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The Importance of π-Bonded Intermediates in Hydrocarbon Reactions on Transition Metal Catalysts

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The significance of π-bonded intermediates in reactions of hydrocarbons on transition metal catalysts is generally discussed. Mechanisms are briefly reviewed in the light of this theory for the exchange of paraffins, olefins, and aromatics with deuterium, for hydrogenation, dehydrogenation, and isomerization reactions. It is shown that a rational explanation of many apparently unrelated phenomena in these reactions is afforded on the basis of the proposed theory. The close similarity of the reactions of surface intermediates to homogeneous reactions of corresponding π-bonded ligands in transition metal complexes is also emphasized.

The surface atoms in metals seem to possess chemical properties which are in many ways identical with those of the free atoms or ions. By analogy with the bond strengths in corresponding compounds, heats of chemisorption of π-bonded intermediates, and thus catalytic activity and selectivity should be a function of the position of the metal in the periodic table. This concept is discussed with reference to the hydrogenation of benzene and the decomposition of formic acid. Some selectivity and activity sequences for the hydrogenation of acetylene, ethylene, and diolefins are also considered.

INTRODUCTION

Following the discovery of ferrocene and the elucidation of its structure, some ten years ago, the preparation and properties of an enormous number of π-bonded organometallic compounds have been described. More recently, there has been a rapid increase in the number of publications concerning the role of transition metal ions and complexes as homogeneous catalysts for the oxidation, isomerization, hydrogenation, and polymerization of olefins, acetylenes, and dienes. While the catalytic activity of transition metals and their oxides or sulfides for organic reactions has been known for a much longer period, theoretical developments in the heterogeneous field have paid little attention to the significant advances in the homogeneous field. It may well be the case however, that both fields are intimately related and that the ability of individual metal atoms and ions in the surfaces of solids to form π-bonded complexes with organic ligands is the origin of their catalytic activity for many reactions.

The concept of π-bonded intermediates has been advanced in several recent publications (*1–5*) to explain reactions of hydrocarbons with hydrogen or deuterium on metal surfaces. In particular, the exchange of cycloalkanes and alkylbenzenes with deuterium has provided evidence for this theory and progress has been made in characterizing different π complexes, the conditions under which they are formed, and the manner of their reactivity on several metals.

The first purpose of the present paper is to give a more concise but clearer description of mechanisms suggested previ-

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ously and to show that these ideas can be applied generally. The second purpose is to illustrate the relationship between the heterogeneous and homogeneous chemistry of the transition metals. The third is to show that the theory may help to provide an explanation of the sequences of metals with regard to selectivity and activity in several reactions.

MECHANISMS

The π-bond theory suggests that there are two functions of transition metals which are important in catalyzing reactions of hydrocarbons with hydrogen or its isotopes. One of these is the ability to cause stepwise formation of several π complexes as ligands of the same individual metal atom. The range of intermediates depends on the nature of the reactant, the metal, and the reaction conditions. The second function which is essential for the first to operate is the capacity of the surface for the reversible formation of a hydride, so that the complexes can be successively interconverted. The metal and its hydride are thus providing simultaneously an oxidizing and reducing system. This oxidizing and reducing action of the metal and its hydride, respectively, on the surface complexes can be compared with the reduction of π-bonded ligands in organometallic molecules or ions by the action of aluminum hydride or sodium borohydride and their oxidation by hydride-abstracting agents. Many examples of these homogeneous reactions have been described in a recent review by Fischer (*6*).

Reactions of Olefins and Paraffins with Deuterium

The interconversion of monoadsorbed alkyl and 1,2-diadsorbed alkene is of fundamental importance in the reactions of olefins and paraffins with hydrogen or deuterium. Two possible ways of bonding the diadsorbed species to the surface can be considered, either by two carbon–metal σ bonds to two adjacent metal atoms or by an olefinic π bond to one metal atom. It was suggested previously that only the σ-bonded intermediates may be important (*2*) but subsequently, the possible significance of the alternative type of bonding was emphasized (*4*). We now believe that there is a need to restate some of the earlier ideas, giving a more detailed account of reaction mechanisms in order to describe the theory more clearly. Where possible, general mechanistic schemes will be based on the reactions of cyclohexane and its unsaturated derivatives.

While it has been generally accepted that the diadsorbed intermediate is bonded to two metal atoms, such an intermediate may have little or no significance in hydrogenation, dehydrogenation, or exchange reactions. No direct evidence for this type of species has ever been obtained and although the same is true for the alternative postulate of a π-bonded intermediate, the indirect evidence very strongly supports the latter. Chemisorption of olefins as σ-bonded diadsorbed species implies that acetylenes also chemisorb and react via σ-bonded species. Bond (7) has reviewed the deductions which can be made on the basis of the geometry of such intermediates for the chemisorption of ethylene and acetylene on the fcc metals. It follows that acetylene should only adsorb on the longer interatomic spacings, e.g., on the (100) and (110) but not on the (111) faces, whereas ethylene may adsorb on the shorter interatomic spacings. However, acetylene almost invariably selectively retards the hydrogenation of ethylene and this must imply that the same sites and crystal faces are capable of chemisorbing both molecules. Furthermore, the geometric approach leads to the conclusion that the cph metals, ruthenium and osmium, should show considerably lower activity for acetylene hydrogenation than the fcc metals because the number of sites possessing the required geometry are well reduced in the former. However, recent work (*8*) has shown that this is not the case.

