3	58,8	67,9
75,8	52,2	42,7	4,9	3,7
0,0	-0,10	-0,13	-0,15	-0,19

Table IV. Distribution of C₆ Isomers Using Tri(isopropyl) phosphine

Reaction Path	Products of Dimerization	Percent	C—H Bond Reacted	Addition Type
1	<i>n</i> -Hexenes	1.8	terminal	hydridic
2	4-Methylpentene-2	11.0	(1 + 2):12.8%	(1 + 3):18.2%
3	2-Methylpentene-1	16.4		
			middle	acidic
4	2,3-Dimethylbutenes	67.9	(3 + 4):84.3%	(2 + 4):78.9%

proportion 80% acidic to 20% hydridic with the other phosphines mentioned. In other words, the direction of addition is independent of the nature of the phosphines. What does depend on the nature of the phosphines is the proportion of middle *vs.* terminal C—H bonds "added." In one extreme case ($R = i\text{-Pr}$), 84% of middle C—H bonds reacted, and in the other, ($R = \text{C}_6\text{H}_5$), only about 5% reacted (extrapolated value). Within this range, the propylene dimerization at the moment can be directed "at will."

These results show that:

(1) In the course of propylene dimerization, to a first approximation, it is only *one* propylene molecule which is strongly influenced by the nature of the catalyst (and correspondingly of the phosphine).

(2) This propylene molecule is the one whose C—H bond is, in a formal sense, added and not the one on whose double bond the addition takes place.

The dimerization reaction has been carried out under two different conditions. In laboratory experiments, the reaction is conveniently carried out under 1 or less than 1 atmosphere and at a temperature of -20° to -10°C . These relatively low temperatures are necessary to obtain a sufficient concentration of ethylene or propylene in the catalyst solution. The dimerization catalyst for laboratory experiments is usually prepared by mixing, for example, chlorobenzene solutions of a π -allylnickel halide and an aluminum halide (or alkylhalide) in molar ratio of at least 1:1. The phosphine-modified catalyst is obtained by simply adding 1 mole of a phosphine per mole of nickel to the solution of the catalyst. When ethylene or propylene is introduced into the catalyst solution, reaction starts immediately, as evidenced by a sudden rise in temperature. Dimerization is exothermic to the extent of about 28 kcal./mole propylene dimer. Hence, the mixture must be stirred and cooled intensively during the reaction. Under these conditions (Table V), reaction rates of about 6 kg.

Table V. Reaction Conditions for Propylene Dimerization

Pressure, atm.	Temperature, $^\circ\text{C}$.	Reaction Rate kg. Product/gram nickel/hour	C_6 Olefins, %	C_9 and Higher Olefins, %
1	-10° to -20°	6	95	11
15	$+35^\circ$ to $+40^\circ$	13	89	5

product/gram nickel/hour have been realized. The product from propylene consists of up to 95% propylene dimers. For comparison, some data on propylene dimerization on a pilot-plant scale (*vide infra*) are also given. Under a pressure of 15 atm. and temperature from $+35^\circ$ to $+40^\circ\text{C}$., reaction rates of 13 kg./gram nickel/hour are attained with a

catalyst consumption of 50 mg. nickel per kg. product—*i.e.*, up to 30,000 propylene molecules can be chemically changed by 1 molecule of the catalyst. The product consists of 89% of propylene dimers, 9–10% trimers, and 1–2% higher oligomers.

Technical Aspects of Propylene Dimerization

From the viewpoint of possible technical importance of the propylene dimerization, it was of interest to perform the dimerization with larger quantities and in a continuous process. The following method, suitable for scale-up, was evolved for preparing the catalyst solution.

