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THE SURFACE ORGANOMETALLIC ZOO - CONTINUED

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1. Introduction

In the period 1950–1965 mechanistic investigations of heterogeneous catalytic reactions of hydrocarbons in the presence of hydrogen or deuterium led to substantial evidence for the existence of a rather large number of different surface intermediates which could be considered to be surface organometallic complexes. In a review in 1966 [1] the author presented a list of eleven such species which he called an organometallic zoo. What is the state of the zoo 24 years later? We shall consider here just that department of the zoo consisting of members of the family of adsorbed C_mH_n on Group VIII metals.

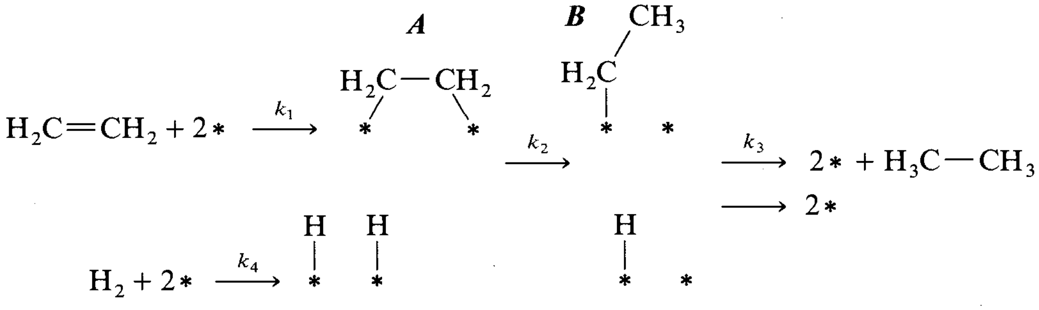
Surface organometallic chemistry started well before molecular organometallic chemistry, but recently the latter has been a major growth industry and the ratio, molecular/surface, has become large. In 1966 the denizens of the zoo were intermediates in catalytic reactions. Spectroscopic studies beginning with Eischens were requiring the opening of a new section of the zoo to harbor "surface chemistry" species. In recent years, workers using spectroscopic techniques applied to single crystal surfaces have worked out the structures of a number of adsorbed hydrocarbon species. Such species properly belong to surface organometallic chemistry, defined here as surface chemistry analogous to molecular organometallic chemistry. Since catalytic sites may constitute only a small fraction of the sites for adsorption, during actual catalytic runs much of the surface of a catalyst may be covered with catalytically irrelevant species. Discovering the exact genetic relationship between the surface species on the rather large crystal planes of surface chemical physics and the intermediates of catalytic reactions which inhabit the surfaces of small metal particles takes further effort. Still more recently, a new section of the zoo has been opened to contain the rather ghostly denizens which are the progeny of quantum mechanics, a development which can receive only casual attention here.

In what follows, the author will primarily be concerned with the establishment of species and matters of priority will not always be a consideration nor will a full historical treatment. Development of the complete ecological aspects of the various species would require a treatise not an article.

A major line of heterogeneous catalysis started with a failed attempt to prepare an organometallic compound. In view of Mond's preparation of the volatile compound, $Ni(CO)_4$, Sabatier syllogized carbon-double bond-oxygen resembles carbon-double bond-carbon, therefore, if CO passed over nickel gives $Ni(CO)_4$, $H_2C{=}CH_2$ passed over nickel powder would give $Ni(H_2C{=}CH_2)_4$. He tried the experiment. Since no volatile nickel compound was formed, the experiment could have been considered a failure. However, something had happened. The nickel had become hot and ethane had appeared in the exit stream. Intrigued by the formation of ethane, Sabatier passed ethylene plus hydrogen over nickel and got ethane and a Nobel Prize [2].

For many years inorganic chemists attempted to make organometallic complexes of transition metals analogous to C_2H_5MgCl, $(CH_3)_2Zn$ and other organometallic compounds of non-transition elements. Universal failure resulted. Ignoring Zeise's compound and the hydrogenation of ethylene on Group VIII metals, inorganic chemists adopted the dogma that organometallic compounds of transition elements could not exist. Thus, from the 1950 point of view, Sabatier's initial experiment was doomed to fail. Indeed, $Ni(C_2H_4)_4$ is still unknown, but a close analog, $Pt(cyclo\text{-}1,4\text{-}octadiene)_2$, is stable enough for its X-ray structure to have been determined [3]. What happened, of course, was that Pauson reported the preparation of ferrocene in 1951 and, following the first olive from the bottle rule, a flood of preparations of diverse organometallic compounds ensued.

Sabatier thought that the hydrogenation of ethylene involved what we would now call the chemisorption of ethylene and hydrogen on the catalyst followed by a surface reaction which liberated ethane, but he never attempted to specify structures of adsorbed species. Horiuti and Polanyi in 1934 [4] were the first to attempt this. Their proposal was Scheme 1.



Scheme 1.

Except for Langmuir's evidence for the dissociative adsorption of hydrogen, the stoichiometry, and the fact that the reaction occurred on a metallic surface, few facts were known against which the mechanism could be tested. Nevertheless, although other mechanisms have been proposed, the H-P mechanism still dominates the field.

Almost coincidentally, Farkas passed ethylene and deuterium over nickel. Two reactions occurred, formation of ethane-d_x and of ethylene-d_y. At that time it was impossible to determine the isotopic distribution patterns of the products, i.e., the specification of the values of D_0, D_1, D_3...where D_i represents the fraction of the exchanged compound containing *i* atoms of deuterium. Farkas proposed that exchange of the olefin occurred by dissociative adsorption of the olefin to form $*$-CH=CH$_2$ (***C***) + $*$H, followed by associative desorption. However, ethylene-*d* could also result from the sequence, ethylene → ***A*** → ***B*** → ***A*** → ethylene-*d*, since in the presence of deuterium much $*$H would be $*$D. In general, the relative importance of these two routes is not yet clear.

Figure 1 is a running list of inhabitants of the zoo which contains species ***A***, ***B*** and ***C*** as well as other species to appear later.

Shortly after the work of Farkas, Morikawa and Taylor discovered isotopic exchange between D_2 and CH_4, C_2H_6 and C_3H_8. Again, isotopic distribution patterns could not be obtained. It was proposed that exchange resulted from the dissociative adsorption of alkane to form monoadsorbed alkane (like ***B***).

