Multilayer Adsorption as a Possible Transition State in Heterogeneous Hydrogenation of C=C Double Bonds

V. Heral

Abstract—Ideas about the mechanism of heterogeneous catalytic hydrogenation are diverse. The Horiuti-Polanyi mechanism is most often referred to base on the idea of a semi-hydrogenated state. In our opinion, it does not represent a satisfactory explanation of the hydrogenation mechanism because, for example, (1) It neglects the fact that the bond of atomic hydrogen to the metal surface is strongly polarized, (2) It does not explain why a surface deprived of atomic hydrogen (by thermal desorption or by alkyne) loses isomerization capabilities, but hydrogenation capabilities remain preserved, (3) It was observed that during the hydrogenation of 1-alkenes, the reaction can be of the 0th order to hydrogen and to the alkene at the same time, which is excluded during the competitive adsorption of both reactants on the catalyst surface. We offer an alternative mechanism that satisfactorily explains many of the ambiguities: It is the idea of an independent course of olefin isomerization, catalyzed by acidic atomic hydrogen bonded on the surface of the catalyst, in addition to the hydrogenation itself, in which a two-layer complex appears on the surface of the catalyst: olefin bound to the surface and molecular hydrogen bound to it in the second layer. The rate-determining step of hydrogenation is the conversion of this complex into the final product. In our opinion, the Horiuti-Polanyi mechanism is flawed, and we naturally think that our two-layer theory better describes the experimental findings.

Keywords—Acidity of hydrogenation catalyst, Horiuti-Polanyi, hydrogenation, two-layer hydrogenation.

I. Introduction

ALMOST the entire chemical industry is built on catalytic processes. We distinguish between homogeneous catalysis, when the catalyst is dissolved in the liquid phase - an example is the production of the vast majority of polymers - and heterogeneous catalysis, when the catalyst is in the form of tablets through which the stream of reactants passes or is, possibly, in the form of a powder dispersed in the liquid or gas phase. This text will focus on heterogeneous catalytic hydrogenation and, more specifically, on olefinic bond hydrogenation.

While the industrial processes are generally perfectly mastered, not much is known about the course of the catalytic action itself. Chemical literature is growing unstoppably, we are bombarded with now studies every day. It is necessary to find means to classify and sort this knowledge. The search for a kind of Systema Naturæ *(according to the terminology of Carl von Linné, 1735)* is therefore a justified effort.

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We consider it useful to present here one more theory of the mechanism of catalytic hydrogenation: our theory will be "two-layer theory".

II. Isomerization

First, we will discuss isomerization, first isomerization in the absence of a hydrogenation catalyst. Olefins are known to isomerize very easily in an acidic environment. The basic types of olefin isomerization are: *cis/trans* isomerization, double bond shift, hydrogen/deuterium isotopic exchange. In a homogeneous medium, isomerization is a reversible reaction catalyzed by a hydrogen cation. An example is *cis/trans* isomerization as shown in Fig. 1.

Fig. 1 Cis/trans isomerization

Thus, acidic, protonic hydrogen is required for isomerization. In a heterogeneous environment, isomerization can also be performed by an acid-base catalyst, such as γ-aluminium oxide.

In the case of a heterogeneous reaction on metal surfaces in the presence of hydrogen, we must assume that the isomerization is a reaction catalyzed – just as in a homogeneous environment – by protonic hydrogen. It is known that hydrogen dissolved in a metal travels under the influence of an electric current, which is considered to be evidence of its presence in a "metallic", i.e., protonic, form.

Hydrogen atoms on the surface of the metal are in equilibrium with protons. In this context, it is good to recall the Nernst equation, according to which the electrode potential of a metal under hydrogen can be written (taking into account the equilibrium $H_2 \leftrightarrow 2H$).

$$E_{H_2} = E_{H_2}^0 - \frac{RT}{F} ln \frac{\sqrt{\frac{P_{H_2}}{P^0}}}{a_{H^+}} \tag{1}$$

Therefore, we believe that acidic hydrogen on the catalyst surface enables "classical" acidic isomerization with intermediates of the type.