Chemisorption of olefins and acetylenes as π complexes does not involve these geometric restrictions and the formation of a di-π-bonded complex from acetylene also explains its preferential adsorption in the presence of ethylene. The bonding in this surface complex is compared with the bonding in $C_2H_2[Co(CO)_3]_2$ in Fig. 1.

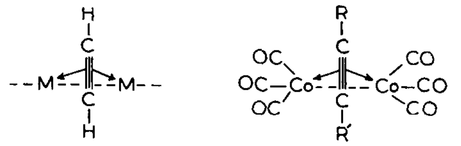


FIG. 1. Corresponding homogeneous and heterogeneous complexes of acetylene.

Since the bonding is the same in both acetylene and ethylene π complexes, both compounds are also expected to chemisorb on the same sites and all the exposed crystal faces may be active.

Very good evidence has been obtained for the participation of π-allylic complexes in the exchange of cycloalkanes with deuterium on palladium films (*2*). The allylic complex and the initial alkyl group are believed to bond to only one metal atom and thus it seems reasonable to assume that the intermediate diadsorbed species is also bonded to the same individual atom. Moreover, current work on homogeneous isomerization and hydrogenation of olefins by transition metal ions clearly indicates that interconversion of σ-bonded alkyl and π-bonded olefin is possible in many systems.

Surface potential measurements also support the view that olefins and acetylenes chemisorb as π complexes. Mignolet (*9*) found that when acetylene and ethylene were adsorbed on nickel films at 20°C positive potentials of 1.00 and 0.83 v, respectively, developed. These values suggest that there is strong donation of charge from the π orbitals of the hydrocarbons to the acceptor orbitals of the metal.

One of the most interesting features of the π-bond theory which arises from experimental observation, is the distinction in reactivity towards hydrogen of olefinic and acetylenic complexes on the one hand and π-allylic, and possibly more delocalized π complexes, on the other. These differences are shown in Fig. 2, where M denotes one metal atom and the asterisk, a site which chemisorbs hydrogen. Interconversion of alkyl and olefinic intermediates occurs in a sterically limited manner which is well illustrated by the exchange of cycloalkanes with deuterium (*2*). Formation of the olefinic complex takes place by loss of a hydrogen atom from the bottom side of the

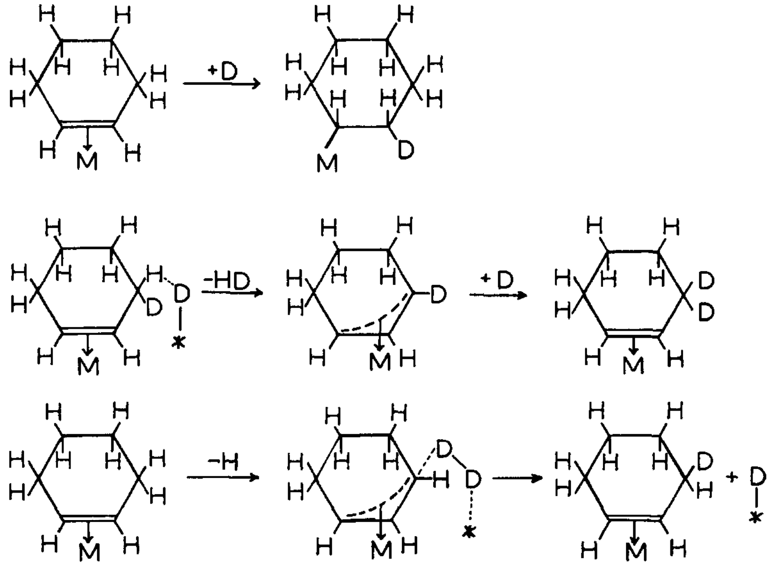


FIG. 2. Interconversion of alkyl, olefinic, and π-allylic complexes.

ring and the reverse step also utilizes a surface "hydrogen" atom (Fig. 2). As a result, this exchange process is restricted to the initial replacement of hydrogen atoms on one side of the ring in cycloalkanes. The exchange of norbornane with deuterium on a palladium catalyst (*10*), where only two hydrogen atoms are initially replaced, provides an interesting test of this idea. Examination of this molecule shows that π-allylic intermediates cannot be formed. The only exchange process which operates is the interconversion of alkyl and olefinic intermediates and the experimental results confirm the view that only *cis* addition of deuterium to the latter is possible. As only two hydrogen atoms are initially replaced, propagation of the exchange reaction must also be forbidden and this may be due to the fact that a bridgehead carbon atom cannot participate in an olefinic linkage. Consequently, these results can also be cited as evidence for the formulation of the diadsorbed intermediate as a π complex.

If only *cis* addition of hydrogen to π-bonded olefin is permitted, the same behavior is also expected with acetylenes when bonded to the metal in the same way as olefins. This is found to be true in the hydrogenation of dimethylacetylene on palladium (*11*) where the sole initial product is *cis*-but-2-ene. A mechanism for this reaction is given in Fig. 3. In this mechanism, *cis*-but-2-ene is formed as a surface complex which may desorb directly or undergo either hydrogenation or isomerization before desorption. Highly selective formation of *cis*-hex-3-ene has also been observed in the hydrogenation of hex-3-yne on a nickel catalyst (*12*).