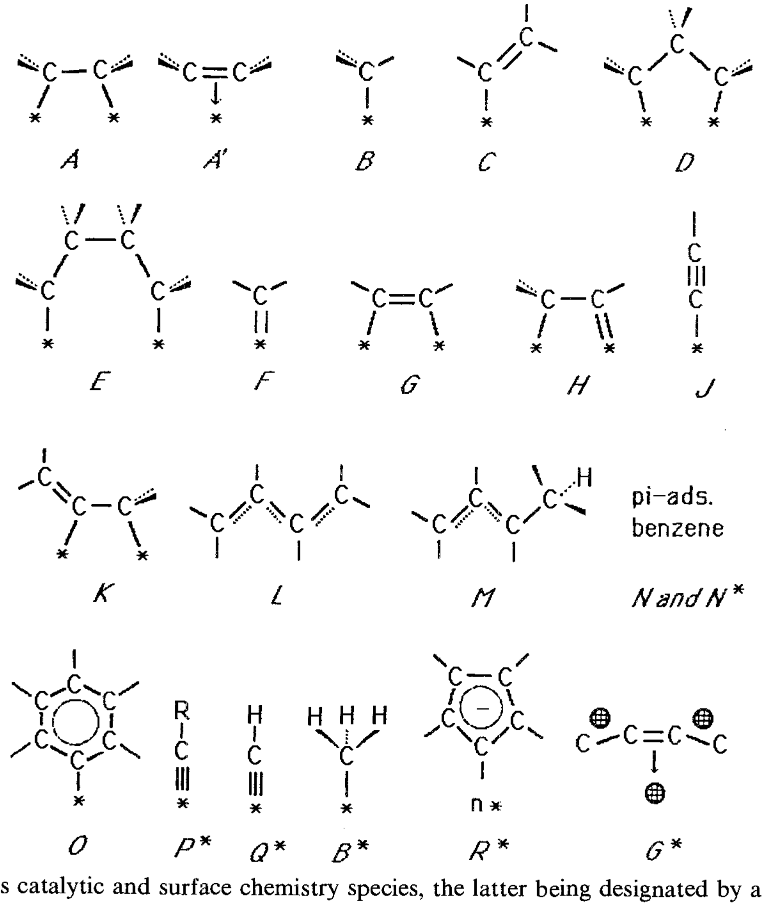


Fig. 1. Various catalytic and surface chemistry species, the latter being designated by a superscript asterisk. An unspecified site is represented by an in-line asterisk. Unterminated chemical bonds may represent binding to H or, where appropriate, alkyl. Cyclic structures may be involved, for example, ***F***, could be α,α-diadsorbed cyclopentane and ***A*** could be diadsorbed cyclohexane. In ***G****** the circles represent atoms in a (111) plane of a cubic close-packed Group VIII metal. ***L***, ***M***, ***R****, and ***G**** represent views looking down at the surface.

Compounds ***A***, ***B*** and ***C*** are surface organometallic complexes which formally violated inorganic theory. However, no controversy arose from this probably because the inorganic and the catalytic chemists moved along lines which at that time were orthogonal.

2. Catalytic species

2.1. DIADSORBED ALKANES AND CYCLOALKANES

The availability of the mass spectrometer after World War II permitted measurement of the D_i's and led to a revival of interest in the mechanism of hydrocarbon reactions as studied by hydrogenation with deuterium and by isotopic exchange between alkanes and deuterium. This work considerably enlarged the organometallic zoo and provided further information about its denizens.

The mass spectrometer gives the distribution of D_i's. In the simple case of one set of uniform sites, this can be considered a function of the ratio $[D*]/[H*]$ and the distribution of N_i's. N_i is the fraction of molecules in which i atoms of hydrogen have been equilibrated with the surface D/H pool. In the products of hydrogenations with D_2, N_0 and N_1 are necessarily zero. In mechanism, it is the N_i's which are of interest rather than the D_i's. When there is exchange between the H atoms of adsorbates and surface $*D$ to generate $H*$, fast desorption of HD leads to a large $[D*]/[H*]$. In the isotopic exchange of alkanes, the ratio is usually large enough to make the distribution of D_i's and N_i's essentially identical. Since desorption of HD is inhibited by alkene, in alkane formed from alkene + D_2, D_{av} is ~ 2, $[D*]/[H*]$ is often near unity, and it may be difficult to reconstruct the N_i's from the D_i's. Therefore, because of the much easier interpretation, studies of isotopic exchange on Group VIII metals were initially more fruitful than those of hydrogenation.

In the 1950's, isotopic exchange between deuterium and a large number of alkanes and cycloalkanes was investigated largely by the Kemball group working with evaporated metal films [5] and the Burwell group working in some cases with evaporated films but mostly with supported metal catalysts [6]. By and large agreement between the work on films and that on supported catalysts was good.

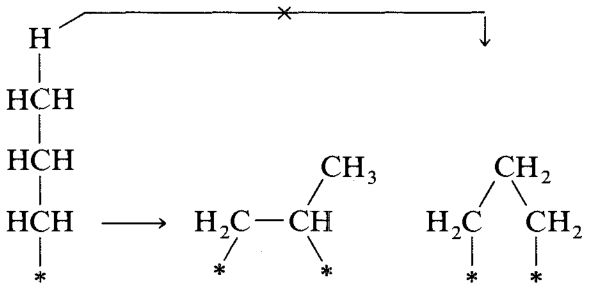
The Kemball laboratory started with methane and worked its way progressively through ethane, propane, isobutane, and cyclopentane to cyclohexane. The other laboratory started with optically active 3-methylhexane, heptane, 3,3-dimethylhexane and 2,2,3-trimethylpentane. These studies helped to populate the organometallic zoo.

Consider the exchange of pentane on W, Mo, Ni, Pt, Pd or Rh at 0 to 80 °C. All D_i's are positive from $i = 1$ to $i = 12$, but the exact distribution pattern depends upon the metal, its pretreatment, the temperature of reaction and the partial pressures of alkane and hydrocarbon. With W and Mo at $T \leqslant 0\,°\mathrm{C}$, D_i decreases monotonically with increasing i, whereas, with Rh, Pd, Pt, and Ni at 0–100 °C, D_i goes through a minimum with increasing i. Suppose that N_{12} equaled unity and $D/H = 10$. Although all hydrogen atoms would have exchanged with the surface D/H pool, D_{11} would be as large as D_{12} as one may calculate with the binomial theorem. Experimentally $D_{12}/D_{11} \gg 1$ except for W and Mo. Thus, at least on most metals, $[D*]/[H*]$ is large for the process leading to the more highly exchanged species. Similar conclusions have been reached for the exchange of a large number of other hydrocarbons.