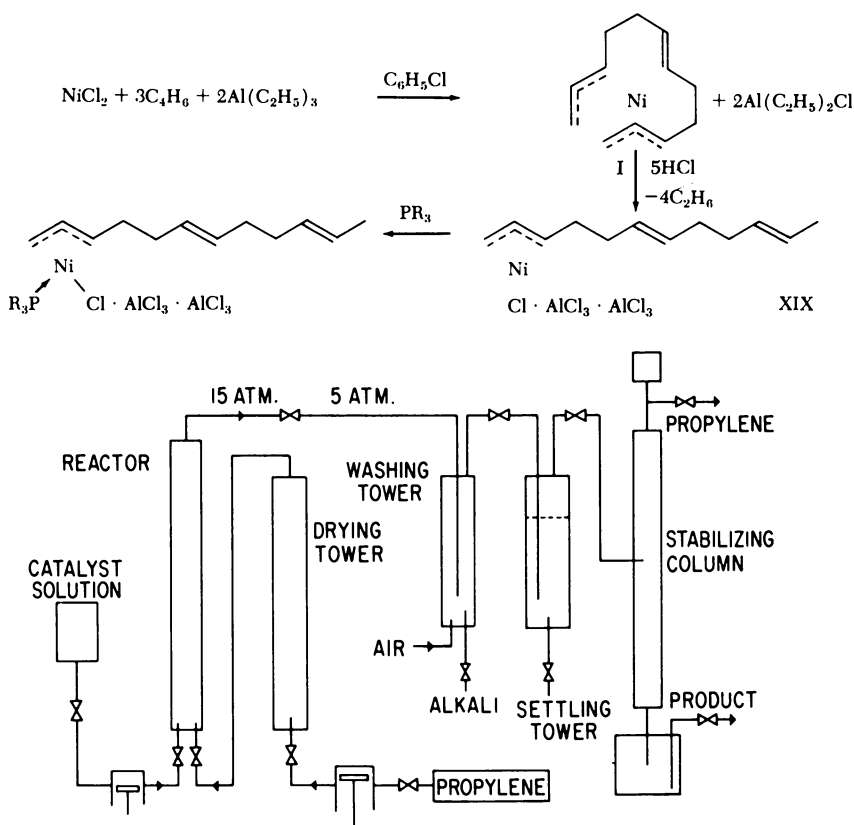


Figure 1. Pilot-plant apparatus for dimerizing propylene

Anhydrous nickel chloride in chlorobenzene suspension is reduced in the presence of excess butadiene with aluminum triethyl. The product is the previously mentioned intermediate, I, of the cyclododecatriene synthesis.

Excess butadiene is pumped off, and gaseous hydrogen chloride is introduced. One π -allyl group in I is cleaved, resulting in a C_{12} - π -allylnickel chloride, XIX, at the same time aluminum chloride as the second catalyst component is formed. Slightly more than 1 mole of the desired phosphine per mole of nickel is now added to the solution. In pilot-plant experiments we used this type of catalyst.

Pilot-Plant Operation

The propylene dimerization on a pilot-plant scale is performed in our institute in the apparatus shown in Figure 1. Liquid propylene is pumped under a pressure of 15 atm. into the reactor through a drying tower containing silica. The reactor is a 15-meter long, double walled tube of 20-liter volume, which is water cooled. The catalyst solution is injected together with propylene at the bottom of the reactor. The catalytic reaction takes place mainly in the first third of the reactor where the temperature rises to 30°–40°C. The product is taken off the top of the reactor, and the pressure is reduced to 5 atm. The product passes through a washing tower, where the catalyst is destroyed with aqueous alkali and air. After passing a settling tower, the mixture is taken to a stabilizing column, where unreacted propylene and product are separated. The capacity of the pilot plant is about 1 ton of propylene per 24 hours.

The following technical aspects of dimeric propylenes obtained with π -allylnickel halide catalysts should be noted:

(1) Mixtures of 2-methylpentenes and 2,3-dimethylbutenes show good properties as antiknock fuel additives in that they raise the octane number in the low boiling ranges of gasoline.

(2) 2-Methylpentenes, which are obtained in about 80% yield, can be used for isoprene production (1).

(3) 2,3-Dimethylbutene, which is obtained in about 70% yield, represents a new and valuable olefin available by a catalytic process. Its dehydrogenation product—2,3-dimethylbutadiene—was once used to produce so-called methyl rubber. The new synthesis of 2,3-dimethylbutene may renew interest in methyl rubber or other synthetic applications of dimethylbutadiene.

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Catalysis at the Atomic Level

Dimerization and Polymerization of Ethylene with Nickelocene and Dibenzenechromium

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Recent developments in catalysis at the atomic level are described. The use of transition metal halides which form intermediate metal π -complexes can promote both the catalytic and stoichiometric coupling of aryl Grignard reagents, the stereospecific coupling of 1,2 disubstituted vinyl groups and the double coupling of ethylene to dimers of butadiene. In the most recent work, nickelocene was decomposed at 200°C. under 600 lb./sq. in. pressure and ethylene thereby selectively dimerized to butene. Similarly, dibenzenechromium was decomposed at 250°C. under 2800 lb./sq. in. pressure, and ethylene was polymerized to a relatively high density polyethylene.

The concept of catalysis at the atomic level involves a new approach to stimulate reaction partly by creating an active metal atom in a favorable environment. The creation of the active zero-valent metal can be accomplished in several ways. It has been shown that homolytic cleavage of σ -bonded aryl metal compounds or homolytic cleavage of an alkyl-metal bond produce an active zero-valent metal. In addition, its creation from the decomposition of either a transitory, unstable, or even stable metal π -complex has been demonstrated. The metal atom thus formed is essential to the catalysis of a given system.

In 1914 Bennett and Turner (1) failed in their attempt to prepare σ -bonded triphenylchromium by refluxing an ethereal solution of phenyl-

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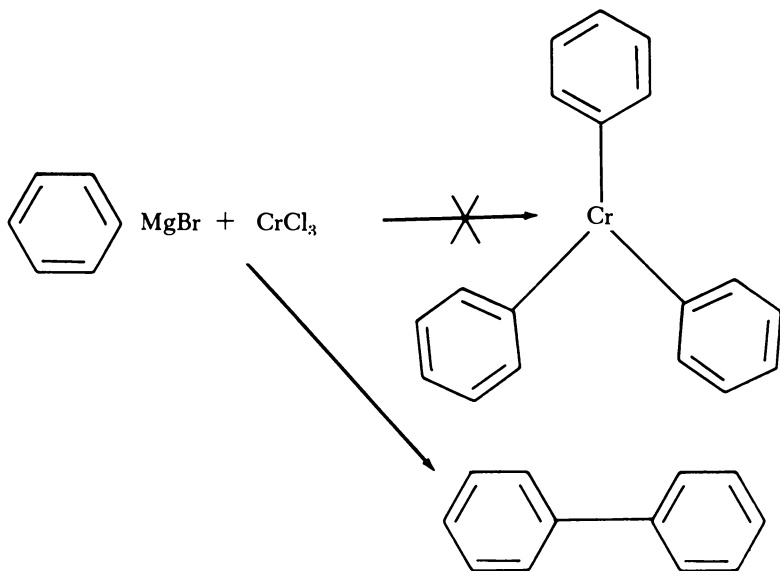