While π-allylic complexes are also capable of reacting with surface hydrogen atoms there seems to be an additional possibility of direct interaction with molecular hydrogen. In the act of fission of the hydrogen molecule, one atom adds to a terminal carbon atom in the allylic complex from above the planar center and the other chemisorbs on the surface (Fig. 2). If this reaction is possible, the formation of an allylic complex by elimination of a hydrogen atom from the upper side of the ring of the cyclohexene intermediate must also be considered. These reactions which involve molecular hydrogen can take place with the inversion of carbon atoms and a mechanism of this nature is undoubtedly required to explain several features which have been observed in hydrogenation and exchange reactions. Some of these are the initial replacement of hydrogen atoms on both sides of the rings in reactions of cycloalkanes with deuterium (*2*), racemization of optically active paraffins during exchange reactions (*10*), and the hydrogenation of disubstituted benzenes and cycloalkenes (*13*) to the corresponding *cis*- and *trans*-cycloalkanes.

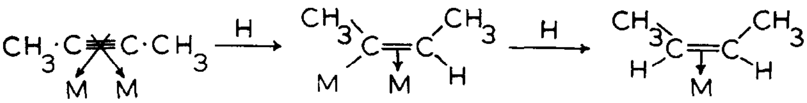


FIG. 3. Mechanism for hydrogenation of acetylenes.

The only obvious reason why olefinic and π-allylic complexes should differ in their reactivity towards hydrogen is that the donor and acceptor orbitals which are utilized in the metal–adsorbate bonds may be different; the allylic species are better classified with ligands such as cyclopentadienyl or benzene. It is commonly believed that the acceptor orbital of the metal atom for olefin–metal bonding is of the σ type, whereas the corresponding orbitals for arene–metal bonding are of the π type. Because of this distinction in bond type, π-allylic complexes may have greater residual bonding activity above the plane of the carbon atoms.

Exchange and Hydrogenation of Benzene

Several experimental observations suggest that benzene is chemisorbed flat on metal surfaces with donation of charge to the metal (*14*, *15*). This supports the view that benzene π bonds to the surface yielding a complex which is similar to arene–metal compounds. At first sight, it may seem surprising that only one metal atom may be mainly involved in the bonding. However, there is the possibility that the electrons acquired by the acceptor orbitals of this atom from the filled π orbital of the ring disperse to some extent to neighboring atoms and throughout the bulk of the crystal. The metal atoms adjacent to the central metal atom of the complex therefore influence the strength of the π bond in a manner which is comparable with the stabilizing influence of electron-accepting ligands such as carbonyl groups, in arene–metal and similar compounds. Dispersion of charge from the surface atoms to the bulk of the metal may be a factor of general importance in assisting the formation of π complexes from hydrocarbons.

The mechanism of benzene exchange with deuterium is of interest, if activation of the aromatic ring through π complexing is important. Addition of a deuterium atom must be the initial step, followed by elimination of the hydrogen atom from the resulting sp^3 hybridized carbon atom. Since the molecule is adsorbed flat on the surface, addition of deuterium must occur either to the top or bottom of the ring followed by elimination from the bottom or top, respectively. These mechanisms are compared with the reversible reduction of the benzene manganese tricarbonyl cation (*16*) in Fig. 4. The behavior of the aromatic ring is, therefore, similar to that of allylic complexes, in that reaction with molecular hydrogen appears to occur. The same intermediates must be involved in exchange and hydrogenation, with successive formation of 1,3-cyclohexadiene and cyclohexenyl complexes from the cyclohexadienyl intermediate. In contrast with the mechanism of exchange, hydrogenation does not require interaction with a hydrogen molecule, but can occur by successive addition of hydrogen atoms. The disproportionation of cyclohexenes and cyclohexadienes on metal surfaces demonstrates that simultaneous oxidation and reduction of π complexes is possible, and a similar disproportionation has been noted (*17*) in the preparation of $(PdCl\cdot\pi\text{-}C_6H_9)_2$ from cyclohexene and palladous chloride. While simultaneous hy-

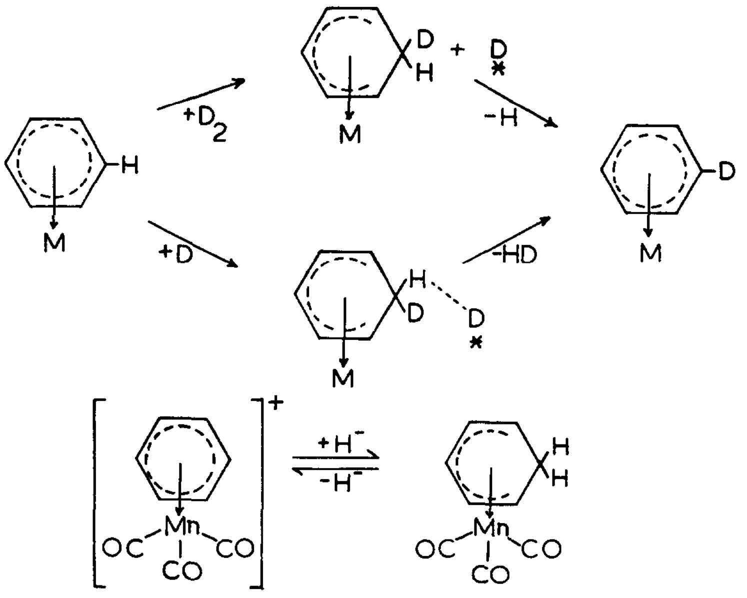


FIG. 4. Mechanisms for exchange and hydrogenation of benzene.

drogenation and dehydrogenation of surface species is readily observed with six-membered rings, because aromatic hydrocarbons are stable compounds, it is possible that this type of surface reaction is quite general with other cyclic and acyclic olefins and dienes (*18*).