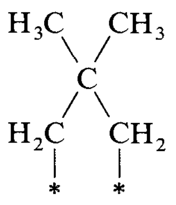
Anderson and Kemball [7] proposed that exchange occurred by alkane(g) $\rightarrow \boldsymbol{B} \rightarrow (\boldsymbol{A} \rightarrow \boldsymbol{B})_n \rightarrow$ alkane-d_i. This permits movement of the point of attachment in ***A*** along the chain and formation of perdeuteroalkane. For example, 1-monoadsorbed butane → 1,2-diadsorbed butane → 2-monoadsorbed butane → 2,3-diadsorbed butane → 3-monoadsorbed butane etc. Thus, the following relations apply to the processes of Scheme 1 on Pt, Pd, Rh, and Ni which lead to the more extensively exchanged species: $r_4 = r_{-4} \gg r_3 = r_{-3}$ and $r_{-2} = r_2 \gg r_3$. The formation of large amounts of highly exchanged alkanes establishes that rotations about C–C bonds in monoadsorbed alkane must be fast.

It was recognized early that sites with only one value of k_{-2}/k_3 could not lead to an isotopic distribution pattern with a deep minimum. Such patterns were interpreted as resulting from two sets of sites, one with k_{-2}/k_3 much larger than the other [7,8].

It was also found early [9] that a single branch in a hydrocarbon chain did not impede the exchange of all hydrogen atoms (heptane vs. 3-methylhexane), but that a gem-dimethyl group was a block to full exchange. Thus, $C_3D_7C(CH_3)_2(C_2H_5)$ was large in 3,3-dimethylhexane, but D_8 and up were zero. Throughout this paper the results quoted are for low conversions and, thus, for one period of residence on the catalyst surface. One concludes that at 50–100 °C monoadsorbed alkane ***B*** readily reacts to form α,β-diadsorbed ***A*** but not to form α,γ-diadsorbed alkane ***D***.



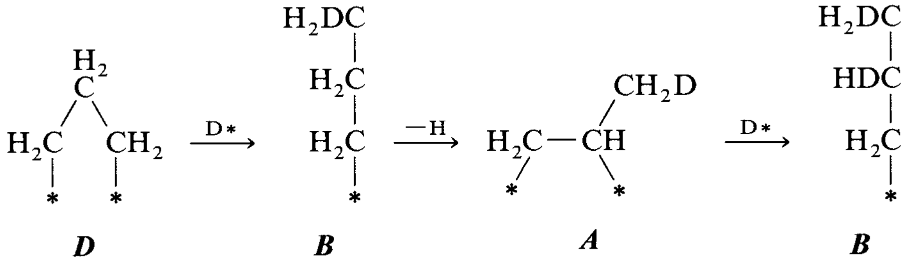
B ***A*** ***D***



D′

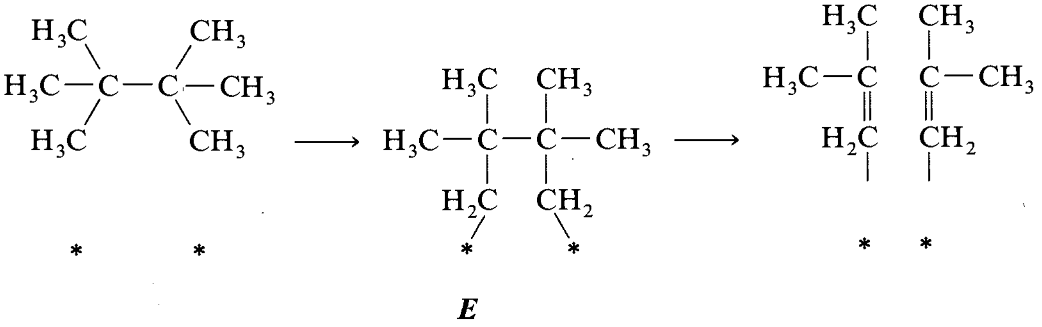
A number of Group VIII metals catalyze the hydrogenolysis of cyclopropanes at room temperatures and it had been proposed that species like ***D*** were intermediates in this reaction. However, reaction between cyclopropane and D_2

could not be used to test this idea. Suppose that cyclopropane reacted with a metal surface to form 1,3-diadsorbed propane ***D*** which then reacted with $*D$ to form (***B***). Before ***B*** could desorb, it



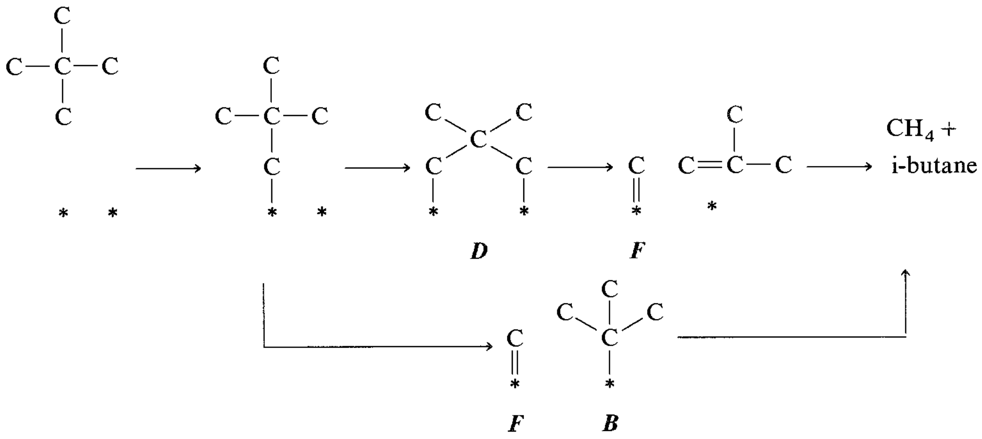
would alternate with ***A*** and information as to the initial mode of adsorption of cycloproane would be obliterated. Chevreau and Gault [10] cleverly hydrogenolyzed 2,2-dimethylcyclopropane with deuterium. In this cyclopropane, ring opening occurs almost exclusively opposite the gem-dimethyl group to give neopentane. On most metals the neopentane was $(CH_3)_2C(CH_2D)_2$ which would be formed by initial adsorption as ***D*** followed by reaction with two $*D$. The gem-dimethyl group prevents that further exchange which would obliterate information as to the position of initial adsorption. Cyclopropane is a higher energy molecule than monadsorbed alkane. Presumably, it is the strain energy and the nature of the orbitals in cyclopropane which facilitates its reaction to form 1,3-diadsorbed alkane.