Figure 1. Stoichiometric aryl coupling reaction

magnesium bromide with chromic chloride. They obtained biphenyl in nearly quantitative yield (Figure 1). Largely through the efforts of Zeiss and Tsutsui (6, 14, 15), this simple aryl coupling reaction was expanded, and a mechanism involving intermediate metal π -complexes was proposed (Figure 2).

By varying the reaction conditions, either biphenyl and/or stable metal π -complexes can be isolated. In Figure 2 the divalent state of the metal is used for simplicity. The first step of this stoichiometric aryl coupling reaction involves the formation of a σ -bonded diphenylchromium compound, I. Homolytic cleavage, II, results in the formation of a hypothetical diradical π -complex, III, or a half-sandwich π -complex, IX. Divalent chromium is reduced to zero-valent chromium at this stage, a two-electron reduction. In the final stage of the reaction biphenyl is produced under vigorous reaction conditions at room temperature or by refluxing. Under milder conditions ($-10^\circ\text{C}.$) or in the presence of additional phenylmagnesium bromide, mixed arene π -complexes and biphenyl are isolated.

A mechanism proposed for a catalytic coupling reaction is illustrated in Figure 3. This reaction, reported by Kharasch and Fields (4) involves the formation of biphenyl by adding an organic halide such as bromobenzene to a mixture of phenylmagnesium bromide and a trace of a transition metal halide. The reaction is striking since (a) organic halides do not react with arylmagnesium compounds or with metal halides, and

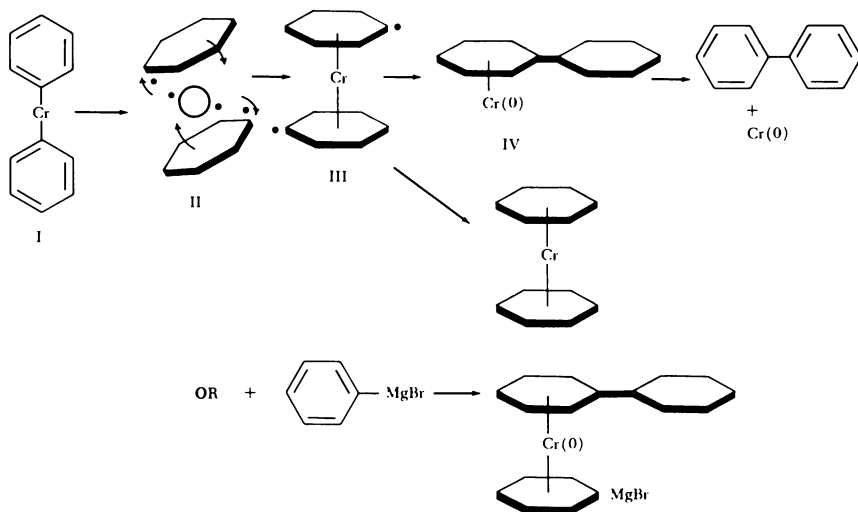


Figure 2. Mechanism of stoichiometric aryl coupling reaction

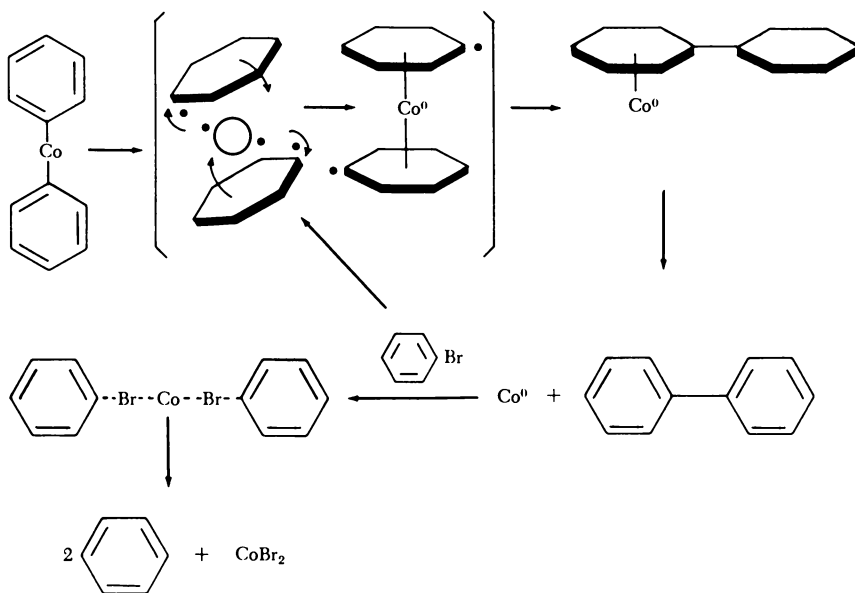


Figure 3. Mechanism of catalytic aryl coupling reaction

(b) metallic halides couple stoichiometrically not catalytically with aryl Grignard reagents. Diphenylcobalt may cleave as described for the stoichiometric mechanism giving biphenyl and an active zero-valent cobalt atom. The cobalt atom can react with bromobenzene, producing

