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The Structure of Reactive Sites on Platinum Metal Catalysts for the Hydrogenation of Unsaturated Hydrocarbons[1]

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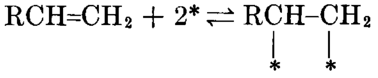
The reactive sites, on platinum metal catalysts for the hydrogenation of unsaturated hydrocarbons and related reactions, are proposed to be the most coordinatively unsaturated exposed metal atoms. To simplify the discussion, the surface atoms are divided into three groups with one, two, or three units of coordinative unsaturation (corresponding to the number of monodentate ligands which may become attached) and are symbolized by ^{1}M, ^{2}M, and ^{3}M. When exposed to hydrogen the first structures formed are ^{2}MH$_2$ and ^{3}MH$_2$ which are transformed, in part, to ^{2}MH and ^{3}MH by diffusion of hydrogen from the edge to other surface sites or to the interior of the crystallite. The proportions of ^{3}M and ^{3}MH present during a reaction are a function of the metal and the conditions of preparation and use. These structures bear a formal relationship to the structure of the complexes $ClRh(PPh_3)_2$(1) and $HRhCO(PPh_3)_2$(2) which are formed through the dissociation of $ClRh(PPh_3)_3$ and $HRh(CO)(PPh_3)_3$, respectively. The catalytic functions of both 1 and 2 appear to involve the same kinds of elementary processes, but the presence of the hydrido group in 2 leads to recognizably different phenomena (kinetics, stereochemistry, deuterium exchange reactions). Accordingly, the characteristics of hydrogenations catalyzed by platinum metals may be rationalized by considering the elementary processes which may occur at each category of site.

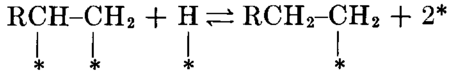
INTRODUCTION

The mechanisms of the reactions of hydrocarbons with hydrogen or with deuterium which are catalyzed by platinum metals are described customarily as a sequence of elementary processes which are represented in the way used by Horiuti and Polanyi to write the mechanism of the addition of hydrogen to an alkene [Eqs. (1–4)] (*1*, *2*).

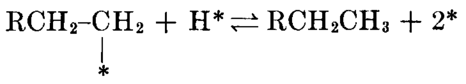
$$H_2 + 2^* \rightleftharpoons 2H^* \qquad (1)$$



$$RCH{=}CH_2 + 2^* \rightleftharpoons \underset{*}{\underset{|}{RCH}}-\underset{*}{\underset{|}{CH_2}} \qquad (2)$$



$$\underset{*}{\underset{|}{RCH}}-\underset{*}{\underset{|}{CH_2}} + \underset{*}{\underset{|}{H}} \rightleftharpoons RCH_2-\underset{*}{\underset{|}{CH_2}} + 2^* \qquad (3)$$



$$RCH_2-\underset{*}{\underset{|}{CH_2}} + H^* \rightleftharpoons RCH_2CH_3 + 2^* \qquad (4)$$

The asterisks represent surface sites of unspecified character and the usual symbol for a covalent bond represents a valence of 1 (*2*). Since these early proposals, the descriptions of the structures of surface-bound intermediates have evolved with

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the improvements in structural theory and particularly with the increase in knowledge of the structures of organometallic compounds (*3–14*).

Few of the theories of catalysis by metals, however, have described the structure of the reactive sites or the structural relationship between the site and the reactants which are involved in each elementary process. An early example is from Balandin who proposed that the reactive sites consist of ensembles of atoms on the surface, "sextets" or "duplets," which are arranged so as to permit a smooth transition from absorbed reactants to adsorbed products through the simultaneous breaking and forming of the appropriate chemical bonds (*15*). The emphasis on concertedness for the overall surface reaction made the theory inappropriate for explaining results in which intermediates are indicated.

The goodness of the geometrical fit of reactants to the array of atoms on the low-index planes of metal crystallites has been offered as an explanation for some catalytic phenomena. For example, Twigg and Rideal found support for the chemisorption of alkenes through the opening of the double bond by showing that the distance between neighboring nickel atoms would accommodate an unstrained two-carbon bridge (*16*). They also calculated that the entire surface of the (110) plane of nickel could be covered by adsorbed ethylene without appreciable interaction between neighboring molecules. The lack of free sites was said to account for the almost complete inhibition of the H_2–D_2 equilibration. Larger alkenes do not pack so efficiently, and accordingly, the H_2–D_2 equilibration which was observed could occur on the uncovered sites (*16*). Conceptually related models of the adsorption of ethylene on particular crystal faces of tungsten have been presented recently to explain the results of flash desorption studies of ethylene and hydrogen on tungsten (*17*). The most direct evidence for the structure of an adsorbed molecule on a metal, however, has been obtained through the interpretation of the scattering patterns of low-energy electrons diffracted from selected planes of a single crystal of platinum which has been exposed to acetylene (*18*). On the (111) plane, the acetylene appears to be bound to a triangular site similar to the manner in which diphenylacetylene is bound in the metal cluster compound $Ni_4[CNC(CH_3)_3]_4[\mu_3(\eta^2)–C_6H_5C{\equiv}CC_6H_5]_3$ (*19*). A triangular array of platinum atoms has been proposed to be the reactive site for the isomerization of neopentane to isopentane, and the proposal is claimed to account for the marked change in the selectivity of this reaction, relative to hydrogenolysis, as a function of the dispersion of platinum on the catalyst's support (*20, 21*). Presumably, the triplet sites make up a larger portion of the surface of a small crystal than of a large one (*21*).

The demonstration that a wide variety of unsaturated groups are bound as π-complexed ligands to a single metal atom in transition metal coordination compounds led to the postulation that alkenes, alkynes, and arenes, or unsaturated intermediates arising from their interaction with hydrogen, might be attached to a single atom of the catalyst (*3–6*). The transfer of hydrogen to these adsorbed structures, however, either was stated explicitly to involve neighboring atoms of the surface (*5, 8*) or the nature of these elementary processes was not stated clearly (*6, 7, 9–14*). For example, in an attempt to develop a more precise description of some of the elementary surface processes which involve hydrogen or deuterium and hydrocarbons, one of us represented these reactions as occurring at a diatomic site located along a hypothetical crystal edge so that each atom of the site could associate with two groups (ligands) (*8*). This arrangement permitted the elementary process for the adsorption of hydrogen to be represented in accordance with the model used by Sherman *et al.* for their calculation, which was based upon absolute reaction rate theory, of the activation energy (*22*). Also, the dissociative adsorption of an alkene, or the isomerization of an alkene by either the associative or the dissociative mechanism, was represented as occurring at a monatomic site, but the exchange with deuterium employed the cooperative action of an adjacent site. The fact that coordination complexes of transition metals such as $ClRh(PPh_3)_3$ (*23*) and $HRh(CO)(PPh_3)_3$ (*24*) catalyze hydrogenation and exchange reactions of alkenes, however, indicates that appropriately structured monoatomic sites, which are located on the surface of a metal, should catalyze the same reactions (*25*). Accordingly, in this paper we shall explore some of the consequences of this hypothesis. Our objective will be to develop a systematic method for representing the elementary processes which occur upon the surface of a platinum metal in order to account for the multifaceted details of hydrogenation and deuterium exchange reactions. Hopefully, this will provide a new perspective for the formulation and testing of rate equations as well as for the interpretation of the results of other experimental methods used in investigating the mechanisms of surface-catalyzed reactions.