It is difficult to avoid the following mechanism for the hydrogenolysis of 2,2,3,3-tetramethylbutane via ***E*** (Scheme 2).



Scheme 2.

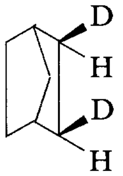
For example, the hydrogenolysis of tetramethylbutane on Rh/SiO_2 at 220 °C goes 86% by Scheme 2 and 14% by a process forming methane and 2,2,3-trimethylbutane [11]. It is difficult to avoid one of the following sequences for the similar process which occur in the hydrogenolysis of neopentane [12] (Scheme 3).

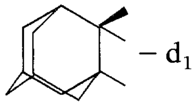


Scheme 3.

Both mechanisms introduce an α,α-diadsorbed alkane (F) which is also a likely intermediate in the formation of multiply exchanged methane in isotopic exchange between methane and deuterium. There are close molecular mechanistic analogs to Schemes 2 [12] and 3 [13].

What is the conformation of the α,β-diadsorbed alkane? Is it eclipsed or staggered (or either)? The maximally exchanged species in the isotopic exchange of bicycloheptane [14] and adamantane [15] are shown below.





The two deuterium atoms in bicycloheptane are rigidly held in eclipsed conformations. The adjacent bridgehead positions are staggered with respect to the methylene units. Thus, α,β-diadsorbed alkane A can exist in the eclipsed conformation but not in the staggered one. All adjacent hydrogen atoms in adamantane are staggered. Monodeuteroadamantane is the maximally exchanged species. This confirms that A cannot exist in the staggered conformation.

The discovery of organometallic compounds containing π-complexed ethylene led to the suggestion that A occurred not in the structure originally suggested by Horiuti and Polanyi but rather as a π-complex. A'. However, in a π-complex, the four bonds attached to the C=C unit are bent back from C=C and the separation between the two atoms of C is substantially increased. Thus, the geometry of the π-complexed species differs rather little from that of the di-σ-adsorbed form. It has been the opinion of the author that the two forms could not be distinguished by isotopic exchange experiments [1]. Both forms have been seen by infrared spectroscopy [16] and both forms are converted to alkane in the presence of hydrogen, but which form is involved in olefin hydrogenation is not yet clear. Perhaps both are.

At about 100 ° C in the presence of hydrogen, optically active 3-methylhexane is racemized by Ni/SiO_2 [9] at a rate,

$$\text{rate} = \left(k_0\, e^{-13100/T}\right)\left(p_{H_2}^{-0.6}\right)\left(p_{3MH}^{0.5}\right) \tag{1}$$

which is unaltered upon replacing the hydrogen with deuterium. Thus the adsorption process is likely to involve simple dissociative adsorption rather than reactive adsorption,

$$RH + H* \longrightarrow R* + H_2.$$

As already described, the 3-methylhexane is isotopically exchanged with all values of D_i being finite and D_{16} being a maximum. At 110 ° C, the ratio, (molecules exchanged/molecules racemized) was about 1.6 on Ni/SiO_2 [8] and 1.25 on Pd/Al_2O_3 [14]. Considering the significantly finite values of $D_1 - D_4$, nearly every exchange of the hydrogen at the tertiary position must have been accompanied by racemization. No process in Scheme 1 would give racemization.

An important step in the development of the organometallic zoo was the investigation by Anderson and Kemball of isotopic exchange between cyclopen-

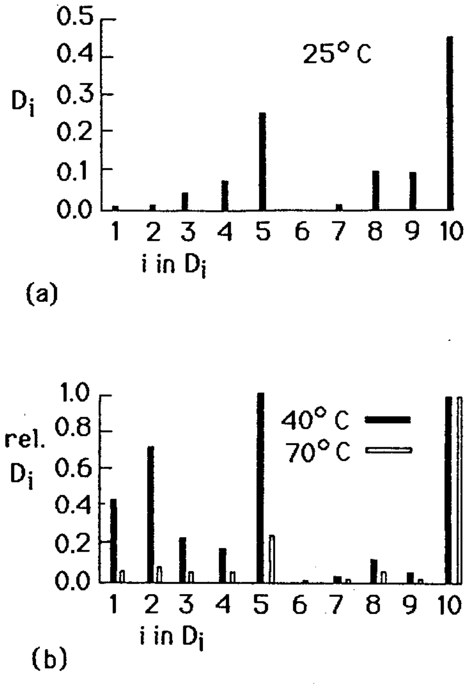


Fig. 2. Isotopic exchange of cyclopentane on palladium catalysts. (a) D_i vs. i on Pd flim at 25 ° C from ref. [7]. (b) D_i relative to $D_{10} = 1.0$ vs. i on Pt/Al_2O_3 at 40 and 70 ° C.

tane and deuterium on evaporated palladium films [17]. Figure 2 shows the results for reaction at 25 °C and also for reaction on Pd/Al_2O_3 at 40 and 70 °C [18].

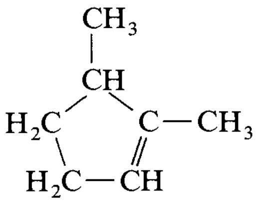
If α,β-diadsorbed alkane is cis-eclipsed, then the sequence cyclopentane(g) → $\boldsymbol{B}(\rightarrow \boldsymbol{A} \rightarrow \boldsymbol{B})_n \rightarrow$ cyclopentane(g) in Scheme 1 would exchange only those hydrogen atoms on that side of the ring upon which the cyclopentane was originally adsorbed. That is, the maximally exchanged cyclopentane would be $H_5C_5D_5$. Clearly then, some additional process provides for transfer of the position of attachment from one side of the cyclopentane ring to the other. This process is likely to be related to that which gives racemization, a supposition confirmed by the interepimerization of cis- and trans-dimethylcyclopentane which accompanies the exchange of these molecules [19]. It was assumed in the cyclopentane work that the two sets of hydrogen atoms of cyclopentane were those on opposite sides of the ring, an assumption not easily avoided. However, Faro et al. have recently proved by deuterium NMR that the original assumption was correct [20].

Increasing p_{D_2} or lowering the temperature reduces the values of the D_i's for larger i's [15]. The effect of p_{D_2} accords with exchange involving intermediates which have lost more than one hydrogen atom.