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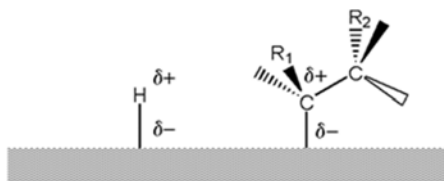Vol:18, No:9, 2024

Fig. 2 Polarity of surface adsorption

The total amount of protonic hydrogen on the surface of the catalyst is probably related to the ability of individual metals to dissolve hydrogen. An extreme case is palladium, which is able to dissolve 350-850 times more hydrogen than its own volume [1] - a solid solution of hydrogen in palladium with the composition Pd_2H is even considered a defined compound. In contrast, in platinum, at normal temperatures and pressure, only $10^{-7}\,cm^3\,H_2/cm^3$ Pt dissolves [2]. There is an obvious connection with the fact that isomerization reactions (and also hydrolytic reactions) take place on platinum only to a small extent, on palladium usually to a considerable extent. The hydrogen-metal bond can then be regarded as an acid, which dissociates under suitable conditions.

One observation on often mentioned heterogeneity of the catalytic surface: Regardless of possible deviations in the activity of individual active centers, a global characteristic can be attributed to the surface. For example, in (1), the global property is the electrode potential. It would be useless here to deal with *a priori* and *induced* heterogeneity - by *induced* heterogeneity we mean, for example, the fact that the adsorption of one mercury atom on the surface of the catalyst displaces 10 hydrogen atoms from it [3].

In our opinion, olefin isomerization during hydrogenation is caused by protonic, "acidic" atomic hydrogen chemically bonded to the catalyst surface. The alkyl complex formed by the addition of olefin to acidic hydrogen on the surface of the catalyst then has a positive charge. If it is indeed a "semi-hydrogenated state", the next step is the would have to be the reaction of the positively charged alkyl complex with the negatively charged hydride ion,

$$CH_3\text{-}CH_2^+ + H^- \rightarrow CH_3\text{-}CH_3$$
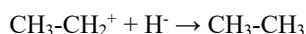
However, in the sense of the Nernst equation, the negative hydride ion is excluded on the homogeneous catalytic surface. The hydrogenation of olefins by hydrogen on metal surfaces must take place in a different state than via a semi-hydrogenated state as hypothesized by Horiuti-Polanyi theory.

In a homogeneous environment, ionic hydrogenation naturally exists. A suitable reducing agent must be used such as certain silane [4], alkali metal, magnesium, aluminum and other metals, metal hydrides, complex hydrides, metal salts, but also non-metal compounds: hydrazines, or many others [5]. Although these are very diverse reagents, different with their effectiveness and specificity, there are many similarities in their action. These agents generally do not hydrogenate isolated olefinic bonds, the catalytic hydrogenation of which is, on the contrary, very easy. A double bond can only be hydrogenated by reducing agents if it is activated in some way, e.g., by the

neighborhood of a polar group (e.g. -OH). The configuration on the saturated bond during hydrogenation with reducing agents indicates a trans-addition of hydrogen, while in catalytic hydrogenation it is a cis-addition of the entire hydrogen molecule, that is, both hydrogens approach from the same side of the double bond. If hydrogenation with a mixture of H_2 and D_2 is carried out on platinum, products with two hydrogen or two deuterium atoms are formed. Against this, we can cite the example of deuteration of ethylene in a solution of $SnCl_2$ + $MoCl_5$ in a protonic solvent (tetrahydrofuran methanol), when monodeuteroethane was mainly formed [6]. In general, hydrogenation with reducing agents is a *trans* addition and proceeds similarly to ionic addition of hydrogen halides, hydration, addition of acids and other *trans* additions that initiates electrophilic particles by forming a π-complex. In the case of olefinic compounds, a carbonyl ion is formed, to which a nucleophilic agent (hydride component) is then added.

To complicate matters a little, let us state that modification of the heterogeneous metallic catalyst with a metal salt, e.g., of platinum: ferric salts deactivate it for the hydrogenation of olefinic compounds, but at the same time increase its activity towards the aldehyde group [7], [8]. Impregnation of nickel catalysts with cadmium, zinc or lead gives similarly surprising results [9]-[11]. We will not deal here with those cases where a foreign metal acts, very likely, as a hydride hydrogen donor.

III. HYDROGENATION

We have some reservations about the heterogeneous hydrogenation mechanism proposed by Horiuti and Polanyi. This mechanism is illustrated, for example, as in Fig. 3.

We have already stated the first objection: the isomerization of olefins under the conditions of hydrogenation has a distinctly polar character, while the hydrogenation itself is a cis - addition of a complete hydrogen molecule.