THE STRUCTURE OF THE REACTIVE SITES

To be a catalyst, a reactive center must be unsaturated coordinatively at some stage of its function in order to bind one or more of the reactants to itself (*26*). Accordingly, the degree of coordinative unsaturation of a primitive site (atom) on the surface of a crystal appears to be the most important index upon which to base a classification of sites with respect to the kinds of elementary processes which can take place upon the surface (*17*). Upon exposure to hydrogen new structures are created, and because hydrogen is involved in all of the reactions which we shall consider in this paper, certain of these will be given special attention.

We shall assume that the number of groups which can be bound to any atom on the surface is limited by its position on the lattice, but the maximum coordination number may be lower because of the bulk of the attached groups (*27, 28*). Because we are basing our model upon the chemistry of coordination compounds of the platinum metals, we assume that the metal atoms adjacent to a monatomic site serve as the fixed ligands, while the reactants, in associating with the reactive center, tend to complete an "octahedral" arrangement of groups about the site. In a face-centered cubic crystal, an interior atom has a coordination number of 12. To conform to octahedral symmetry, therefore, the neighboring atoms must be specified in pairs (*29*). Similarly, paired atomic vacancies at the surface generate "octahedral" vacancies about a surface site. An ambiguity in specifying the maximum number of ligands which may become attached to a monatomic site arises if the number of atom vacancies is odd. We shall not try to resolve this ambiguity here but simply assume, that depending upon its location on the surface, a monatomic site may be bound at most to one, two, or three monodentate ligands.

To facilitate the discussion we will designate the monatomic primitive sites (before exposure of the surface to hydrogen) by the sumbols $^1\mathbf{M}$, $^2\mathbf{M}$, and $^3\mathbf{M}$, the superscript indicating the degree of coordinative unsaturation. Upon exposure to hydrogen, the oxidative addition of molecular hydrogen to $^2\mathbf{M}$ and $^3\mathbf{M}$ produces the structures $^2\mathbf{MH}_2$ and $^3\mathbf{MH}_2$, respectively. These in turn can be transformed to $^2\mathbf{MH}$ and $^3\mathbf{MH}$ through the transfer of atomic hydrogen to an adjacent site or to the interior of the crystal. These transformations are represented in Eqs. (5–8) where $^{0}\mathbf{M}$ designates an interior atom of a crystallite.

$$^{2}\mathbf{M} + H_2 \rightleftharpoons {}^{2}\mathbf{MH}_2 \qquad (5)$$

$$^{3}\mathbf{M} + H_2 \rightleftharpoons {}^{3}\mathbf{MH}_2 \qquad (6)$$

$$^{2}\mathbf{MH}_2 + {}^{1}\mathbf{M} \rightleftharpoons {}^{2}\mathbf{MH} + {}^{1}\mathbf{MH} \qquad (7)$$

$$^{3}\mathbf{MH}_2 + {}^{0}\mathbf{M} \rightleftharpoons {}^{3}\mathbf{MH} + {}^{0}\mathbf{MH} \qquad (8)$$

In this manner, structurally different sites are produced; however, we believe that two types, $^{3}\mathbf{M}$ and $^{3}\mathbf{MH}$, are of particular significance for the hydrogenation of unsaturated hydrocarbons and the related exchange and isomerization reactions, and a third, $^{2}\mathbf{MH}$, may have also a significant role in the isomerization of alkenes (*30*).

The proportion of sites such as $^{3}\mathbf{M}$ and $^{3}\mathbf{MH}$ which are present during a catalytic reaction will be a function of the metal and the history of the catalyst; in particular, the conditions of its exposure to hydrogen including the temperature, the pressure of hydrogen, and the presence of molecular species which may compete with hydrogen for adsorption at the **M** centers.

ELEMENTARY PROCESSES

We shall make use of current knowledge of the mechanism of reactions of coordination compounds to specify the elementary processes which may take place at each category of site. Excluding the transfer of hydrogen atoms between neighboring sites, neither free radicals nor atoms will be assumed to separate from a site (*31*). Our intention is to limit the discussion to a category of mechanism in which ordinary molecular species are involved. Ionic mechanisms will be excluded, although in the presence of suitable solvents, they might replace, in part, the molecular mechanisms which we will discuss (*32*).

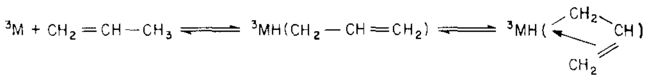
All of the sites which possess at least one vacant coordination position can associate with donor molecules (monodentate ligands) such as CO, NR_3, PR_3, alkene, alkyne, etc. If two vacancies exist on a single site, then as noted previously, hydrogen may add oxidatively and the oxidative addition (dissociative adsorption) of an alkane [Eq. (9)] or of an alcohol [Eq. (10)] also is allowed.

$$^{2}\mathbf{M} + CH_4 \rightleftharpoons {}^{2}MH(CH_3) \qquad (9)$$

$$^{2}\mathbf{M} + ROH \rightleftharpoons {}^{2}MH(OR) \qquad (10)$$

Obviously each such site could associate with two monodentate ligands or both vacant cordination positious could be filled by one bidentate ligand.

A divalent site is required to hold an allyl group as a π-complex (*33*). However, the elementary process for the interconversions of the σ- and π-forms of an allyl ligand is of significance only for reactions at $^{3}\mathbf{M}$ or $^{3}\mathbf{MH}$ sites. For example, the dissociative adsorption (oxidative addition) of propylene to the $^{3}\mathbf{M}$ site initially creates a structure with two ligands, an hydrido and a σ-allyl group. This process may be followed by the conversion of the σ-allyl to the π-allyl structure [Eq. (11)] (*33*).



$$^{3}M + CH_2{=}CH{-}CH_3 \rightleftharpoons {}^{3}MH(CH_2{-}CH{=}CH_2) \rightleftharpoons {}^{3}MH(\overset{CH_2}{\leftarrow}CH \underset{CH_2}{}) \qquad (11)$$

At a $^{3}\mathbf{MH}$ site, the oxidative addition of propylene must be followed by the reductive elimination of hydrogen before a π-allylic structure can be formed.