Isomerization of Olefins

The chemisorption of olefins as π complexes suggests two mechanisms for double-bond isomerization, namely interconversion between olefinic and alkyl intermediates, and interconversion between olefinic and π-allylic complexes. These mechanisms are shown in detail for the *n*-butenes in Figs. 5(a) and 5(b), respectively. Although both mechanisms may occur simultaneously, their relative importance should depend on the metal and the experimental conditions. The interconversion of olefinic and π-allylic intermediates may be less important at low temperatures for most metals, except palladium. This follows from the

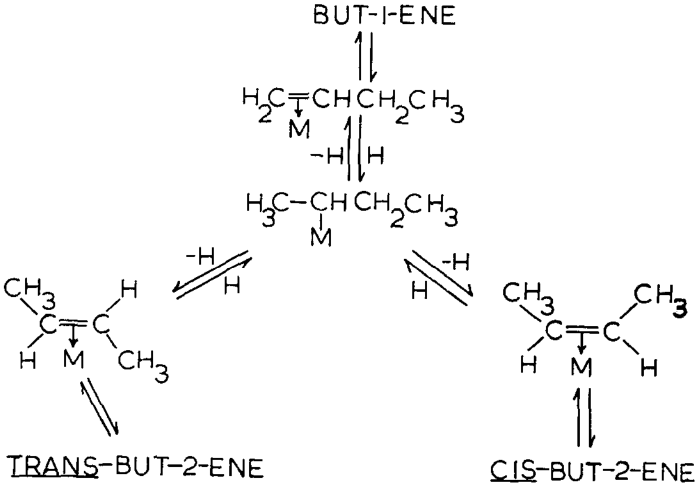


FIG. 5(a). Alkyl reversal mechanism for the isomerization of the *n*-butenes.

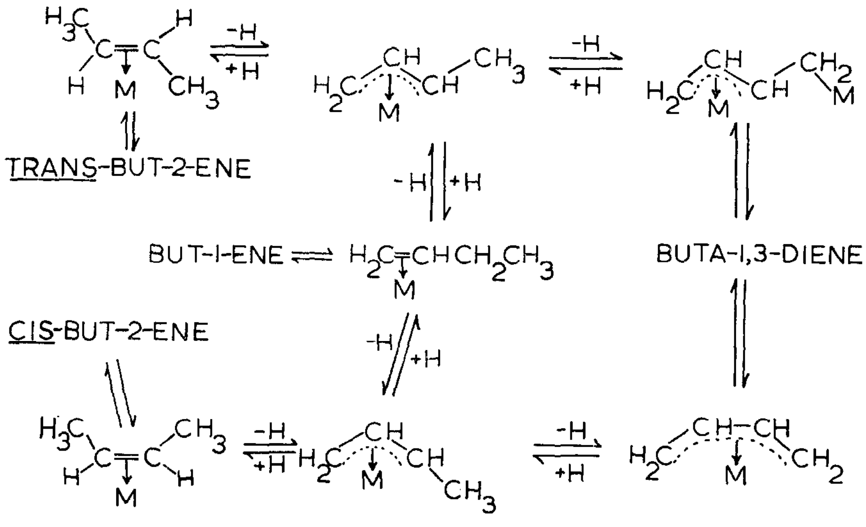


FIG. 5(b). Mechanism for the isomerization of *n*-butenes involving π-allylic intermediates.

observation that π-allylic complexes play an important role in exchange reactions of cycloalkanes with deuterium on palladium (*2*) but are relatively insignificant in the same reactions on platinum, nickel, and rhodium at ambient temperatures. The exchange studies also showed that, with increasing temperature, π-allylic complexes participate to a greater extent in the surface processes. At low temperatures and high hydrogen pressures, the results of isomerization of the *n*-butenes may therefore reflect the characteristics of the mechanism of isomerization by alkyl reversal. Considering this mechanism [Fig. 5(a)], it is obvious that if desorption of butenes is not rate-controlling, the rates of reversal of the *sec*-butyl group will determine the relative proportion of the but-2-enes formed from but-1-ene. If the activated complexes in these steps resemble the resulting π-complexed but-2-enes, then the strengths of adsorption of the latter will influence their rates of formation. Measurements have shown that *cis* olefins form more stable π complexes with Ag^+ ions than the corresponding *trans* isomers (*19*). The order of stabilities of corresponding olefinic complexes on metal surfaces is probably the same and thus preferential formation of *cis*-but-2-ene might be expected initially when but-1-ene is isomerized by the mechanism of alkyl reversal. These conclusions are supported by the observations that when pent-1-ene is hydrogenated on nickel catalysts (*12*) under conditions where π-allylic complexes are likely to be of no importance, *cis*-pent-2-ene is formed well in excess of *trans*-pent-2-ene.