The second doubt pertains to whether fragments of molecules travel on the surface as required by this mechanism. The principle of microscopic reversibility states that if a reaction proceeds in one direction through certain intermediates, then a reaction in the opposite direction will proceed through the same intermediates. In the case of hydrogenation, it is necessary to increase the temperature significantly to cause the opposite reaction. However, the questions arise: Why would hydrogen travel far on the surface after splitting. Is it possible for hydrogen to jump from one adsorption site to another? In general, the theory requires that there would be only one transition state between the initial and final states of a chemical reaction, and that this transition state should be as symmetrical as possible.

The third doubt stems from the observation that during the hydrogenation of 1-alkenes in the liquid phase, by increasing the hydrogen pressure, a state can be reached where the reaction is zero-order with respect to both components, i.e., both with respect to the olefin concentration and with respect to the hydrogen pressure. Let us assume that when increasing the concentration of one reactant it gradually fills the entire catalytic surface, so further increasing its concentration will no longer affect the occupation of the surface and thus the speed of

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the chemical reaction, the speed will become independent of the concentration of this component. But this cannot apply to two components at the same time: In competitive adsorption, both cannot occupy the entire catalytic surface. We will return to this matter in more detail, as we still have to mention the theory of two surfaces. According to this theory, there are two types of adsorption centers on the surface of the catalyst, one of which activates one component (olefin) and the other activates the second component (hydrogen). These activated components then somehow interact and a hydrogenation product is formed. For us, such an idea is unacceptable, including ideas that both components are activated on or near the surface of the catalyst to the extent that they then react together in space, outside the surface of the catalyst [12].
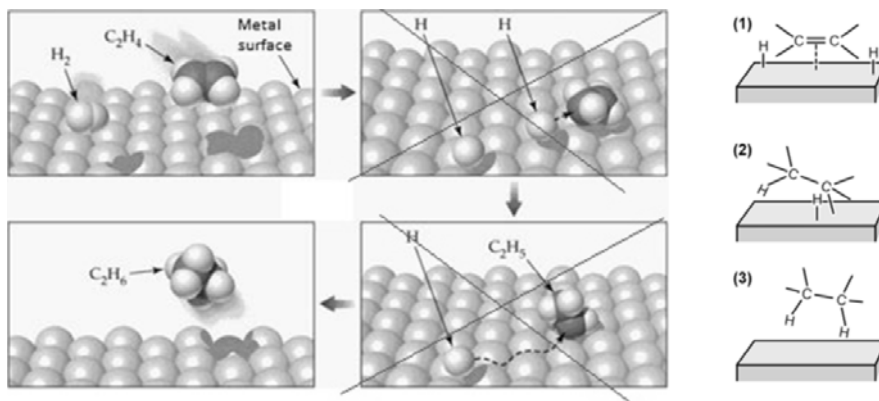

Fig. 3 Horiuti–Polanyi mechanism (double view)

Now is the time to discuss the nature of the active sites on the catalytic surface. We believe that in catalytic hydrogenation, the entire operation takes place on a single metal atom of the catalytic surface. Our own experience with the hydrogenation of 1-alkene on Wilkinson's homogeneous catalyst, chloridotris(triphenylphosphine)rhodium(I), leads us to this. As the concentration of the catalyst increases, the limiting activity is quickly reached, because there is a doubling between the Rh atoms of two molecules of the catalyst, which thus becomes catalytically inactive [13]. If a single metal atom acts in homogeneous hydrogenation, it can be the same in heterogeneous hydrogenation.

It is known that Benzene/cyclohexane conversion on a metal catalyst occur only when the metal surface forms a triangular structure with a distance between neighboring atoms between 2.40 and 2.77 Å. Metals with distances outside this range or with a different surface geometry are inactive. A hexagon can then be nicely drawn into such a structure, which represents six carbons, as shown in Fig. 4.
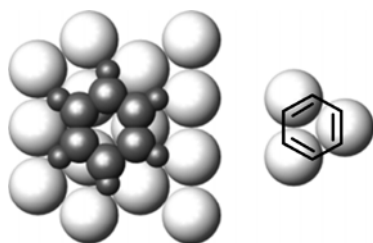

Fig. 4 Origins of "multiplet theory"

If we look at the benzene nucleus as a grouping of three double bonds, then the rule is confirmed that only one metal atom is enough to hydrogenate one double bond. By the way, Fig. 4 stood at the birth of the theory of multiplets, i.e., the idea that specific and special groupings of metal atoms are always needed for hydrogenation [14]-[17]. Boreskov [18] calls the followers of this theory "hunters of active centers". Our conclusion is exactly the opposite: one metal atom is enough for one double bond.