The interconversion of a methyl and methylene group plus hydrogen, in principle, also requires only a divalent site; however, with the restriction we have adopted for the discussion of mechanism, this change is likely to have significance only at either a $^3\mathbf{M}$ or $^3\mathbf{MH}$ site [Eqs. (12) and (13)] (*12*).

$$^3\mathbf{M} + CH_4 \rightleftharpoons {}^3MH(CH_3) \rightleftharpoons {}^3MH_2(-CH_2) \quad (12)$$

$$^3\mathbf{MH} + CH_4 \rightleftharpoons {}^3MH_2(-CH_3) \overset{-H_2}{\rightleftharpoons} {}^3M(-CH_3) \rightleftharpoons {}^3MH(-CH_2) \quad (13)$$

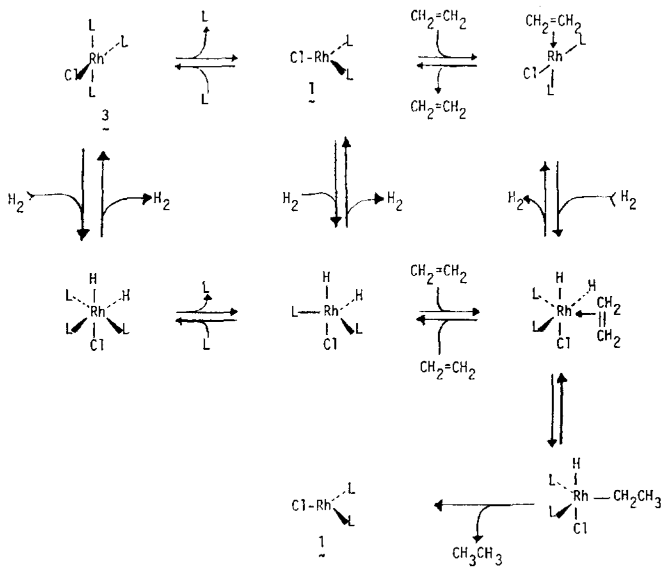
The scheme of binding methylene carbene to the metal resembles the binding of CO in that each of these ligands, formally, not only is an electron pair donor but also possesses a vacant *p* orbital which can overlap with a filled metal *d* orbital of the same symmetry (*34*).

The sites $^3\mathbf{M}$ and $^3\mathbf{MH}$ bear a formal relationship to the structures of the complexes $ClRh(PPh_3)_2$(**1**) and $HRhCO(PPh_3)_2$(**2**) which are formed through the dissociation of a triphenylphosphine (PPh_3) ligand from the principal species in solutions of chlorotristriphenylphosphinerhodium(I) (**3**) and hydridocarbonyltristriphenylphosphinerhodium(I) (**4**), respectively. The species **1** may combine simultaneously with a molecule of hydrogen (oxidative addition) and a molecule of alkene on the path to the formation of alkane (Scheme I). To accomplish the same result with **2**, however, requires first the addition of alkene followed by the rearrangement of the intermediate to a four-coordinated species, $Rh(CO)(PPh_2)_2$(alkyl), which is able to add molecular hydrogen oxidatively to form a complex which extrudes the alkane in reforming **2** (Scheme II).

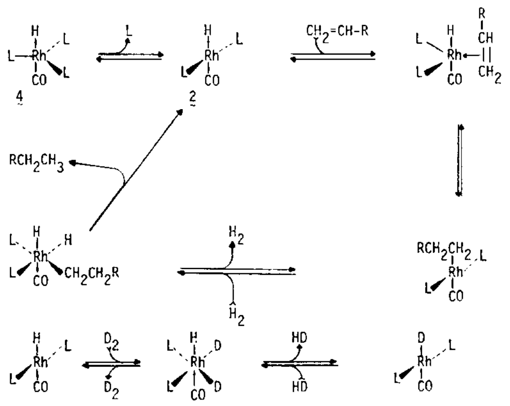
Most strikingly, **4** (via **2**) catalyzes the (H_2–D_2) equilibration, whereas **3** does not do so except in conjunction with the exchange or isomerization of an alkene. The elementary processes involved in these changes also appear to occur in the reactions of other transition metal complexes, although at rates which must vary over a wide range as a function of the metal, the ligand, and other independent variables (*35*).

RELATIONSHIP OF PROPOSAL TO SOME CHARACTERISTICS OF CATALYSIS BY PLATINUM, PALLADIUM, NICKEL, AND RHODIUM

Many of the catalyzed reactions which involve hydrogen are among those which have been called "facile" because the activity per unit surface area of the catalyst was found to be insensitive to the particle size of the metal or to the nature of the supporting material (*21*). This characteristic is believed to indicate that for such reactions, special structural surface features are not required.



SCHEME I. The hydrogenation of alkenes catalyzed by $ClRhL_3$; L = PPh_3 (*23*).



SCHEME II. Mechanism of alkene hydrogenation and H_2-D_2 equilibration catalyzed by $HRh(CO)L_3$; L = PPh_3 (*24*).

In contrast, studies on single crystals of platinum by Somorjai and his associates show that atomic steps are the preferred surface sites for breaking H–H and C–H bonds (*36*). The rate of the H_2–D_2 exchange on stepped crystals was found to be at least 10^4 times as rapid as on the (111) surface (*37*a). Dehydrogenation of cyclohexane or cyclohexene to benzene occurs at an appreciable rate only on stepped platinum surfaces (*37*b). Whereas the rate of dehydrogenation of cyclohexene is proportional to the step density, the rate of dehydrogenation of cyclohexane to benzene is independent of the number of steps provided that there are some. The rate of the hydrogenolysis of cyclohexane to hexane increases with increasing step density but increases much more rapidly with an increase in kink density. This later reaction, involving C–C bond scission, is similar to the hydrogenolysis of neopentane which is categorized by Boudart as a "structure-sensitive" reaction (*21*). The hydrogenolysis of cyclopropane to propane, however, apparently is insensitive to the presence of steps (*38*).

That only a fraction of the surface sites which can adsorb hydrogen, CO, or various unsaturated hydrocarbons is able to catalyze hydrogenation and deuterium exchange reactions is apparent from other studies. For example, Aben *et al.* found that for a group of platinum–alumina catalysts, the specific activity for hydrogenating benzene correlated with a specific low-temperature desorption peak obtained from the temperature-programmed desorption of hydrogen rather than the H/Pt ratio determined by chemisorption of hydrogen (*39*). Support for this conclusion is found in the studies by Primet *et al.* of the reversible adsorption of hydrogen on a Pt/Al_2O_3 catalyst (*40*).