phenyl radicals and cobaltous bromide. The trace quantity of transition metal halide is maintained, and the catalytic role of the transitory radical cobalt π -complex and cobalt metal is sustained. It is not unreasonable that the bromobenzene may attack the cobalt complex directly. Dibenzene-cobalt is not expected to possess any degree of stability since cobalt does not easily accept 12 electrons from the two benzene rings. However, even a transitory existence can be postulated since it has been shown that the biphenyl phenyl groups originate from phenylmagnesium bromide and not from bromobenzene. The over-all concept of catalysis by zero-valent transition metals is also being developed by others (2, 16).

We have thus far assumed that the initial step in all of these reactions involves the formation of a σ -bonded transition metal compound undergoing homolytic cleavage (a σ - π rearrangement) (Figure 4). It was shown that isolable σ -bonded triphenylchromium tetrahydrofuranate could be rearranged to π -dibenzenechromium under heat and reduced pressure (17). We have introduced this mechanism as π -radical hybridization (6). It was proposed that the stabilizing tetrahydrofuran ligands were removed under these conditions, resulting in the homolytic cleavage of the chromium phenyl linkages, creating a radical arene and a freshly prepared radical-type zero-valent chromium atom. In the arene environment, overlap of the vacant $3d$ orbitals and arene π -electrons results in the isolation of the π -dibenzenechromium complex. Thus, the reaction proceeds in the same manner whether we start with the Grignard reagent,

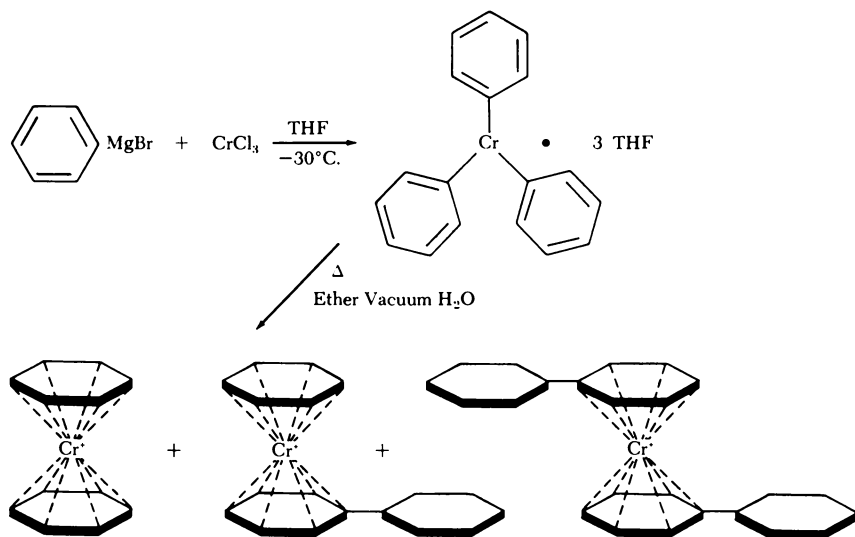


Figure 4. σ - π Rearrangement of triphenylchromium tetrahydrofuranate to diarenechromium π -complexes

as in the aryl coupling reactions or with the isolable first stage. Further, some measure of proof for the existence of a radical homolytic type cleavage was afforded by EPR spectroscopy (11).

Basically, we have shown thus far that we can produce a particular type of zero-valent transition metal atom. It matters little whether we call this an active zero-valent metal atom, a nascent metal, or highly excited reactive metal. The important fact remains that we may use this metal atom for (a) the catalytic formation of biphenyl, and (b) for the formation of various arene π -complexes. The difference is the reaction conditions and general environment surrounding its creation. We can now proceed further into the development of this concept, ultimately involving polymerization.