As would be expected, cycloöctane exchanged on Pd/Al_2O_3 exhibits no break between D_8 and D_9 [14]. The cyclooctane ring is large enough so that an adjacent pair of trans hydrogen atoms can be eclipsed. Thus an adsorbed secondary olefin (di-σ-adsorbed or π-complexed) can exist in either the cis-eclipsed or the trans-eclipsed form.

In exchange with deuterium, methylcyclopentane exhibits two sets of hydrogen atoms, one with 4 and one with 8 atoms [14]. On the principles derived above, the 4 hydrogen atoms on the same side of the ring would constitute one set and the 5 hydrogen atoms on the other side of the ring plus the 3 atoms in the methyl group would constitute the other set [15]. The results of exchange of a large number of other alkanes and cycloalkane accord with the principles derived above.

What process leads to two-set exchange of cyclopentane? Anderson and Kemball [17] proposed that it involved the intermediate, 1,1-diadsorbed cyclopentane [$\boldsymbol{F}$]. In this model, a frequently formed $\boldsymbol{F}$ would be $*{=}H_4C_5D_4$ in which one side of the ring would have four H atoms, the other, 4 D atoms. Addition of D could occur in two ways, to give the species monoadsorbed on the side of the ring with the 4 H atoms, or on that with the 4 D atoms. The first could proceed to C_5D_{10}, the second could only form $C_5H_4D_6$ without again passing through the α,α-diadsorbed species. On this model, if both D_5 and D_{10} have substantial values, D_6 should also be large. On both Pd film and Pd/Al_2O_3, D_6 and D_7 were nearly zero. Further, an α,α-intermediate cannot cause racemization and epimerization to accompany isotopic exchange. Two-set exchange requires either an intermediate or a transition state which is symmetric (racemization and epimerization). One such species is a desorbed cyclopentene, for example in the exchange of 1,2-dimethylcyclopentane,

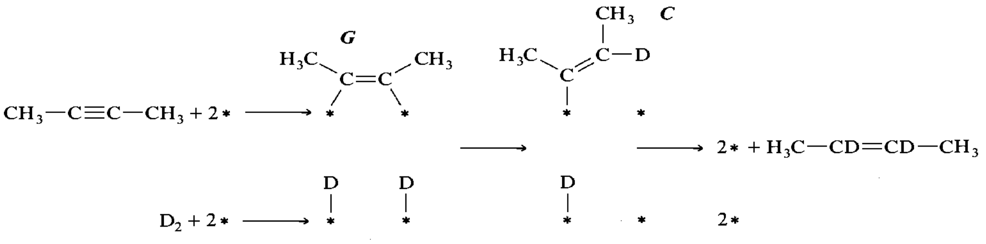


However, the activation energy for liberation of desorbed cyclopentene is too large, at least equal to the heat of hydrogenation of cyclopentene [18]. A cyclopentene oriented vertically with respect to the catalyst surface and weakly bonded to it would be a possible intermediate energetically and this species is probably involved in the two-set exchange of cyclopentane [15,20,21]. This process has been called a *rollover* process [15]. If one considers desorbed cyclopentene as the limit of rollover, it is apparent that the maximally exchanged cyclopentane formed by one rollover is $C_5H_2D_8$ and, indeed, cyclopentanes exchanged on palladium at temperatures below 100 ° C always exhibit a maximum at D_8. On Pt, D_6 is not near zero and any maximum at D_8 is much less clear. Two set exchange on Pt may well involve at least some contribution from α,α-diadsorbed cyclopentane [22].

Hilaire et al. [23] have reported that exchange between deuterium and methyl- and dimethylcyclobutanes at 0–100 ° C on Pd films resembles that of the corresponding cyclopentanes. However, another paper [24] reported a very different exchange pattern for cyclobutane itself on Pd films. D_1 was large and following which D_i declined rapidly with increasing i. It is likely that some artefact distorted the results of this work. However, the question of the mechanism or mechanisms of two-set exchange does not appear to be fully resolved.

2.2. SPECIES IN THE HYDROGENATION OF ACETYLENES AND DIENES

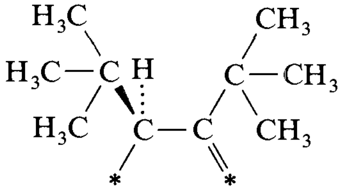
When dimethylacetylene is hydrogenated on palladium catalysts, *cis*-dimethyl-2-butene is the nearly exclusive initial product. Further reaction of the butene is inhibited as long as any acetylene remains unreacted. With deuterium, the butene is *cis*-CH_3–CD=CD–CH_3 and no exchanged butyne is formed [25]. The likely mechanism is presented in Scheme 4.



Scheme 4.

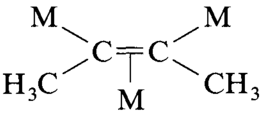
In hydrogenation on Pd only very small amounts of *trans*-ene and ane are formed initially, but other metals usually give more. The hydrogenation of di-t-butylacetylene illuminates the origin of *trans*-ene and ane [26]. The steric strain between the two t-butyl groups in cis-di-t-butylethylene vs trans-di-t-butylethylene is large, 42 kJ, and the intraadsorbate strain in ***G*** should also be substantial. Nevertheless, 69% of the product is the strained *cis*-ene formed by the sequence yne → ***G*** → ***C*** → ene. However, with 3-hexyne the percentage of cis-ene (here unstrained) is much larger. Scheme 2 provides no way in which ***G*** can lead to trans-2-butene nor in which ***G*** or ***C*** can become converted to ***A*** or ***B*** and thus lead to alkane. Thus, with di-t-butylacetylene the intraadsorbate strain in ***G*** must promote some surface reaction which is slow in molecules like 3-hexyne. It seem likely that the intermediate leading to trans-ene and ane is species ***H***.

H



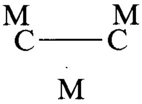
In comparison with 3-hexyne, conversion of ***G*** to ***H*** rather than to ***C*** is favored by release of intraadsorbate strain. ***H*** will add an atom of hydrogen to form trans-***A*** (trans-diadsorbed di-t-butylethane) which may either react with two H* to liberate alkane or desorb as *trans*-di-t-butylethylene, a process favored by release of surface-adsorbate strain [26]. ***H*** is likely to be the source of ane and trans-ene in the initial products of the hydrogenation of acetylenes in general.

The question as to the relative contribution of σ- and π-binding has arisen for ***G*** as well as for ***A***. Here, for the first time in this paper, we come to evidence from single crystal studies. On Pt(111) at 300 K, as judged by electron energy loss spectroscopy (EELS), 2-butyne adsorbs to form ***G**** in which the plane of the di-σ-adsorbed 2-butene unit is bent over to π-complex with a third surface atom [27]. The asterisk indicates that the species derives from surface chemistry rather than from catalysis.