That edge sites are the loci of the reactive centers for the hydrogenation of unsaturated hydrocarbons is also indicated by the ease of addition of hydrogen to compounds such as di-t-butylacetylene and di- and tri-t-butylbenzenes or derivatives of tryptycene (*11*, *41*, *42*). The geometry of these compounds prevents the binding of their unsaturated centers to a site which is located on a planar surface. In apparent contradiction to this conclusion we should note that the turnover number for the hydrogenation of di-t-butylacetylene is larger on the less dispersed than on the more dispersed Pt/Al_2O_3 catalyst (*43*). In competition with cyclopentene, however, the relative reactivity of di-t-butylacetylene is greater on platinum catalysts of high dispersion.

The catalytic sites differ among one another with respect to the mechanism as well as the specific rate for a given category of reaction; e.g., addition of hydrogen, alkene isomerization, or deuterium exchange with C–H bonds. Observing the noncorrelated variations in the isotopic distribution patterns of cyclopentane which had exchanged with deuterium on a series of palladium catalysts, Schrage and Burwell concluded that at least five different types of sites are involved in the exchange reaction (*44*). Similar arguments led to the conclusion that at least two different sets of sites were involved in the same exchange reaction on supported platinum catalysts (*45*). The relative rates of exchange of deuterium with the methyl and ring hydrogens of toluene on freshly deposited films of nickel is markedly altered when the films are sintered or a small amount of CO is adsorbed (*46*). These exchange reactions are likely to proceed by different mechanisms (*8*, *12*). Phillipson and Burwell concluded that the distribution of deuterium in the products of the platinum-catalyzed exchange and addition of deuterium to alkenes can be explained only by assuming the presence of at least two kinds of sites at which the effective ratio of (D/H) as well as the mechanism of exchange and/or addition differ (*47*). Similarly, Hilaire and Gault concluded that on palladium surfaces, the deuteration of dimethylcyclopentenes does not proceed by the same mechanism as the double-bond migration and alkene exchange, and they suggested that these reactions occur on different sites (*48*).

APPLICATIONS

To illustrate the application of our proposals to the rationalization of catalytic phenomena, we have selected experimental results which we believe are informative or may have influenced the development of commonly expressed views of the mechanism of hydrogenation and exchange reactions. One such idea is that the chemisorption of hydrogen produces absorbed atoms which rapidly mingle with other hydrogen or deuterium atoms on the surface. This is the mechanism for the H_2–D_2 equilibration on metals according to Bonhoefer and Farkas (*49*). However, the strength of binding a hydrogen atom to the surface of a metal is a function of the location of the binding site as is the rate of dissociative adsorption of molecular hydrogen (*36*). Clearly the presence of other molecular species on the surface must effect both the rate of adsorption and the rate of the surface migration of hydrogen. The question that is pertinent for mechanistic considerations, therefore, is whether the rate of the surface migration of hydrogen to a reactive center during the observed catalysis is greater or less than the rate of dissociative adsorption of molecular hydrogen at the reaction site. Accordingly, we shall consider results which have been obtained under conditions commonly used in investigating catalytic hydrogenations (*50*).

Addition of D_2–H_2 to alkynes. The addition of deuterium to 2-butyne on palladium is remarkably stereoselective and yields almost exclusively *cis*-2,3-dideuterobutene (*51*). If a mixture of H_2 and D_2 is used in place of deuterium, however, the distribution of C_4H_8, C_4H_7D, and $C_4H_6D_2$ appears as a random distribution of the added hydrogen and deuterium. Also observed is a kinetic isotope effect, $k_H/k_D = 1.6$, which must refer to the relative rates of adsorption of H_2 or D_2 because little HD is evolved. Meyer and Burwell conclude that the hydrogen and deuterium are dissociated into atoms on the surface, and any required surface migration is fast enough to scramble the adsorbed atoms, H* and D*.

We propose an alternative to the above explanation. Suppose the reactive sites have the structure designated as ^{3}**MH**. The mechanism of addition would then proceed as in Fig. 1. Note that the coordination of the alkyne with the reactive center inhibits the H_2–D_2 equilibration. The insertion reaction proceeds with the formation of a vinyl intermediate, and a second coordination site is vacated. A molecule

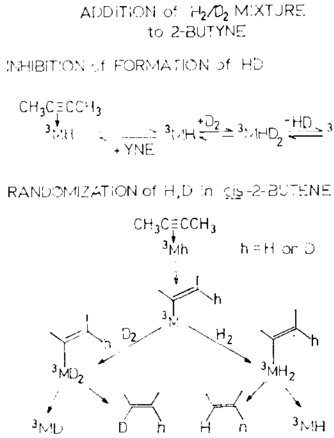


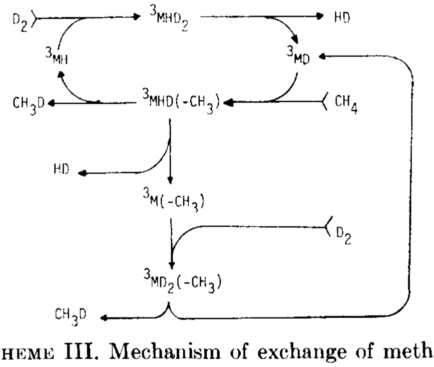
FIG. 1. Addition of H_2–D_2 mixture to 2-butyne. Inhibition of the formation of HD and randomization of H, D in the product, *cis*-2-butene.

of either hydrogen or deuterium now is enabled to add oxidatively to the metallic center, and this elementary process is followed by the reductive elimination of *cis*-2-butene. The distribution of H and D atoms in the product will be randomized because the two atoms added (H, D) cannot come from the same molecule of H_2 or D_2. Interestingly, the observed kinetic isotope effect (1.6) is close to the value (1.47) reported for the hydrogenation of 1-hexene catalyzed by $HRh(CO)(PPh_3)_3$ in which the oxidative addition of hydrogen to a four-coordinated rhodium complex is rate controlling (*24*). If the reactive site had the structure ^{3}**M**, one would have expected that the product would have consisted of *cis*-2-butene(C_4H_8) and *cis*-2,3-dideutero-2-butene with none of the monodeutero species. Presumably, there are few such sites, and/or the rate of addition of hydrogen to the alkyne is lower at the ^{3}**M** sites than at the ^{3}**MH** sites.