During hydrogenation at the expense of hydrogen dissolved in the catalyst, it was found that more isomers (double bond migration) are always formed in this way than during normal hydrogenation under hydrogen on the same catalyst. It was found [19], [20] that on osmium, iridium, platinum, ruthenium and rhodium blacks (black – metal oxide, reduced in situ) the strongly adsorbed form of hydrogen, i.e., atomic hydrogen, takes part in the displacement of the double bond, while in hydrogenation the weakly adsorbed form, i.e., molecular hydrogen [19], [20]. During the hydrogenation of ethylene in the gas phase on various metals, the ethylene molecule exchanges several hydrogens before saturation [21]. In the absence of hydrogen, the exchange does not occur [22].

It has been found that if the metal is dehydrogenated prior to the hydrogenation of the olefin, it loses its isomerization capabilities. A nickel catalyst, on which 1-octyne was hydrogenated previously loses its ability to isomerize 1-hexene, while its ability to hydrogenate this olefin remains unchanged [23]. The same was observed when the nickel catalyst was dehydrogenated by thermal desorption. Attempts to isomerize on metal surfaces in the absence of hydrogen tend to fail [22, p. 418], [24]-[26].

The conclusion is obvious: hydrogenation and isomerization occur simultaneously, but essentially independently. Atomic hydrogen directly bound to the surface of the catalyst plays a role in isomerization, but it does not play any role in hydrogenation. In our opinion, the hydrogenation of olefins occurs by the reaction of a surface-bound olefin with molecular hydrogen adsorbed in the second layer. We will now discuss

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this in more detail.

IV. Langmuir and Hinshelwood Kinetic Model

Concentrations usually play the role of activities in the rate equations of homogeneous reactions. For reactions on surfaces, the activity is defined as the proportion of surface active sites occupied by the respective reactant to the total number of surface active sites. Adsorption on the surface is competitive and takes place according to the Langmuir adsorption isotherm. We will assume that the following adsorption complexes are present on the surface (Fig. 5).
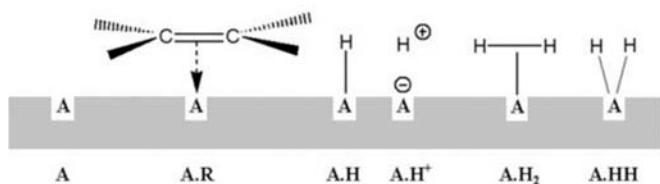

Fig. 5 Monolayer surface adsorption balance

We express the Longmuir equilibrium graphically in Fig. 5 and then by (5):

| [A.R]$_T$		[A.H]$_T$	[A.H$_2$]$_T$	A
A$_T$				

Fig. 5 Surface complexes in the first layer

$$[A]_T = [A] + [A.R]_T + [A.H]_T + [A.H_2]_T \qquad (2)$$

where A$_T$: total number of active surface sites; A: unoccupied active sites; [A.R]$_T$: active sites occupied by olefin; [A.H]$_T$: active sites occupied by atomic hydrogen (A.H, A.H$^+$); [A.H$_2$]$_T$: active sites occupied by molecular hydrogen (A.H$_2$, A.HH).
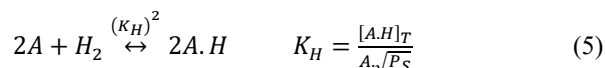
An adsorption equilibrium constant can be defined for each adsorbed component:

$$A + R \overset{K_R}{\leftrightarrow} A.R \qquad\qquad K_R = \frac{[A.R]_T}{A \cdot c} \qquad (3)$$
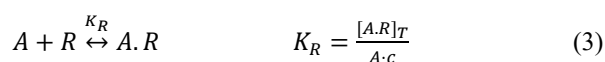
where c is the activity *(concentration)* of the olefin in solution:

$$A + H_2 \overset{K_{H2}}{\leftrightarrow} A.H_2 \quad K_{H2} = \frac{[A.H_2]_T}{A.P_S} \qquad (4)$$
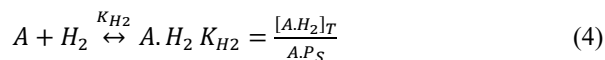
where PS is the activity of hydrogen *(expressed as its partial pressure at the surface of the catalyst).*

$$2A + H_2 \overset{(K_H)^2}{\leftrightarrow} 2A.H \qquad K_H = \frac{[A.H]_T}{A.\sqrt{P_S}} \qquad (5)$$