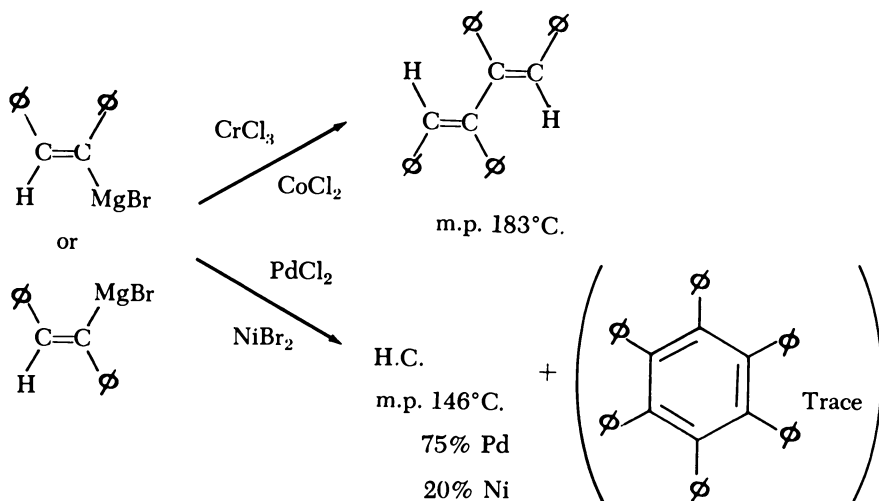


Figure 5. Stereospecific coupling of disubstituted vinyl groups

Creation of an active zero-valent metal also promotes the stereospecific coupling of 1,2-disubstituted vinyl groups. The major inference lies in the fact that variation of the transition metal halide employed results in the formation of either *cis-cis* or *trans-trans* products because of the selective configuration of the transition metal employed. As shown in Figure 5 when either *cis*- or *trans*-stilbenemagnesium bromide reacts with chromic chloride or cobaltous chloride, *cis-cis*-1,2,3,4-tetraphenylbutadiene, m.p. 183°C., is formed. When palladium bromide or nickel bromide is used, the *trans-trans*-1,2,3,4-tetraphenylbutadiene, m.p. 146°C., is formed, along with a trace of hexaphenylbenzene. However, the absolute configuration of these hydrocarbons have not been firmly established. In any event, those transition metal halides exhibiting octahedral d^2sp^3

hybrid orbitals give one configuration, and those exhibiting a square planar dsp^2 or tetrahedral sp^3 hybrid orbitals give a second distinct configuration. It is again postulated that homolytic cleavage of a σ -bonded intermediate promotes the formation of an active metal, in the presence of a stilbene radical; coupling is then influenced by the orbital overlap requirements of the particular metal (Figure 5) (9).

We can carry this idea further in a two-step or double-coupling reaction as shown in Figure 6 (10). Four moles of vinylmagnesium bromide and 1 mole of titanium tetrachloride produce 4-vinylcyclohexene-1 plus 1,4-*trans*-polybutadiene. These products are dimers of butadiene, which in turn is a dimer of ethylene. Hence, we call this a double-coupling reaction.

The first step involves the formation of σ -bonded tetravinyltitanium. Homolytic cleavage produces vinyl radicals and an active titanium atom. Two moles of 1,3-butadiene can be formed, which constitute the first coupling. The 1,3-butadiene thus produced is free to form a π -complex with the active titanium atom. Further cleavage of this unstable complex results in the formation of the isolable products, primarily 4-vinylcyclohexene-1 as well as some 2,6-octadiene, 3-methyl-1,5-heptadiene, and 3-methyl-1,4,6-heptatriene. Many other interesting catalysts at the atomic level have been reported and are reviewed (5, 7, 8).

At this point, it becomes apparent that we need not rely only on the preparation of an intermediate σ -bonded organotransition metal compound to produce an active metal; it may be supplied by the destruction of a π -complex itself. Figure 7 reveals that nickelocene (dicyclopentadienylnickel) may act as the source of an active metal (12).

Selective dimerization has been achieved with some success over boron trifluoride, pure nickel, cobalt over charcoal, nickel oxide, silica, and alumina, trialkylaluminum titanates, and zirconates to name a few. However, in most cases, the catalysts are complex mixtures of several components since the selectivity for butene production is not prominent.

Specifically, we have found a system for selectively dimerizing ethylene to butene. Ethylene was added to a heptane solution of 1 gram nickelocene under nitrogen. Reaction occurred at 200°C., 600 lb./sq. in. over an 18-hour period. The colorless liquid obtained was found by gas chromatography to consist of butene in 89% yield along with *cis*- and *trans*-2-butene and butane. The catalyst in the reaction system was decomposed, and some higher oligomers were also detected in the reaction mixture. When the reaction was conducted at 300°C., the butene content dropped to about 20% owing to isomerization to 2-butene.

Figure 8 shows a mechanism for this reaction. Under these conditions since nickelocene has two unpaired electrons in its antibonding orbitals, it may be attacked by ethylene, releasing the cyclopentadienyl rings and