Influence of additives upon the selectivity of alkynes to alkenes. The selectivity of the hydrogenation of alkynes to alkenes is often improved by the addition of substances such as quinoline. It is said that the selectivity changes because the additive is more strongly adsorbed at a reactive site than is the product alkene but less than the reactant alkyne. It is easy to show, however, that this mechanism cannot effect a change in selectivity at a single site (*52*). However, the selectivity could be markedly different at structurally different sites, and further, an inhibitor is more likely to be bound to the less, rather than the more, selective reaction center. As noted above, the addition of hydrogen to an alkyne on palladium is well explained by assuming that the reduction occurs at ^{3}**MH** sites. The deuteration exchange reactions of alkenes on palladium indicates that ^{3}**M** sites are also present (see below). The latter would be expected to be the less selective sites, being coordinatively more unsaturated. A similar difference in selectivity for the hydrogenation of alkenes is exhibited by the analogous homogenous catalysts, $HRh(CO)(PPh_3)_3$ and $ClRh(PPh_3)_3$, respectively (*23, 24*). This, of course, is not the only manner by which selectivity may be altered but is likely to be important when mass transport is not a limiting factor.

Exchange of methane with deuterium. Kemball reported one of the first exchange reactions of alkanes to be examined on metals, the exchange of methane with deuterium on nickel films and later on films of rhodium, platinum, palladium, and tungsten (*53, 54*). Remarkably, the initial distribution of products on nickel at 237°C consisted of CH_3D, CH_2D_2, CHD_3, and CD_4 in the ratio 12:3:24:61 (*53*). With tungsten at 151°C, the initial distribution differed in that monodeuteromethane was the main product, the deuterated species being formed in the ratio 76:1:9:14 (*54*). Kemball proposed that the production of CH_3D indicated the formation of adsorbed methyl radicals, while the production of CHD_3 and CD_4 indicated the formation of adsorbed methylene radicals which could interconvert readily with adsorbed methinyl (CH*ads*) or possibly C*ads*.

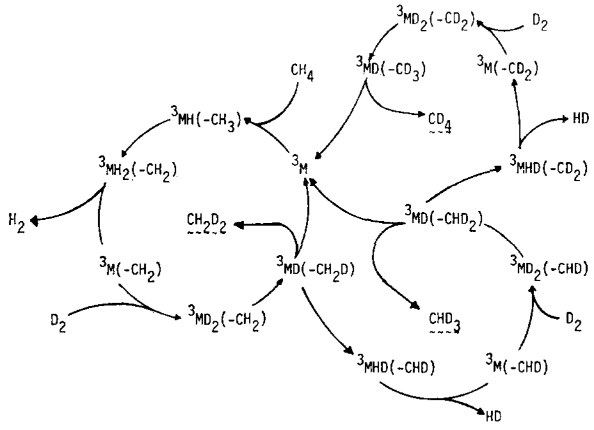
The observed dichotomy in the exchange patterns is reproduced through the allowed elementary processes at the ^{3}**M** and ^{3}**MH** sites. Exchange at ^{3}**MH** sites permits the replacement of only one hydrogen atom by one deuterium atom per sojurn at the site (Scheme III).



SCHEME III. Mechanism of exchange of methane with deuterium at ^{3}**MH** sites.

In contrast, exchange of methane with

deuterium at ^{3}**M** sites requires the formation of a carbene (methylene) intermediate (Scheme IV). Clearly two or more hydrogen atoms may be replaced by deuterium during a single sojourn of dissociatively adsorbed methane at such sites.



SCHEME IV. Mechanism of exchange of methane with deuterium at ^{3}**M** sites.

The relative rates of these two competing exchange mechanisms will depend upon the relative specific rates of each process as well as the proportion of sites of each kind. Both the ability to absorb methane dissociatively as well as the ability to convert adsorbed methyl to adsorbed methylene must be functions of the metal. As noted earlier, methylene can be expected to resemble CO in the manner by which it is bound to a transition metal (*34*); the binding energy must be a function of the metal.

Addition–exchange and isomerization of alkenes. The addition–exchange of deuterium with alkenes and the accompanying exchange and isomerization catalyzed by platinum and palladium catalysts often are thought to occur by different mechanisms (*44, 47, 48, 50*). Generally, the formed alkane contains, on the average, more deuterium atoms per molecule than the exchanged or isomerized alkene. In most instances the distribution of deuterium in the alkane and the isomerized alkene appear unrelated. Presumably the alkane is formed via the classical Horiuti–Polanyi mechanism through the reversible formation of the "half-hydrogenated" intermediate from the adsorbed alkene, a process which is coupled with the rapid replacement of absorbed hydrogen by deuterium atoms (*14*). The exchanged alkene is supposed to be formed via the dissociation of an allylic hydrogen, and subsequent changes have been given in detail by Hilaire and Gault (*48*).

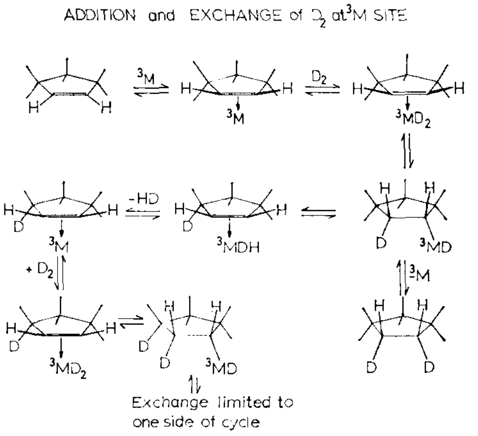
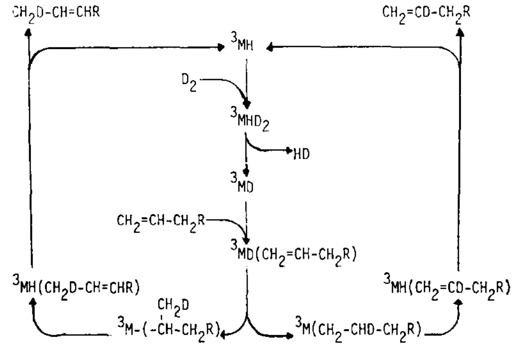


FIG. 2. Addition and exchange of D_2 with cyclopentene at a ^{3}**M** site.