By substituting into the default balance (2), we get:

$$[A]_T = [A] + [A]K_R c + [A]K_H\sqrt{P_S} + [A]K_{H2}P_S \qquad (6)$$

The activity of the olefin on the catalytic surface is then:

$$a_R = \frac{[A.R]_T}{[A]_T} = \frac{K_R c}{1 + K_R c + K_H\sqrt{P_S} + K_{H2}P_S} \qquad (7)$$

Similarly, for atomic hydrogen:

$$a_H = \frac{[A.H]_T}{[A]_T} = \frac{K_H\sqrt{P_S}}{1 + K_R c + K_H\sqrt{P_S} + K_{H2}P_S} \qquad (8)$$

If practically all active centers are covered by adsorbed olefin,

$$K_R c \gg 1 + K_H\sqrt{P_S} + K_{H2}P_S \qquad (9)$$

Equation (7) takes the form:

$$a_R = 1 \qquad (10)$$

Further increasing the concentration practically does not change the activity, i.e., the reaction is of zero order to the olefin. The activity towards hydrogen is then *(for atomic hydrogen):*

$$a_H = \frac{K_H\sqrt{P_S}}{K_R c} \qquad (11)$$

In this case, the proportion $1/K_R \cdot c$ is practically constant, so the order of the reaction towards hydrogen will be non-zero. Similarly, if the surface is covered with hydrogen and the olefin is deficient, then the order of reaction with respect to hydrogen will be zero; but, the order with respect to olefin cannot be zero. This applies quite generally: *in the case of competitive adsorption of two reactants, the order of the reaction cannot be zero at the same time with respect to both.* If, therefore, a zero-order reaction with respect to both reactants was observed during the hydrogenation of olefins under higher pressure, then - as we have already stated - this is not compatible with the theory of the semi-hydrogenated state.

V. Two-Layer Adsorption Theory

We tacitly accepted various simplifications in the Langmuir and Hinshelwood rate equations. Thus, we consider the number of active surface sites to be constant, independent of the degree of occupation of the surface by individual adsorbed substances, and we consider all active centers to be equivalent. However, these and other simplifications do not affect the overall (that is, qualitative, not quantitative) validity of our conclusions.

In general, the surface covered by adsorbed particles can become a site of adsorption in other layers (recall that BET isotherms are based on multilayer adsorption). We will examine only the first two layers; we will extend Hinshelwood's theory to two-layer adsorption. We consider the surface complexes according to Fig. 6.

We express the equilibrium in both layers in Fig. 7:

[A.R]		[A.R.H$_2$]			
[A.R]$_T$			[A.H]$_T$	[A.H$_2$]$_T$	A
A$_T$					

Fig. 7 Surface complexes in two layers

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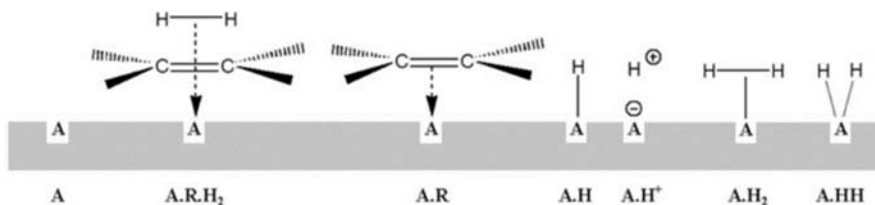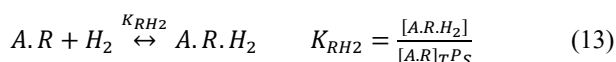Vol:18, No:9, 2024

Fig. 6 Double layer surface adsorption balance

We have already dealt with the balance of the first layer. We assume that hydrogen adsorption in the second layer does not change the equilibrium in the first layer. The balance of the second (upper) layer will be:

$$[A.R]_T = [A.R] + [A.R.H_2] \tag{12}$$

$$A.R + H_2 \overset{K_{RH2}}{\leftrightarrow} A.R.H_2 \qquad K_{RH2} = \frac{[A.R.H_2]}{[A.R]_T P_S} \tag{13}$$

$$\frac{[A.R.H_2]}{[A.R]_T} = \frac{K_{RH2}[A.R]_T P_S}{[A.R]_T + K_{RH2}[A.R]_T P_S} = \frac{K_{RH2} P_S}{1 + K_{RH2} P_S} \tag{14}$$

By multiplying the left and right sides of this equation by the above equation for $a_R = [A.R]_T/[A]_T$ gives:

$$r = kW \frac{K_R c}{1 + K_R c + K_H \sqrt{P_S} + K_{H2} P_S} \cdot \frac{K_{RH2} P_S}{1 + K_{RH2} P_S} \tag{15}$$

where W is the amount of catalyst, K is the rate constant; also includes the amount of active centers AT, per unit amount of catalyst W.