The 1-methyl-π-allyl complexes shown in Fig. 5(b) are geometric isomers. There is little that can be said about their relative stabilities except that the *syn* isomer of the corresponding complexes with cobalt tricarbonyl is converted to the *anti* isomer by heating (*20*), which suggests that the latter is more stable. Consequently, a marked preference for the formation of *cis*-but-2-ene is not expected in but-1-ene isomerization by this mechanism [Fig. 5(b)]. An interesting feature of the interconversion of olefinic and π-allylic complexes is that it cannot give rise directly to *cis–trans* isomerization. The observation that both *cis*- and *trans*-but-2-ene isomerize almost exclusively to but-1-ene at 375°C in the absence of hydrogen on a silver catalyst (*21*) demonstrates the validity of this conclusion, and supports the view that π-allylic complexes are important intermediates in these and other reactions of olefins at high temperatures on metal surfaces.

Hydrogenation of Buta-1,3-diene

The C_4H_7 complexes [Fig. 5(b)] may dissociate readily to adsorbed *syn* and *anti* forms of buta-1,3-diene and the reverse processes of hydrogen addition constitute mechanisms for the hydrogenation of the diolefin. The bonding in the *syn* complex may be compared with that in butadiene iron tricarbonyl where the π electrons of the butadiene molecule are apparently fully delocalized. The adsorption of the *anti* form involves both σ- and π-bonding to adjacent metal atoms. According to Crawford and Kemball (*3*), the benzyl intermediate in the reaction of toluene with deuterium on nickel surfaces is also bonded to the surface in a similar manner.

The complex nature of the mechanisms of hydrogenation of buta-1,3-diene is illustrated by the different distributions of mono-olefins obtained on different metals. Meyer and Burwell (*22*) found that a palladium catalyst at 40°C gave 53.2% but-1-ene, 42.0% *trans*-but-2-ene, and 4.8% *cis*-but-2-ene. On the other hand, a gold catalyst at 200°C gave 70% but-1-ene, 13% *trans*-but-2-ene, and 17% *cis*-but-2-ene (*23*). The isomerization of but-1-ene on this catalyst under the same conditions also gave the same relative proportions of but-2-enes. Meyer and Burwell believe that buta-1,3-diene is chemisorbed mainly in the *anti* configuration as a π complex which undergoes both 1,2 and 1,4 addition of hydrogen atoms. Predominant adsorption of the buta-1,3-diene in the *anti* configuration seems reasonable as some 95% of the molecules adopt this form in the gas phase (*24*). The mechanisms given in Fig. 5(b) then provide a satisfactory explanation for the results obtained on the palladium catalyst. It may be noted that direct formation of a π-allylic complex in the chemisorption of buta-1,3-diene is postulated. Similar reactions occur in the homogeneous field, such as the formation of isomeric 1-methyl-π-allyl cobalt tricarbonyls from buta-1,3-diene and cobalt carbonyl hydride (*20*).

However, the markedly different distributions of products obtained on the gold catalyst suggest that the mechanism of hydrogenation in this case may differ considerably from that shown in Fig. 5(b). The high yield of but-1-ene indicates that 1,2 addition of hydrogen atoms predominates so the route to π-allylic complexes may be less direct on this metal. Although the diolefin may still adsorb mainly in the *anti* configuration, the bonding in the surface complexes must be different on palladium. It is possible that either one or both of the olefinic functions independently react with a separate metal atom without the direct formation of a π-allylic derivative (Fig. 6). Addition of the first hydrogen atom to the terminal carbon atom gives a σ-bonded butenyl intermediate which on further addition of hydrogen can only give but-1-ene. Before this occurs, there may be partial conversion of the σ-bonded butenyl complexes to the corresponding π-bonded intermediates so that some but-2-enes are formed directly. The mechanism for but-1-ene isomerization (Fig. 6) also includes the σ-bonded butenyl group as an essential intermediate in the conversion of the olefinic complex to the corresponding π-allylic derivatives. The intervention of this σ-bonded species in the interconversion of olefinic and π-allylic complexes may be necessary to account for the same distribution of but-2-enes obtained from the hydrogenation of buta-1,3-diene and the isomerization of but-1-ene. As distinct from the mechanism in Fig. 5(b), its inclusion allows the possibility of direct *cis–trans* isomerization of the but-2-enes in addition to double-bond shift.