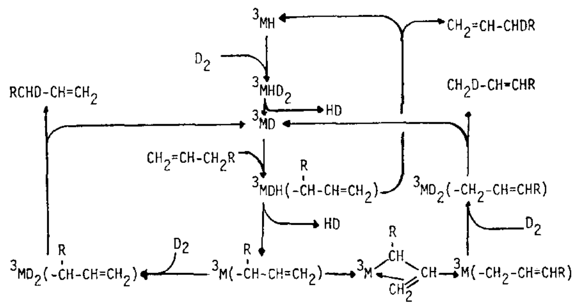
Consider how our proposals would be used to account for such phenomena. The more extensive exchange–addition of deuterium with a cycloalkene would proceed at ^{3}**M** sites providing that the desorption of HD or H_2 from the complex ^{3}**MH**$_2$-(alkene) was faster than the desorption of the alkene (Fig. 2). To obtain deuterated species containing more than the number of hydrogen atoms on one side of a cyclic molecule, some exchanged alkene must desorb and readsorb [an extreme form of Burwells "roll over" mechanism (*11*, *44*)], and a portion should appear as exchanged cycloalkene. If a second mechanism of isomerization were occurring at the same time, then the observed distribution in the exchanged cycloalkene would be a composite of two patterns.

Several isomerization mechanisms can be expected at the ^{3}**MH** sites. The most probable is the associative mechanism which would yield both deuterated and undeuterated isomerized products in a distribution which would depend upon the relative rates of the elementary processes indicated in Scheme V. No more than one hydrogen atom could be replaced by deuterium during one sojourn of a molecule of alkene at this site.



SCHEME V. Isomerization and exchange of alkenes at ^{3}**MH** sites; associative mechanism.

A dissociative exchange mechanism could also occur at the ^{3}**MH** sites (Scheme VI); however, it too would result in only a single exchange for each sojourn of a molecule of alkene at this site.



SCHEME VI. Isomerization and exchange of alkenes at ^{3}**MH** sites; dissociative mechanism.

At a ^{3}**M** site, dissociative adsorption at an allylic position could lead to isomerization without any accompanying exchange of D for H. Such a result, has been reported to occur on palladium films (*55*). Which of these isomerization mechanisms is followed is likely to be a function of the metal, the structure of the unsaturated hydrocarbon, and the concentration of molecular species which may be adsorbed in competition with the unsaturated hydrocarbon.

An increase in the pressure of deuterium can be expected to cause a change in the dominating mechanism of isomerization and may account for the following results. Smith and Burwell treated 9,10-octalin with deuterium at 1 atm in the presence of reduced platinum oxide (*56*). Upon comparing the distribution of deuterium in the *cis*- and *trans*-decalins with the distribution of deuterium in the recovered 9,10-octalin, they concluded that although part of the *cis*-decalin was formed by the classical Horiuti–Polanyi mechanism for addition, most was produced via the addition of (H, D) to 1,9-octalin which was formed via a dissociative mechanism. On the other hand, Weitkamp isolated 9,10-octalin from the reaction of 1,9-octalin with deuterium at high pressure on a platinum catalyst and, using Smith and Burwell's mathematical analysis of the distribution of deuterium in the products, concluded that *cis*- and *trans*-decalin and the 9,10-octalin were formed through a common intermediate, presumably the half-hydrogenated state of Horiuti and Polanyi (*57*). This change in the mechanism of isomerization with an increase in pressure would be consistent with our proposals if isomerization at the $^3\mathbf{MH}$ sites were to be inhibited through the competitive adsorption of $D_2(H_2)$ [Eq. (14)].

$$^3\mathbf{MH} + D_2 \leftrightarrows {}^3\mathrm{MHD}_2 \qquad (14)$$

The hydrogenation of ethylene which is catalyzed by $IrH(CO)(PPh_3)_3$ apparently exhibits such a mechanism of inhibition by hydrogen (*58*).

Philipson and Burwell have conducted deuterations of cyclic olefins on platinum/alumina in solutions of solvents containing exchangeable deuterium atoms such as CH_3OD or ethanolamine-d_3 (*47*). Their aim was to increase the proportion of deuterium atoms on the surface so that the underlying pattern of the distribution of deuterium in the products would not be hidden by the hydrogen released in the exchange reactions. The strategy was successful and they deduced that there are at least two sets of surface sites. "One is characterized by large (D^*/H^*), some simple addition hydrogenation, all or most of the exchange–addition hydrogenation leading to ane-d_3, ane-d_4, ..., and a substantial rate of $H^* + ROD = D^* + ROH$. The second set involves only or mainly simple addition hydrogenation, formation of exchanged olefin and a relatively small rate of $H^* + ROD = D^* + ROH$. There are differences among the solvents; CH_3-COOD gives much the most exchange–addition hydrogenation, ethanolamine gives much the most simple addition hydrogenation" (*47*).

Although our proposal recognizes two categories of sites at which the mechanisms of exchange and addition would occur, it would suggest a different relationship than that deduced by Philipson and Burwell. We would assume that the exchange addition reactions would occur at $^3\mathbf{M}$ sites. However, the increase in the (D^*/H^*) ratio would result from the accompanying exchange of the released H_2 or HD with ROD at $^3\mathbf{MH}$ sites. As indicated above, the exchange and addition reaction of alkenes at the later site would appear to involve a surface pool of (H, D) in which the ratio of D/H could be effectively less than 1, depending upon the relative rate of the exchange, isomerization, and addition reactions.

Hydrogenation of 1,4-di-t-butylbenzene. That two kinds of sites are present on a rhodium catalyst is indicated by the effect of large changes in the pressure of hydrogen upon the rate of hydrogenating 1,4-di-t-butylbenzene and its derivative, 1,4-di-t-butylcyclohexene (*59*). At low or moderate pressures of hydrogen (0.2–1.5 atm), the rate of hydrogenating the arene dissolved in cyclohexane is first order in the pressure, and the principal initial product is the cycloalkene (ca. 85%) whose rate of reduction is approximately 0.5 order in the pressure of hydrogen. If the pressure is increased to 50–100 atm, however, the rate of hydrogenation of the arene is decreased. At 50 atm, allowing the reactants to stand for 30 min in the presence of hydrogen before agitation of the mixture is started results in a lower rate of hydrogenation than if stirring is begun immediately. In contrast to the results at low pressure, at high pressure the intermediate cycloalkene is hydrogenated more rapidly than is its arene precursor.

The above results are accommodated by the two-site model. The proportion of the two types of sites, $^3\mathbf{M}$ and $^3\mathbf{MH}$, will depend upon the history of the catalyst, in particular the conditions of its exposure to hydrogen including the temperature, the pressure of hydrogen, and whether molecular species are present which may compete with hydrogen for adsorption at the **M** centers.

We believe that the hydrogenation of the arene occurs exclusively on $^3\mathbf{M}$ sites. Although alkenes may add hydrogen at either $^3\mathbf{M}$ or $^3\mathbf{MH}$ sites, in the low pressure range the $^3\mathbf{MH}$ sites are liable to be the more effective, because if the ratio of hydrogen to alkene in the vicinity of a site is low, most sites will be occupied by either arene or alkene. Further, the relative rate of the oxidative addition of hydrogen to a reactive center can be expected to increase in the order $^3\mathbf{M}$–alkene < $^3\mathbf{M}$–arene < $^3\mathbf{M}$ < $^3\mathbf{MH}$, $^3\mathbf{M}$–alkyl, formed rapidly from **MH**-(alkene), because the rate should be a function of the electron density at the metallic center as well as of the availability of two vacant coordination sites (*60*).