The equation must be understood as semi-quantitative – a lot of simplification was adopted in its derivation. However, it is certain that, if:

$$K_R c >> \left(1 + K_H \sqrt{P_S} + K_{H2} P_S\right) \text{ and } K_{RH2} P_S >> 1$$
$$r = k \cdot W \tag{16}$$

i.e., zero order to both reacting components, within a certain range of concentrations of reacting components, is possible.

Anyway, we can conclude that from the kinetic point of view, the theory of the two-layer activated complex is satisfactory. On the other hand, we recommend approaching the generally accepted "semi-hydrogenated state theory" - *to put it politely* - only with a large margin.

VI. Running of Hydrogenation in Two Layers

The data on hydrogenation kinetics are best suited by the assumption that the rate-determining step of hydrogenation is the breakdown of the two-layer complex of alkene and molecular hydrogen at the active site, i.e., at the transition metal atom of the catalytic surface. Accordingly, at the beginning of the reaction, the unsaturated substance is bound to the surface by a strong bond (chemisorption) and it is weakly bound to it (physical sorption) by hydrogen in the second layer.

The fundamental question of whether hydrogen is bound to a double bond "from above" or "from below" has already been the subject of many discussions. The opinion that hydrogen

bonds from below is held by, for example, Burwell [27]. This is evidenced by the ease with which trans-cyclohexene is hydrogenated, in which the conformation of the cycle is said to completely protect the upper side of the double bond against attack by an external reagent. Similarly, Smith [28] found that on PtO_2, isomeric *cis*- and *trans*-cyclodecenes hydrogenate at practically the same rate, although in the latter case the polymethylene chain must hinder addition from the upper side of the chemisorbed double bond to a greater degree. The objection would be valid if we accept the collision theory, where hydrogenation occurs by "bombarding" the adsorbed olefin with hydrogen molecules from the solution. In our theory, which is an activated state theory, there is always enough hydrogen, since hydrogen adsorption is not the rate-determining step.

During hydrogenation of complex structures, it sometimes appears that hydrogen approaches from the less sterically protected side of these molecules, i.e., from the side where it binds to the catalytic surface. However, this can be explained by the previous isomerization: the migration of the double bond is usually fast. The direction of the migration of the double bond is given by polarization of the double bond due to the induction effect - in the case of hydrogen moving to another place in the carbon chain, to the point of branching. When interpreting the experimental data, however, it must be remembered that isomerization is an equilibrium reaction, so the double bond is isomerized as well from the point of branching to a straight section. The isomeric olefin can then be stabilized by direct binding to the catalytic surface and subsequently hydrogenated. Tri-substituted olefinic compounds that cannot be hydrogenated on platinum (*low isomerization ability*) can therefore be hydrogenated on palladium (*high isomerization ability*), or on a metal deposited on an acidic aluminum oxide support (γ-Al_2O_3) or in a mixture with aluminum oxide. It may happen that under hydrogenation conditions only the most stable isomer is the product of the reaction [29].
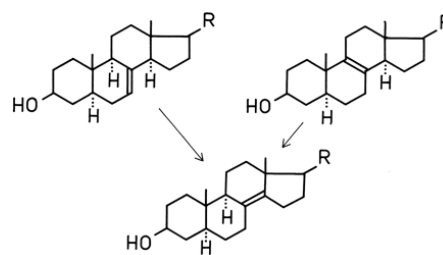

Fig. 8 Steroids under hydrogenation conditions

The entire reaction mechanism of hydrogenation is shown in

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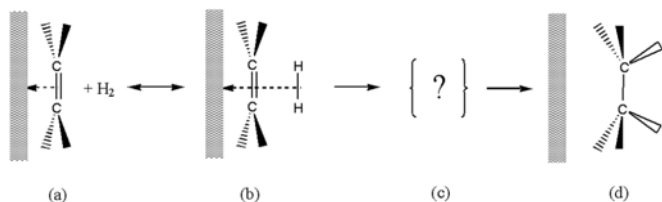Vol:18, No:9, 2024

Fig. 9.