ACTIVITY AND SELECTIVITY

The concept of π-bonded intermediates in catalytic reactions suggests that the chemical properties of individual surface atoms in metals may be of importance in catalysis, rather than bulk properties. If this is true, an explanation of the sequence of activities or selectivities of different metals for a particular organic reaction may be found by comparing the strengths of the metal–ligand bond in appropriate organometallic compounds where the ligand is identical with the postulated surface intermediate. Examples already exist which encourage the belief that correlations of this type may have widespread sig-

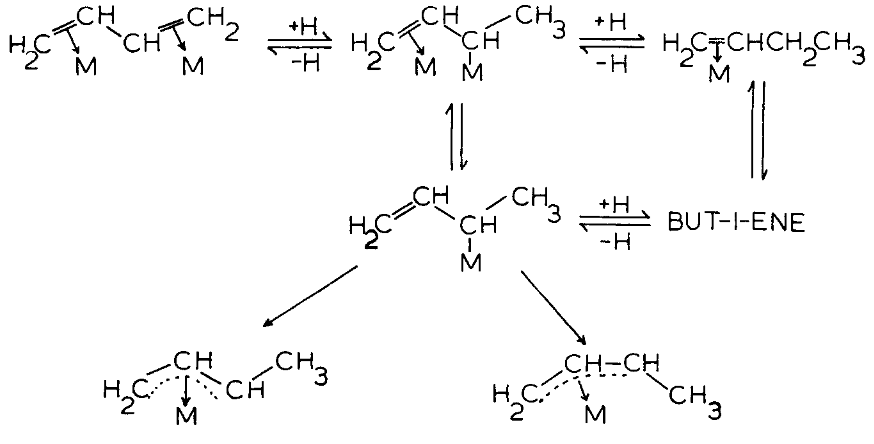


FIG. 6. Mechanism for the hydrogenation of buta-1,3-diene.

nificance. Roberts (*25*) has shown the existence of a relationship between the heats of chemisorption of oxygen and the heats of formation of the corresponding oxides. Similarly, the activities of metals for formic acid decomposition (*26*) have been expressed as a function of the heats of formation of the metal formates. The application by Dowden (*27*) of crystal field theory to explain the catalytic behavior of transition metal oxides also illustrates the advantages of treating chemisorption from the point of view of compound formation.

Although there is as yet little quantitative information regarding the strengths of π bonds in organometallic compounds, some general trends have been established. The stabilities of compounds such as the *bis*-cyclopentadienyls of a particular transition series are very dependent upon the total number of electrons in the valency shell of the metal atom. Similar variations in bond strengths of π-complexed intermediates on surfaces of metals in a particular series might also be expected. There is, however, an important distinction between the bonding involved in compounds and in corresponding surface complexes. In the former, the molecular orbitals are limited to definite boundaries, whereas in the latter they include the surface complex and the whole of the metal crystallite. Consequently, the charge acquired by a surface atom from the donor orbital of the ligand may be partly dispersed through the bulk of the metal. This would permit the electron content of the valency shell of the surface atom to vary to some extent in order to meet the requirements for optimum strength of π-complexing. The differences in stabilities of a particular surface complex with metals of the same transition series may therefore be less marked than differences in bond strengths of the corresponding compounds.

There is often a considerable increase in bond strengths in corresponding organometallic compounds as the atomic number of metals in the same group increases. For example, the stabilities of ferrocene, ruthenocene, and osmocene increase in that order and a similar trend is observed with olefinic complexes of the general formula $(C_2H_4)_2M_2Cl_4$ where M is nickel, palladium, or platinum. The increase in stabilities is probably due to increased donation from the π orbitals of the ligands to acceptor orbitals of the metal. This effect may be associated with a change in the degree of ligand field splitting of the degenerate *d* orbitals as the atomic number increases. Orgel (*28*) states that the energy difference between the t_{2g} and e_g orbitals in an octahedral field increases by as much as 30% from the first to the second transition series and by a similar amount from the second to the third.

Where solid metals are of concern, the crystal structure should have some influence on the type of ligand field splitting of the *d* orbitals of the surface atoms, but the degree of splitting should also vary with atomic number. Such a variation in atomic properties is likely to have a significant influence on the strengths of bonds between intermediates and metal surfaces and the stabilities of a particular complex should change systematically for metals in the same group or subgroup.

It follows from the above arguments that the strength of binding of a particular intermediate to the surface depends upon the position of the metal in the periodic table, and this should be an important factor in determining activity and selectivity in several reactions. In order to provide a valid test for this theory, only metals which have the same crystal structure should be considered. It is fortunate that the metals of subgroups $VIII_2$ and $VIII_3$, which are widely used as catalysts all possess the fcc structure.

The significance of the position of the metal in the periodic table is discussed in the following sections in reference to some well-known reactions.

Hydrogenation of Benzene

The relative activities of several silica-supported metals for the hydrogenation of benzene at 100°C (*29*) are given in Table

TABLE 1
RELATIVE ACTIVITIES OF SILICA-SUPPORTED METALS FOR BENZENE HYDROGENATION AT 100°C [log k (Rh) = 0]

Fe	Co	Ni
−2.3	−1.1	−1.2
Ru	Rh	Pd
−0.1	0	−0.2
Os	Ir	Pt
—	—	+0.4

1. There is clearly a systematic increase in activity with increasing atomic number for metals in the same subgroup. When corresponding metals of subgroups $VIII_2$ and $VIII_3$ are compared, the differences in activities are small although the metals of the former subgroup are slightly more active. Anderson and Kemball (*30*) also observed that in the reaction of benzene with deuterium on metal films, the ratio of the rates of hydrogenation and exchange increase from nickel to palladium to platinum.

These systematic trends can be interpreted in terms of the mechanisms given in Fig. 4. Certain additional items of information concerning nickel catalysts are also relevant in this context. First, benzene exchanges with deuterium without undergoing hydrogenation on nickel films at lower temperatures (*30*). Secondly, Selwood (*31*) has observed that cyclohexene dissociates to give a stable C_6H_8 complex on a bare nickel surface at room temperature and that the system must be heated before further dissociation occurs. These observations suggest that the cyclohexadienyl complex is unstable relative to chemisorbed benzene or 1,3-cyclohexadiene.