The rate of hydrogenation of either the arene or alkene at a $^3\mathbf{M}$ site will increase with increasing pressure until all such sites are saturated with hydrogen ($^3\mathbf{MH}_2$); however, the hydrogenation of an alkene at a $^3\mathbf{MH}$ site can be expected to exhibit a maximum rate at some intermediate pressure beyond which the rate will *decrease* with *increasing* pressure. This would occur because of the increasing fraction of **MH** sites which would be present as $^3\mathbf{MH}_3$ (*58*). Accordingly at high pressure, virtually all of the addition of hydrogen, whether to arene or to alkene, must occur at $^3\mathbf{M}$ sites where an alkene may be expected to react more rapidly than an arene in keeping with the characteristic reactivity of $H_2RhCl(PPh_2)_2$, the analog of $^3\mathbf{MH}_2$ (*23*).

The slowed rate of hydrogenation of the arene at high pressure, which is accentuated if the mixture is allowed to stand undisturbed for a time before vigorous stirring is begun, is indicative of the further conversion of the $^3\mathbf{M}$ structures to $^3\mathbf{MH}$, presumably through the diffusion of one of the hydrogen atoms at a $^3\mathbf{MH}_2$ center to another position on the surface.

The above phenomena are not readily apparent when *m*- or *p*-xylene is hydrogenated using the rhodium catalysts. Presumably, it is due to the fact that the xylenes are more strongly absorbed than 1,4-di-t-butylbenzene and thus slow the rate of conversion of $^3\mathbf{M}$ to $^3\mathbf{MH}$ sites.

CONCLUSION

In the preceding discussion we assumed that the elementary processes which make up the catalytic reactions of hydrogen and hydrocarbons on platinum metals are centered upon single coordinatively unsaturated surface atoms. The neighboring atoms correspond to the fixed ligands whose electronic characters affect the energy of changes at the reaction center. These "ligand" atoms, however, may be involved in a more specific manner. For example, a hydrogen atom which is bound to a reactive center may occupy a bridging position to a neighboring surface atom. However, if the pattern of the distribution of deuterium in the products is to correspond to that predicted in the present proposal, then the bridging hydrogen atom should not migrate from the catalytic center or exchange with deuterium except through the elementary processes which occur at the center. This restriction could arise if organic fragments were bound strongly to these neighboring atoms. That such a situation does occur is indicated by the formation of chiral products from achiral reactants when the catalyst has been modified with optically active substances (*61, 62*). Furthermore, there is ample evidence that much of the surface of a platinum metal catalyst which has been exposed to hydrogen and hydrocarbons is largely covered by relatively unreactive hydrocarbon species (*63*).

The possibility that transition metal cluster complexes may serve as models for catalysis by metal surfaces has stirred considerable interest in their chemistry (*64*), and perhaps certain of their peculiar structural features are required to catalyze some of the changes which are observed in catalysis by the platinum metals. Undoubtedly a deeper insight into the mechanism of catalysis of metallic surfaces will be gained through detailed comparisons of catalysis by the metals with the several categories of transition metal complexes, mononuclear as well as bi- and polynuclear.

As suggested frequently, a variety of reactive sites probably exist simultaneously on the surface; their relative importance in a particular overall change is likely to be a function of the metal as well as of the independent variables. The proposals we have discussed are likely to apply mainly to reactions which occur at relatively low temperatures. As the temperature is raised, the migration of organic groups as well as hydrogen from one metallic center to another becomes more likely. Further experiment and detailed analysis of the results should show whether our proposals afford an appropriate description of catalysis by any of the platinum metals.

REFERENCES

1. Horiuti, I., and Polanyi, M., *Trans. Faraday Soc.* **30**, 1164 (1934).

2. (a) Boudart, M., "Kinetics of Chemical Processes," Chap. 2. Prentice-Hall, Englewood Cliffs, N. J., 1968; (b) "Manual of Symbols and Terminology for Physicochemical Quantities and Units," Appendix II, Part II. Prepared for publication by Burwell, R. L., Jr., *Pure Appl. Chem.* **46**, 71–90 (1976).

3. Fukushima, D. K., and Gallagher, T. F., *J. Amer. Chem. Soc.* **77**, 139 (1955).

4. Halpern, J., *Advan. Catal.* **11**, 301 (1959).

5. Rooney, J. J., Gault, F. G., and Kemball, C., *Proc. Chem. Soc.*, 407 (1960).

6. McQuillin, F. J., Ord, W. O., and Simpson, P. L., *J. Chem. Soc.*, 5996 (1963).

7. (a) Rooney, J. J., *J. Catal.* **2**, 53 (1963); (b) Rooney, J. J., and Webb, G., *J. Catal.* **3**, 488 (1964).

8. Siegel, S., *Advan. Catal.* **16**, 123 (1966).

9. Bond, G. C., *Discuss. Faraday Soc.*, 200 (1966).

10. Ugo, R., *in* "Catalysis" (J. W. Hightower, Ed.), Vol. 1, p. B-19. North-Holland, Amsterdam, 1973.

11. Burwell, R. L., Jr., *Intra-Sci. Chem. Rep.* **6**, 135 (1972).

12. Kemball, C., *Catal. Rev.* **5**, 33 (1972).

13. Moyes, R. B., and Wells, P. B., *Advan. Catal.* **23**, 121 (1973).

14. Clarke, J. K. A., and Rooney, J. J., *Advan. Catal.* **25**, 125 (1976).

15. (a) Balandin, A. A., *Z. Physik. Chem.* **B2**, 289 (1924); (b) Balandin, A. A., *Advan. Catal.* **10**, 96 (1958).

16. Twigg, G. H., and Rideal, E. K., *Trans. Faraday Soc.* **36**, 533 (1940).

17. Rye, R. R., *Acc. Chem. Res.* **8**, 347 (1975).

18. Buchholtz, J. C., and Somorjai, G. A., *Acc. Chem. Res.* **9**, 333 (1976).

19. Thomas, M. G., and Muetterties, E. L., *J. Amer. Chem. Soc.* **98**, 4645 (1976).

20. Anderson, J. R., and Avery, N. R., *J. Catal.* **5**, 446 (1966).

21. Boudart, M., Aldag, A. W., Ptak, L. D., and Benson, J. E., *J. Catal.* **11**, 35 (1968).

22. Sherman, A., Sun, C. E., and Eyring, H., *J. Chem. Phys.* **3**, 49 (1934).

23. (a) Osborn, J. A., Wilkinson, G., and Young, J. F., *Chem. Commun.* **1**, 17 (1964); (b) Osborne, J. A., Jardine, F. H., Young, J. F., and Wilkinson, G., *J. Chem. Soc. A*, 1711 (1966); (c) Hussey, A. S., and Takeuchi, Y., *J. Amer. Chem. Soc.* **91**, 672 (1969).