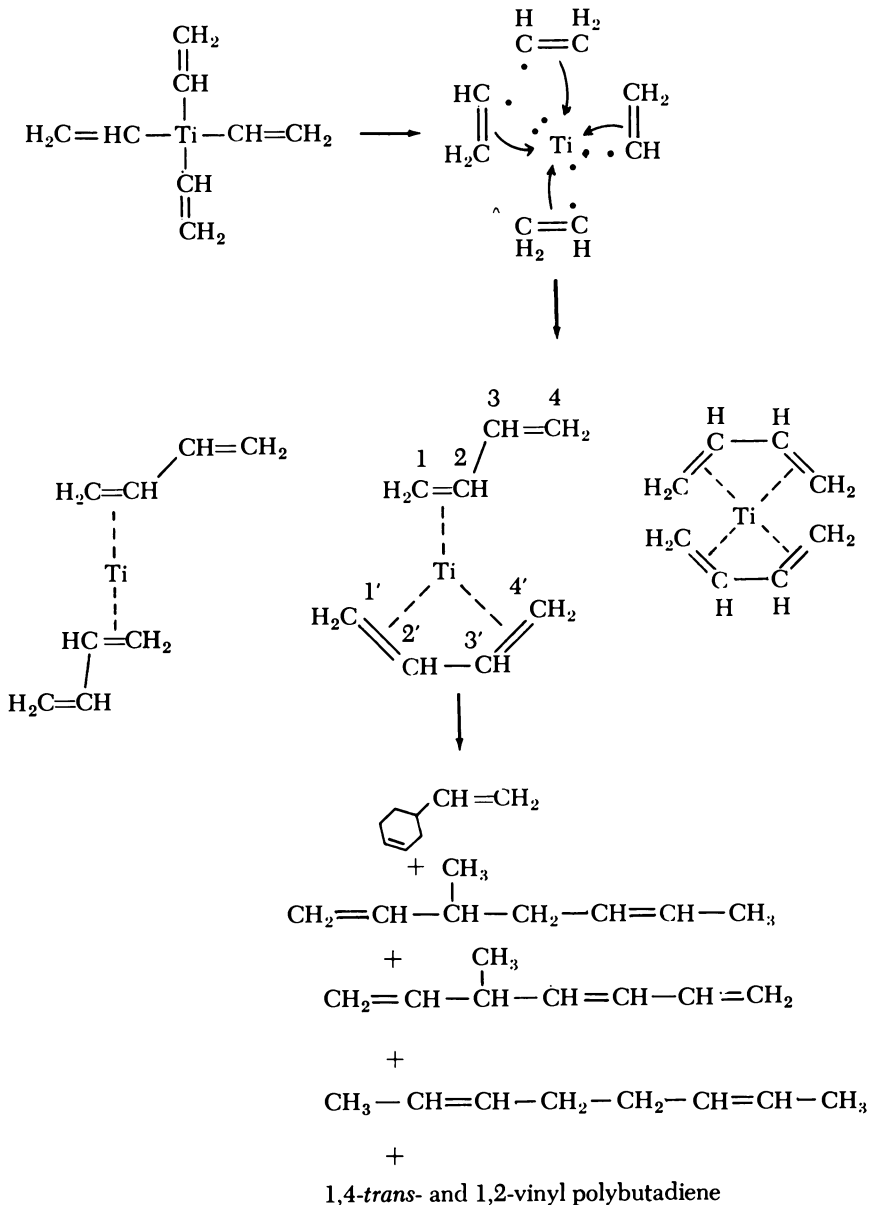


Figure 6. Double-coupling reaction of vinyl groups

forming a π -complex with ethylene, V. Dimerization occurs by the coupling of ethylene on the surface of the nickel metal, VI. Simultaneously, another ethylene molecule attacks the complex, VII, and selectively yields a butene complex by the shift of a hydrogen radical. No further coupling

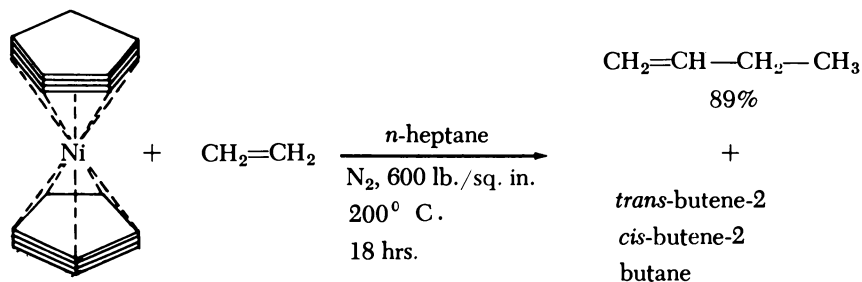


Figure 7. Dimerization of ethylene with nickelocene

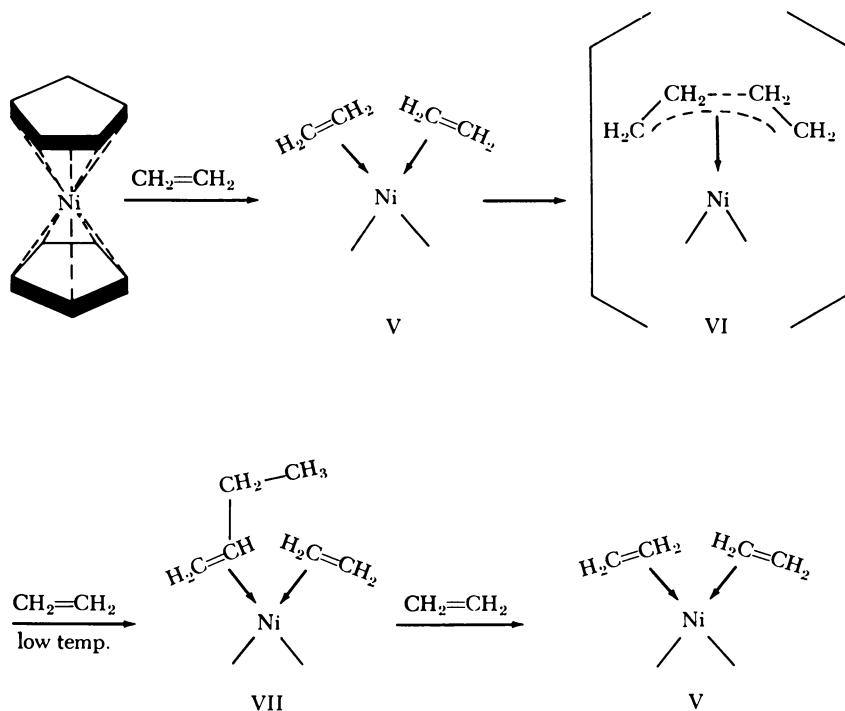


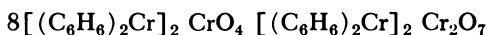
Figure 8. Mechanism for dimerizing ethylene by nickelocene