In the following mechanism for exchange and hydrogenation of benzene, steps (1, 3), and possibly (4) are believed to be slow compared with step (2).

$$C_6H_6 \underset{-H\ (2)}{\overset{+H\ (1)}{\rightleftharpoons}} C_6H_7 \underset{-H\ (4)}{\overset{+H\ (3)}{\rightleftharpoons}} C_6H_8$$

The slow step in exchange is reaction (1), whereas the slow step in hydrogenation is reaction (3). Since the rate of hydrogenation is a function of the rate of addition of hydrogen to the cyclohexadienyl complex, the lifetime of this species is an important factor. The more labile the cyclohexadienyl complex, the more readily will it dissociate back to benzene, and on nickel films dissociation is so rapid at low temperatures that further addition of a hydrogen atom is prevented. The cyclohexadienyl complex increases in stability from nickel to palladium to platinum and consequently, the rate of hydrogenation and the ratio of the rates of hydrogenation and exchange increase in that order. The bond strength in the benzene complex should also increase with atomic number of the metal and this may also result in more rapid formation of the cyclohexadienyl complex.

Hiroto (*32*) has observed that the exchange of p-xylene with deuterium oxide occurs on alumina-supported but not on silica-supported nickel. This difference is probably due to the electron-accepting properties of the alumina affecting the metal with a consequent increase in donation of electrons from the π orbitals of the ring to the acceptor orbitals of the metal. Moreover, the effect of the support was more pronounced at low metal concentrations, which is not unlikely if enhanced donation of charge from benzene to the metal helps to activate the molecule for exchange.

Selectivities in Acetylene and Diolefin Hydrogenation

Wells (*33*) has recently summarized selectivities for the hydrogenation of acetylene and some diolefins on the noble Group VIII metals. Selectivity was defined as the ratio of the yield of mono-olefin to the total yield of olefin and paraffin and some values of this parameter for the reaction of acetylene, allene, and buta-1,3-diene, respectively, on alumina-supported metals are reproduced in Table 2. Invariably, selectivity decreases markedly down each subgroup, and with the exception of iridium, which shows anomalously low values, there is a systematic decrease from right to left across the periodic table.

TABLE 2
Selectivities in Hydrogenation Using the Noble Group VIII Metals Supported on Alumina

Acetylene			Allene			Buta-1,3-diene		
Ru	Rh	Pd	Ru	Rh	Pd[a]	Ru	Rh	Pd
0.82	0.93	0.95	0.84	0.92	1.00	0.73	0.92	1.00
Os	Ir	Pt	Os	Ir	Pt	Os	Ir	Pt
0.67	0.22	0.83	0.73	0.36	0.89	0.69	0.25	0.81

[a] Pumice supported.

With doubly unsaturated hydrocarbons it is possible to obtain π complexes which contain two metal–ligand bonds. Consequently, it would be expected that these compounds will be more strongly adsorbed than the corresponding olefins. Thus acetylene and diolefin can effectively prevent the readsorption of mono-olefins after the latter have been eliminated from the surface. It follows that initial hydrogenation of doubly unsaturated molecules to paraffins takes place during one sojourn of the hydrocarbon species on the surface and is not due to readsorption and further reaction of olefinic products, although this may be important during the latter stages of the reaction (*33*). Selectivity is therefore a function of the ratio of the rate of desorption of olefins and the rate of further addition of hydrogen to adsorbed olefins. Since the rate of desorption of the olefin decreases with increasing strength of adsorption, selectivity should likewise decrease in the same direction. It can be concluded, therefore, that the stabilities of olefinic complexes increase down the periodic table. There should also be an increase in bond strength corresponding to a decrease in selectivity from right to left across the table if the above postulates are correct. Previously determined heats of adsorption of ethylene on metals (*34*) are in agreement with this view.

The Decomposition of Formic Acid

The reciprocal of the absolute temperature T_r, at which the logarithm of the rate of decomposition of formic acid attains a value of —0.8 mole/site^{-1} sec^{-1} has been measured for various supported metal catalysts (*35*). These values are plotted as a function of the transition series number in Fig. 7. Apart from the Group IB metals, the rates increase markedly for corresponding metals from the first to the third transition series. It has been shown previously (*35*) that these increases in rates are due to a decrease in the heat of adsorption when the kinetics approximate to zero order, and that a decrease in rate is also caused by a decrease in the heat of adsorption when the kinetics approximate to first order, as on silver and gold. There is, therefore, a general decrease in heats of adsorption on passing from corresponding members of the first transition series to those of the third. The relationships between $10^3/T_r$ and series number are linear and virtually parallel for Subgroups $VIII_2$ and $VIII_3$. This emphasizes that there is a systematic variation in activity both across and down the periodic table, the trend down the table being the more important.