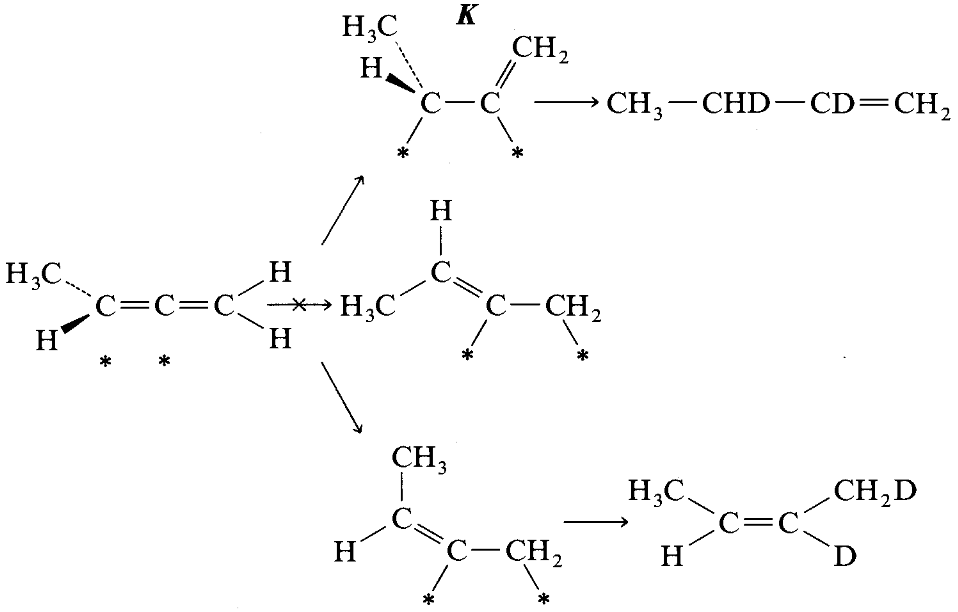
At 170 K, *cis*- and *trans*-2-butene adsorb to form the appropriate epimer of 2,3-di-σ-adsorbed butane. Both react at 300 K to form ***G****. Also for the first time in this paper, identification of a species depends upon the use of a molecular organometallic complex as a spectroscopic reference, in this case, $Os_3(CO)_9(\mu_3\text{-}\eta_2\text{-}C_4H_6)$. This compound contains an equilateral triangle of osmium atoms to which the acetylene unit is bonded as shown above. Hydrogenation of 2-butyne with deuterium could not serve to distinguish between ***G*** and ***G****. From EELS, Avery concludes that below 330 K the structure of adsorbed acetylene is also ***G****

[28]. And for a first mention of a quantum mechanical species, Silvestre and Hoffmann have calculated that acetylene is located on Pt(111) as shown below [29]



The hydrogenation of 1-butyne with D_2 unlike that of 2-butyne leads to some butene-d_3. About 12% of the residual hydrogen atom at C-1 in $CHD{=}CD{-}C_2H_5$ was exchanged during hydrogenation on Pd/Al_2O_3 at 35 °C [30]. Small amounts of $DC{\equiv}C{-}C_2H_5$ were also formed. The species ***J***, $*C{\equiv}C{-}R$, is probably involved.

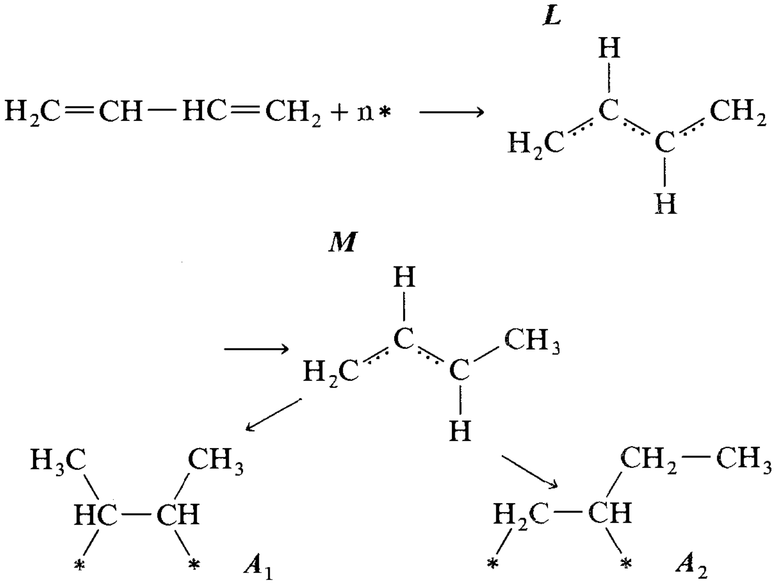
The hydrogenation of methylallene, $CH_3HC{=}C{=}CH_2$, with D_2 on Pd/Al_2O_3, forms $CH_3{-}CHD{-}CD{=}CH_2$ and $CH_3{-}CH{=}CD{-}CH_2D$ [30]. In the presence of unreacted allene, further reaction of the butenes is inhibited. The 2-ene is almost entirely cis and only very small amounts of butene-d_3 are formed. In methylallene, $CH_3HC{=}C{=}CH_2$, the planes of CH_3HC and CH_2 are perpendicular. Scheme 5 shows the probable mechanism.



Scheme 5.

Here, the allene adsorbed at one of the double bonds to form ***K***. The middle species of ***K*** in Scheme 5 would lead to the thermodynamically favored *trans*-2-butene, but this form of ***K*** is disfavored by adsorbate-surface strain. Indeed, on a flat surface like Pd(111) the methyl group would be closer to the surface than the carbon atoms which are bonded to it. Thus, the scheme accords with the experimental observation that the thermodynamically disfavored *cis*-2-butene is heavily favored catalytically over *trans*-2-butene.

The hydrogenation of 1,3-butadiene on Pd/Al_2O_3 at about 40 °C, gives roughly equal amounts of 1-butene and *trans*-2-butene [30] but much less *cis*-2-butene than that corresponding to the cis/trans equilibrium ratio. Since the presence of butadiene inhibits further reaction of butenes, butadiene must be adsorbed considerably more strongly than butene and therefore not as $C{*}H_2{-}C{*}H{-}CH{=}CH_2$, i.e., only at one double bond. Further, in competitive hydrogenations, 2-butyne and 1,3-butadiene hydrogenate at about equal rates. Thus, butadiene probably adsorbs as some species like ***L*** which then reacts with H* to form ***M***, probably a π-allylic species (Scheme 6).