occurs on the metallic surface because the bulkiness of the dimer prevents the metal orbital overlap with another ethylene molecule. After butene is expelled from the complex by an approaching ethylene, the interaction proceeds in the same manner. Thus, the reaction continues catalytically. Figure 9 shows that at higher temperatures, a biradical propagation reaction may occur soon after the initial interaction of the ethylene molecules. The butene complex does not form under these conditions

because of the retardation of the proton shift by thermal agitation producing higher oligomers. Thermodynamically, it is difficult to obtain pure butene at high temperatures owing to isomerization to 2-butene.

Hagihara and Yamazaki reported the use of dibenzenechromium in the presence of oxygen as an effective catalyst for polymerizing ethylene (3). The results show that polymerization can proceed at temperatures of about 60°C. even at ordinary pressures. They were able to vary the molecular weights of the polymer from 50,400 to 1,660,000 by varying the temperatures (160°C. max.) and by using (SiO₂-Al₂O₃) silica-alumina supports. The polyethylene formed was highly linear in structure, showing strong absorption at 905 cm.⁻¹, indicative of a terminal vinyl polymer.

Efforts were made to determine the structure of the oxygenated dibenzenechromium. Based on analysis, ultraviolet and infrared spectra, the following composition was assigned to the catalyst:



For verification, dibenzenechromium bichromate [(C₆H₆)₂Cr]₂Cr₂O₇ was prepared from the reaction of dibenzenechromium hydroxide and chromic oxide (C₆H₆)₂CrOH CrO₃. The resultant catalyst showed catalytic activity analogous to the original catalyst.

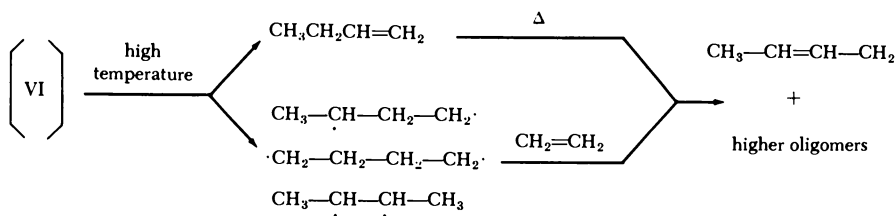


Figure 9. Dimerization of ethylene by nickelocene at 290°C.

It was later reported that the yields and nature (*e.g.*, density, molecular weight and terminal vinyl content) could be altered by varying hydrogen pressure in the oxygenated dibenzenechromium catalyst. This type of catalysis is not considered to be catalysis at the atomic level although dibenzenechromium arene π -complex was employed. The seemingly essential role of freshly prepared zero-valent transition metal is not apparent.

However, if we add ethylene to dibenzenechromium in nitrogen-saturated heptane at 2800 lb./sq. in. and 250°C. for 7 hours, we obtain a notable reaction (Figure 10) (13). It should be noted that under conditions used for the nickelocene catalysis—namely 630 lb./sq. in. at 200°C. for 16 hours, no reaction was indicated. The reaction temperatures cor-

respond to the decomposition temperatures for nickelocene and dibenzenechromium, respectively. The catalyst was found decomposed in the reaction mixture. A white solid polyethylene was formed. According to infrared analysis, the polymer seems to contain only an internal trans double bond (965 cm^{-1}). The density was 0.966 by the density gradient tube method. This value corresponds to 88% crystallinity. The melting point observed under a polarization microscope was 126°C . The intrinsic viscosity measured in Tetralin at 130°C . was 0.99 from which the molecular weight calculated by Tung's equation was 34,000.

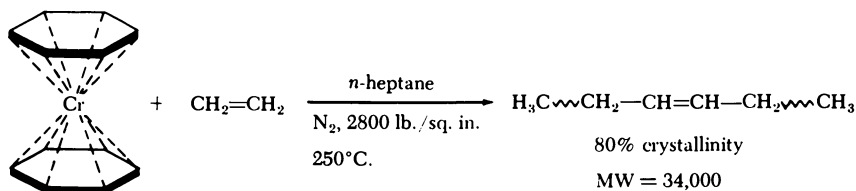


Figure 10. Ethylene polymerization with dibenzenechromium(0)

It appears that the polymerization may proceed by atomic level catalysis since the reaction begins at a temperature close to the decomposition point of dibenzenechromium. The trans double bond in the polymer implies that the double bond was fixed to the catalyst during the propagation reaction and the chain grew from both sides independently. The mechanism which we propose is reviewed in Figure 11. Soon after metallic chromium is formed from the thermal decomposition of dibenzenechromium, the surrounding ethylene molecules start interacting with the vacant d orbitals of the metal to form π -bonding VIII. Since the active chromium shows a strong ability to dehydrogenate organic groups forming chromium hydride, the ethylene ligands form a biradical olefinic chain, IX. Each radical can add additional ethylene molecules assisted by the central metal which can interact with the ethylene π -system, X. Thus, the successive radical propagation continues catalytically, XI to XIII, until the hydrogen radicals from the decomposition of chromium hydride finally terminate the reaction (Figure 11). During the polymerization, the internal double bond is preserved by π -bonding to the catalyst. As a result of the restricted propagation on the metal surface, an unusually high density polyethylene is produced despite a sort of radical-type polymerization.