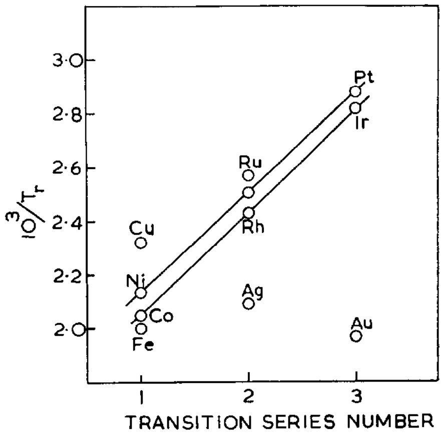
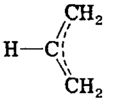
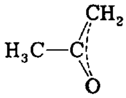
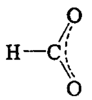


Fig. 7. Activities of metals for the decomposition of formic acid. T_r is the temperature at which log(rate) = —0.8 mole site^{-1} sec^{-1}.

The dependence of activity on the position of the metal in the periodic table suggests that the intermediate involved in the decomposition is the formate radical, covalently bonded to the metal, in agreement with the conclusions of Eischens (*36*). Moreover, the complex is probably of the π type bonded to one metal atom so that there is a close comparison with π-allylic derivatives. Additional support for this formulation is provided by the evidence obtained by Kemball and Stoddard (*37*) that a triadsorbed species is important in the catalytic exchange of acetone with deuterium on metal films. The following intermediates may be compared:







where a methylene group is successively replaced by an isoelectronic oxygen atom. The electronegativity of the oxygen atoms will markedly affect the degree of donor and acceptor interaction of the π orbitals in the formate radical with the metal orbitals. Transfer of charge from the metal to the formate group is believed to be of major importance in determining bond strengths whereas donation from ligand to metal is thought to be decisive in stabilizing bonds between π-complexed hydrocarbons and surface atoms. Thus the strongest bonding of the formate group is found with the metals of the first transition series while hydrocarbons appear to form most stable π complexes with the members of the third series. The formate complex may, therefore, have considerable ionic character, which together with the bond strength, decreases as the atomic number of corresponding metals increases. This interpretation is supported by the conclusions of Eischens and Pliskin (*38*) that complexes of the carboxylic acids with platinum have a higher degree of covalent bonding than the corresponding complexes with nickel.

Rates of Hydrogenation of Ethylene and Acetylene

The relative activities of various metals for the hydrogenation of ethylene (*39, 29*) are summarized in Table 3. It can be seen that the second row metals possess higher activities than those of the first or third series. A value for osmium is absent, but recent work (*33*) has shown that this metal is somewhat less active than ruthenium. The second row metals are also the most reactive for acetylene hydrogenation (*40*). The higher activity of the second row metals is unexpected if the strength of chemisorption of ethylene and acetylene control the rate of hydrogenation and therefore this factor must be of little importance. This conclusion is also supported by the observation that the activation energies for ethylene hydrogenation are independent of the metal (*29, 39*). It is possible that the rate-controlling step in these reactions is the rate of dissociative adsorption of hydrogen on surfaces which are already substantially covered with hydrocarbon species. The invariance of the activation energies for hydrogenation may therefore be due to the fact that the differences in the initial heats of adsorption of hydrogen on these metals are quite small, and would be even less on surfaces already well-covered with hydrocarbon species.

TABLE 3

Relative Values of the Logarithms of the Specific Activities of Metals for Ethylene Hydrogenation at 0°C

[log k_s(Rh) = 0]

Silica-supported metals			Metal films
Fe	Co	Ni	Ni
−3.4	−2.1	−1.5	−2.5
Ru	Rh	Pd	Pd
−0.3	0.0	−0.9	−0.8
Os	Ir	Pt	Pt
—	−2.0	−1.5	−1.65

Conclusions

While the theory outlined in the foregoing sections is only qualitative, it may help to serve as a guide towards a better understanding of activities and selectivities of different metals for catalytic reactions. However, there are still many details of catalytic behavior which are peculiar to the individual metals concerned and bear no relationship to their position in the periodic table. For example, palladium (*2*), cobalt (*41*), and iron (*18*) films readily convert olefinic complexes to π-allylic derivatives. In reactions of olefins and paraffins where there is the possibility of forming both types of intermediates, the order of importance of π-allylic complexes on different metals appears to be:

$$\mathrm{Fe} > \mathrm{Pd} > \mathrm{Co} > \mathrm{Ni} \sim \mathrm{Pt} > \mathrm{Rh}.$$

On the other hand, approximately the reverse order of activities is observed in promoting the exchange of cycloalkanes and other paraffins with deuterium (*18, 41, 42*). This suggests that when the bonding orbitals of the surface atoms are highly appropriate for the formation of π-allylic complexes they are less suited to the dissociative chemisorption of paraffins as alkyl groups and hydrogen atoms which are both σ-bonding entities. There is no obvious explanation why there should be this apparent conflict between σ- and π-bonding characteristics of atomic orbitals of different metals, but it may be noted that palladium forms π-allylic complexes more readily in homogeneous reactions than nickel, platinum, or rhodium (*21*).

Much more detailed information about the precise nature of the metallic bond is required before a full description of surface π complexes is possible. It is obvious therefore, that many of the ideas described in this paper are preliminary in character and will require further modification and development. However, they may help to clarify the type of approach which appears to be necessary if progress is to be achieved in understanding the fundamental origins of catalytic activity of the transition metals for organic reactions.

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