24. (a) O'Connor, C., and Wilkinson, G., *J. Chem. Soc. A*, 2665 (1968); (b) Ueda, T. *in* "Catalysis," Proceedings of the Fifth International Congress of Catalysis, Vol. 1, Paper 26, p. 431. North-Holland/American Elsevier, Amsterdam and New York, 1973.

25. This proposition has been discussed with respect to the catalysis of such reactions on cobalt oxide. Siegel, S., *J. Catal.* **30**, 139 (1973).

26. Collman, J. P., *Acc. Chem. Res.* **1**, 136 (1968).
27. Shaw, B. L., and Stainbank, R. E., *J. Chem. Soc. Dalton Trans.*, 223 (1972).
28. Tolman, C. A., *J. Amer. Chem. Soc.* **92**, 2956 (1970); **96**, 53 (1974).
29. Kahn, O., and Salem, L., Paper A2, the Sixth International Contress on Catalysis, London, July 1976.
30. Ando, N., Maruya, K., Mizoroki, T., and Ozaki, A., *J. Catal.* **20**, 299 (1971).
31. Recently, a free radical mechanism was proposed for the cobalt carbonyl catalyzed hydrogenation of aromatic hydrocarbons: Feder, H. M., and Halpern, J., *J. Amer. Chem. Soc.* **97**, 7189 (1975). A similar mechanism might occur at high temperature on platinum metals.
32. van Rantwijk, F., Kieboom, A. P. G., and van Bekkum, H., *J. Mol. Catal.* **1**, 27 (1975).
33. Vrieze, K., and Volger, H. C., *J. Organometal. Chem.* **9**, 527 (1968).
34. Mallo, A. S., and Redhouse, A. D., *J. Chem. Soc. A*, 1274 (1969).
35. James, B. R., "Homogeneous Hydrogenation," pp. 229–237. Wiley, New York, 1973.
36. Somorjai, G. A., *Acc. Chem. Res.* **9**, 248 (1976).
37. (a) Bernasek, S. L., and Somorjai, G. A., *J. Chem. Phys.* **62**, 3149 (1975); (b) Blakely, D. W., and Somorjai, G. A., *J. Catal.* **42**, 181 (1976).
38. Kahn, D. R., Peterson, E. E., and Somorjai, G. A., *J. Catal.* **34**, 294 (1974).
39. Aben, P. C., van der Eijk, H., and Oelderick, J. M., *in* "Catalysis" (J. W. Hightower, Ed.), Vol. 1, p. 717. North-Holland, Amsterdam, 1973.
40. Primet, M., Basset, J., and Mathieu, M., *J. Chem. Soc. Faraday I*, **70**, 293 (1974).
41. Burwell, R. L., Jr., Barry, D., and Kung, H. H., *J. Amer. Chem. Soc.* **95**, 4466 (1973).
42. van Bekkum, H., Buurmans, H. M. A., van Minner-Pathius, G., and Wepster, B. M., *Rec. Trav. Chim. Pays-Bas.* **88**, 779 (1969).
43. Kung, H. H., Pellet, R. J., and Burwell, R. L., Jr., *J. Amer. Chem. Soc.* **98**, 5603 (1976).
44. Schrage, K., and Burwell, R. L., Jr., *J. Amer. Chem. Soc.* **88**, 4549 (1966).
45. Roth, J. A., Geller, B., and Burwell, R. L., Jr., *J. Res. Inst. Catal. Hokkaido Univ.* **16**, 221 (1968).
46. (a) Phillips, M. J., Crawford, E., and Kemball, C., *Nature (London)* **197**, 487 (1963); (b) Crawford, E., and Kemball, C., *Trans. Faraday Soc.* **58**, 2452 (1962).
47. Phillipson, J. J., and Burwell, R. L., Jr., *J. Amer. Chem. Soc.* **92**, 6125 (1970).
48. Hilaire, L., and Gault, F. G., *J. Catal.* **20**, 267 (1971).
49. Bonhoeffer, K. F., and Farkas, A., *Trans. Faraday Soc.* **28**, 242, 561 (1932).
50. Burwell, R. L., Jr., *Catal. Rev.* **7**, 25 (1973).
51. Meyer, E. F., and Burwell, R. L., Jr., *J. Amer. Chem. Soc.* **85**, 2877, 2881 (1963).
52. Burwell, R. L., Jr., *in* "Actes Du Deuxieme Congress International de Catalyse," Vol. 1, p. 1005. Editions Technip, Paris, 1960.
53. Kemball, C., *Proc. Roy. Soc. Ser. A* **207**, 539 (1951).
54. Kemball, C., *Proc. Roy. Soc. Ser. A* **217**, 376 (1951).
55. Touroude, R., Hilaire, L., and Gault, F. G., *J. Catal.* **32**, 279 (1974).
56. Smith, G. V., and Burwell, R. L., Jr., *J. Amer. Chem. Soc.* **84**, 925 (1962).
57. Weitkamp, A., *J. Catal.* **6**, 431 (1966).
58. Burnett, M. G., and Morrison, R. J., *J. Chem. Soc. A*, 2325 (1971); *J. Chem. Soc. Dalton, Trans.*, 632 (1973).
59. Siegel, S., and Garti, N., *in* "Proceedings of the Sixth Conference on Catalysis in Organic Synthesis" (G. V. Smith, Ed.). Academic Press, New York, in press.
60. Empsall, H. D., Hyde, E. M., Jones, C. E., and Shaw, B. L., *J. Chem. Soc. Dalton Trans.*, 1980 (1974).
61. Izumi, Y., *Angew. Chem. Int. Ed.* **10**, 871 (1971).
62. Groenewegen, J. A., and Sachtler, W. M. H., Paper B-40, the Sixth International Congress on Catalysis, London, July 1976.
63. (a) Blakely, D. W., and Somorjai, G. A., *J. Catal.* **42**, 181 (1976); (b) van Meertan, R. Z., Verhaak, A. C. M., and Coenen, J. W. E., *J. Catal.* **44**, 217 (1976).
64. Smith, A. K., and Basset, J. M., *J. Mol. Catal.* **2**, 229 (1977).