The mechanisms for dimerizing ethylene by nickelocene and polymerizing of ethylene by dibenzenechromium(0) are of course only speculative, based on the products obtained.

Several factors contribute to the difference in catalysis between nickel (16) and chromium at the atomic level. Presumably, it is caused partly

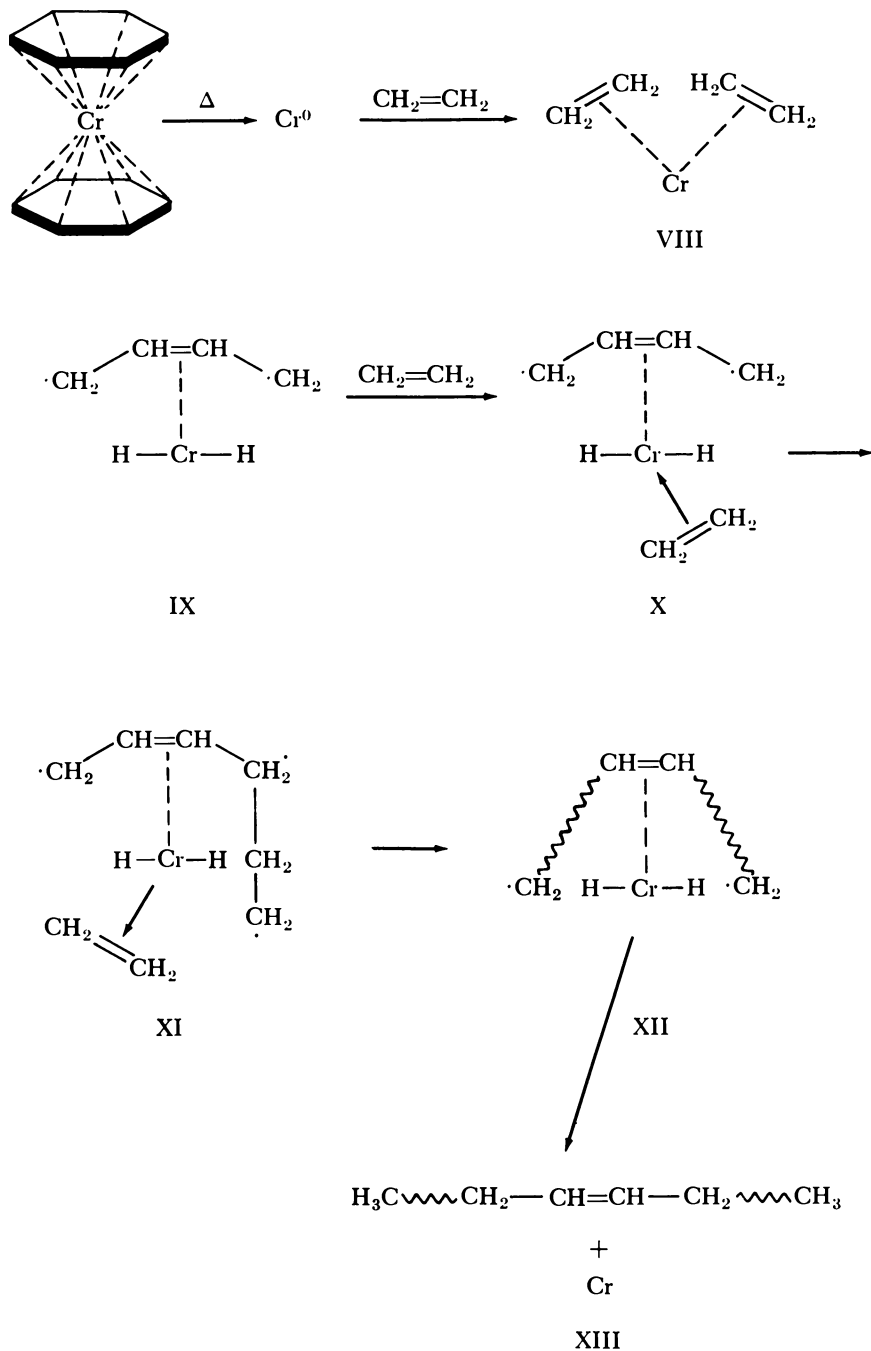


Figure 11. Mechanism of ethylene polymerization with dibenzenechromium(0)

by the difference in electronic configuration and geometry. Zero-valent nickel forms tetrahedral complexes while zero-valent chromium can accept as many as six ligands in an octahedral environment. Thus, the intermediate dimerized chromium complex can couple more easily with additional ethylene molecules. Evidently, the nickel complex breaks as additional ethylene molecules approach the metal perpendicular to the square plane.

Acknowledgment

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