Scheme 6.

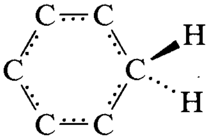
Because of intraadsorbate strain, species ***L*** would be largely in the anti form and would proceed on to *trans*-2-butene. Further reaction of H* with ***M*** would form A_1 or A_2. Addition to ***M*** at C-1 would generate 2,3-diadsorbed 2-butane A_1, at C-3, 1,2-diadsorbed 1-butane A_2. Since species of type *A* do not appear in the catalytic sequences of schemes 4 and 5, initial formation of butenes would not be expected there. However, with 1,3-butadiene, one must assume that the strongly adsorbed butadiene causes desorption of the species *A* as butenes rather than $A \rightarrow \boldsymbol{B} \rightarrow$ butane. In hydrogenation of 2-butyne with deuterium on Pd, D_2 for butene is nearly unity; for hydrogenation of methylallene, about 0.85; but for that of 1,3-butadiene, only about 0.69 with D_3 and D_4 accounting for the remainder. Unreacted butadiene does not become deuterated. Thus, the conversion of ***L*** to ***M*** must be partly reversible. NMR indicated that the *trans*-butene product was primarily $DCH_2{-}CH{=}CH{-}CH_2D$ which accords with the proposed mechanism and would not accord with a mechanism which involved an intermediate like ***C***. The hydrogenation of 1,3-butadiene on a number of other metal catalysts is similar to that on palladium. For results with a number of rhenium catalysts and references to results on other metals, see ref. [31]. Generally similar behavior and mechanistic views have been reported for the hydrogenation of 1,3-butadiene on Pt(111), (110) and (100) except that the selectivity to butane is much larger [32].

Participation of π-allyl species like ***M*** has been proposed in other reactions but not always persuasively. The isotopic exchange of olefin which accompanies hydrogenation with deuterium varies with metal and pretreatment. Microwave spectroscopic determination of the location of D in exchanged propene and 1-butene has been taken to indicate that exchange could proceed under particular conditions by one, two or three of the following process: via vinylic ***C***, via allylic ***M***, or via associative ***B*** intermediates (Scheme 1) [33,34]. Interpretation here is difficilitated by the small ratio D/H which obtains during hydrogenations of olefins with deuterium.

An important intermediate is missing from fig. 1, the intermediate in the interisomerization of methylcyclopentane, hexane, 2-methylpentane, and 3-methylpentane on platinum at about 270 ° C [35]. It must be some kind of an adsorbed methylcyclopentane which can react with one or more $*$H and desorb or which can undergo hydrogenolysis of any of its 5 C–C bonds and desorb as one of the three hexanes. Unfortunately the species is not well enough described to enter in the fig. 1.

2.3. SPECIES DERIVED FROM BENZENE

Because of evidence from chemisorption [36] and the rate of hydrogenation of benzene on Group VIII metals being zero order in benzene, it has been general believed that benzene is adsorbed flat as some kind of π-complex resembling that of molecular complexes of benzene with atoms of transition metals such as bis[hexahaptobenzene] chromium [37]. Since the addition of the first hydrogen atom would lead to the destruction of the resonance energy of benzene, the residual unsaturated C_5 unit must remain complexed with the surface so as to compensate for this loss and probably as [38].



However, this species is a little too uncertain to enter in fig. 1. It would be assumed to react further to form the equivalent adsorbed cyclohexadiene. A somewhat different view is given by Mirodatos et al. [39] in which the surface of Ni is primarily covered by H_2 and the coverage by hydrocarbon intermediates is only 0.01.

On a large number of metals, hydrogenation with D_2 at about 25 °C is accompanied by isotopic exchange to form benzene-*d*. Since the kinetic orders of the two reactions differ and since their rate ratio varies with catalyst pretreatment, they probably involve different sites. The exchange reaction seems to require C_6H_5*, ***O***, as an intermediate. The adsorbed C_6H_7 species shown above might be imagined to be the intermediate, but the principle of microscopic reversibility poses a problem. One would expect the D atom to be added from below and if so the D atom should be removed, not the original H atom. The dissociative adsorption mechanism is supported by the results of exchange of toluene. Exchange of toluene at para and meta positions is fast vs. that at ortho ones [40]. The methyl group should block formation of ortho-***O*** more severely than that of ortho-$CH_3C_6H_5H$(ads).

2.4. ADSORBED HYDROCARBON RESIDUES

Reactions between hydrocarbons and hydrogen on Group VIII metals are accompanied by the deposition of carbonaceous residues as first noted in the hydrogenation of ethylene [2,41,42]. The residue is liberated as an alkane with the same number of carbon atoms as the reactant upon heating in H_2 at slightly above reaction temperatures when $T_{\text{reaction}} \leqslant 25\,^\circ C$. Similar results are obtained at higher T_{reaction}, e.g., Pt/SiO_2 at 81 °C for isotopic exchange between D_2 and pentane or cyclopentane, except that 10% of the residue is liberated only at 300 °C and as methane. Even in neohexane + D_2 on Pt/SiO_2 or Pd/SiO_2 at ~ 100 °C, most of the residue is liberated as unaltered neohexane [43].

It has often been suggested that the residues are composed of highly unsaturated species. But mere unsaturation is not enough. Acetylenes and 1,2- and 1,3-dienes hydrogenate normally. Further, the hydrogenation of vinylacetylene, $H{-}C{\equiv}C{-}CH{=}CH_2$, on $Pd/BaSO_4$ at 25 °C in solution in ethanol appears normal and further reaction of the major product, $H_2C{=}CH{-}CH{=}CH_2$, is inhibited by vinylacetylene [44]. Vinylacetylene is, therefore, bonded to the surface by more than merely the $-C{\equiv}C-$ unit and probably as a species analogous to ***L***. It may be noted that none of the species discussed up to this point contains a $*{\equiv}C-$ unit.

3. Surface chemistry species

Surface chemistry has led to the opening of a new branch of the organometallic zoo. The inhabitants were first examined by the techniques of what can be called surface physical chemistry applied to supported catalysts, in particular, by IR spectroscopy. More recently solid state NMR has been employed. Now-a-days surface species are most frequently studied on single crystal surfaces and by the techniques of surface chemical physics. Despite its rather low resolution, high resolution electron energy loss spectroscopy, EELS has been a particularly useful tool, but angle resolved UV photoelectron spectroscopy and near edge X-ray absorption fine structure have also been employed. Comparison of spectra with those of molecular organometallic compounds of known structure has become common. Such comparison goes back to the assignment of bridging and linear adsorbed CO on supported metal catalysts. Surface chemistry species will be designated by *. The observation of ***A**** and ***A′**** by IR has already been mentioned [16] as has that of ***G**** on Pt(111) by electron energy loss spectroscopy (27). Others to be discussed ar adsorbed alkylidyne ***P****, σ-adsorbed methyl ***B****, adsorbed methine ***Q****, adsorbed cyclopentadienyl$^-$ ***R****, and π-adsorbed benzene ***N****.

One of the most studied in this group is 1,1,1-triadsorbed alkane, adsorbed alkylidyne, $*{\equiv}C{-}CH_2R$, ***P****, first characterized as $*{\equiv}C{-}CH_3$ on the (111) plane of platinum by the Somorjai group at Berkeley [45] but since seen on the surfaces of other metals and on conventional supported catalysts. In most cases the hydrogen-free carbon atom is bonded to an equilateral triangle of metal atoms. Ref. [46] lists 27 previous references to $*{\equiv}C{-}CH_2R$. The EELS spectrum of $*{\equiv}C{-}CH_3$ is compatible with the infrared spectrum of $CH_3C(Co)_3(CO)_9$ (which contains a carbon atom bonded to an equilateral triangle of Co atoms) [45,47]. The rotation of the methyl group in $*{\equiv}C{-}CH_3$ is slow on the IR time scale but fast on that of NMR [48]. The most noteworthy characteristic of $*{\equiv}C{-}CH_2R$ is the slowness with which it is removed from metal surfaces by hydrogen at 50 ° C. ***P**** may well be involved in that low temperature carbonaceous residue which reacts with H_2 to liberate alkane with the some number of atoms of carbon as the original hydrocarbon. However, this would not be the case for reactions with cyclo-C_5 compounds nor for the hydrogenation of secondary alkenes [49].

Carbon atoms on Ru(001) react with H_2 at about 370 ° C to form $*{\equiv}CH$, ***Q****, which was characterized by EELS [50]. This role of this species in catalysis is not yet clear.

Despite the pervasive involvement of monadsorbed alkanes in reactions of hydrocarbons, reports of sightings of ***B**** were rare and possibly mistaken. The problem seems to result from the coupling of two phenomena, the dissociative adsorption of alkanes requires a substantial activation energy and, in the absence of hydrogen, monadsorbed alkanes decompose into $*H$ and adsorbates containing less hydrogen. The presence of hydrogen inhibits decomposition of $R*$, but it also promotes $R* + H* \rightarrow RH(g)$. Thus, in the absence of hydrogen, $R*$ is unstable at a temperature at which alkane reacts to form $R* + H*$. The problem was recently solved by exposing Ni(111) at 140 K to a beam of methane molecules with a translational energy normal to the surface of 17 kcal mol^{-1} [51]. Spectroscopic examination indicated that this procedure prepared surface σ-methyl. ***B**** decomposed at 150 K.

Several calculated structures of $*{-}CH_3$ had been published with disagreeing conclusions. The most recent calculation and the one at the highest level employed nickel clusters and electron correlation. CH_3 prefered to be bonded at a three-fold hollow site with a binding energy of 50–55 kcal mol^{-1} [52]. There was no evidence for agostic interactions (binding between any of the methyl hydrogen atoms and nickel atoms).

Cyclopentane strongly physisorbs on Pt(111) at 90 K. Some of the adsorbed cyclopentane desorbs at ~ 200 K and some loses two atoms of hydrogen to form cis-eclipsed σ-1,2-diadsorbed cyclopentane [53], $A*$. At about 260 K this loses more hydrogen to generate 1,2,3,4,5-pentadsorbed cyclopentane or pentahapto-cyclopentadienyl$^-$, $R*$, which was identified by its C/H stoichiometry and by EELS. The EELS spectrum closely resembled that of molecular metallocene-like species containing a M–(Cp^-) bond. $\boldsymbol{R}*$ is stable to about 480 K.

On many surfaces adsorbed benzene has the virtue that it does not decompose at room temperatures but remains still for examination. Using angle resolved, polarized UV photoelectron spectroscopy, Netzer et al. concluded that benzene adsorbed on Rh(111) has C_{6v} symmetry [54] with the ring centered over an on-top position and the C–C bonds parallel to the close-packed rows of Rh atoms. The adsorbed benzene is ordered and essentially close packed. Using a technique like that just cited, Somers, et al. found a small distortion from C_{6v} towards a single Kekulé structure for Pt(111), larger than for Ni(111), Pd(111) and Rh(111) but smaller than for Ir(111), Os(0001) and Re(0001) [55].

Surman et al. have used EELS to examine isotopic exchange between D_2 and benzene adsorbed on Pt(110) at ~ 320 K [56]. Since adsorbed benzene was stable at up to 346 K, they concluded that the exchange could not proceed dissociatively, i.e., via species $\boldsymbol{O}$ and they adopted an addition-elimination mechanism via C_6H_7*. They did not, however, discuss the problem posed by microscopic reversibility.

4. Postcript

It will have been noted that catalytic techniques, particularly isotopic exchange, and hydrogenation, were rather good at identifying the structural identity of adsorbed intermediates but were ineffective in providing information about the catalytic site or the geometry of the adsorbate-site interaction. On the other hand, the various spectroscopic techniques were effective in providing information on the latter point. A proper understanding of the electronic details of adsorbed intermediates will require further applications of quantum mechanics. Although the species of the surface chemistry section have a perfectly valid existence without applications to other branches of science, one might wish to transfer them to the catalytic section. However, the process is not straightforward. The absence of $H_2(g)$ during use of EELS or photoelectron spectroscopy may lead to the decomposition of species stable in the presence of one atm of H_2. Further, in the examples reported above, EELS was used to examine uniform (well, nearly) surfaces, many micrometers in diameter. The 1–10 nm particles of supported catalysts can have no planes of such a colossal extent. Further, the small particles are apt to be rough [43] and their surfaces may be mobile [57]. Results with stepped and kinked single crystal surfaces suggest that uniform low index planes may not provide perfect models for catalytic particles. Nevertheless, studies on single crystal surface are important in illuminating the background of adsorption and reactions on metals. In some cases it has been established that the surface chemistry and the catalytic species are of the same genus and very likely of the same species.

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