Fig. 9 Two-layer theory: progress of hydrogenation

a) The olefin is adsorbed onto the metal surface – a strong chemical bond.
b) Hydrogen is adsorbed in the second layer – physical or chemical bond.
c) Transitional state: the bond between the olefin and the surface weakens and the bond with the hydrogen atoms strengthens at the same time. The substituents on the carbons deviate towards the catalytic surface, which can prematurely weaken the bond of the olefin to the surface. Therefore, hydrogenation of 1-olefins with two substituents on double bond takes place, while hydrogenation of tri- and tetra-substituted double bonds is excluded.
d) The saturated molecule leaves the surface.

VII. CONCLUSIONS

There are reasons to believe that the isomerization during the hydrogenation is a purely secondary reaction that takes place parallel to the hydrogenation itself. This assumption could be an interesting starting point for further research.
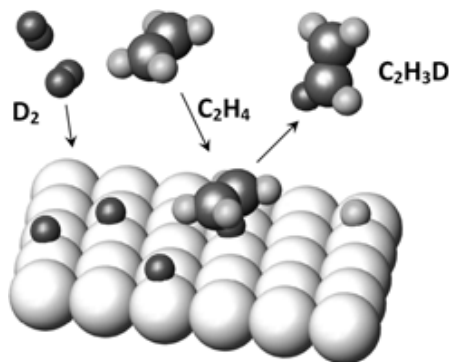

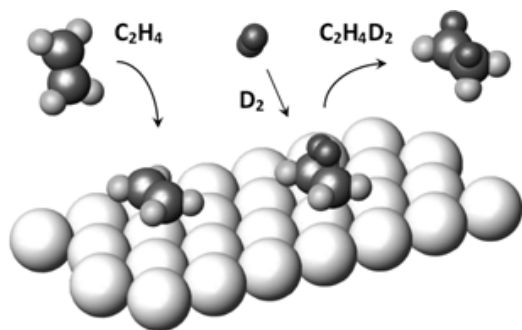Fig. 10 "Two-layer" model of isomerization (here: isotopic exchange)

Fig. 11 "Two-layer" model of hydrogenation (here: deuteration)

REFERENCES

[1] Remy R., *Lehrbuch der anorganischen Chemie*, Vol. 2, Leipzig 1955
[2] Galwey A.K., Gwathmey A.T., Cunningham R.E., *Advances in catalysis* 10, 57 (1998)
[3] Iljushenko V.M., Shligin A.J., *Izv. AN Kaz.SSR, Ser.Khim.* 3,12 (1949)
[4] Parnes Z.N., Bolestova C.I., Kursanov D.N., *Izv. AN SSSR Ser.Khhim.* 1972, 1987, 1989
[5] Khrush A.P., Shilov A.E., *Kinetika i Kataliz* 10, 466 (1969)
[6] Hudlický M., Trojánek J., *Preparativní reakce v organické chemii I – redukce a oxydace*, NČAV Praha 1953
[7] Tuley S.F., Adams R., *J.Am.Chem.Soc.* 47, 3061 (1925)
[8] Adams R., Garvey B.S., *J.Am.Chem.Soc.* 48,447 (1926)
[9] Mitsui S., Nagahisa Y., Tomurura G., Shinoya M., *Shokubai* (Catalyst) 13, 74 (1968) - quoted in Siegel S., *Advances in Catalysis* 16, 123 (1966)
[10] Loewenthal H.J.E., *Tetrahedron* 6, 269 (1959) – quoted in Siegel S., *Advances in Catalysis* 16, 123 (1966)
[11] Siegel S., Smith G.V., *J.Am.Chem.Soc.* 82, 6082 (1960)
[12] Pierre Brun, *Catalyse et catalyseurs en chimie organique*, Masson 1970
[13] Tulupov V.A., *Zhurnal fizicheskoi khimii* 36, 1617 (1962)
[14] Khrush A.P., Shilov A.E., *Kinetika i Kataliz* 10, 466 (1969)
[15] Halpers J., *Canad.J.Chem.* 39, 1372 (1961)
[16] Halpers J., *Canad.J.Chem.* 44, 671 (1966)
[17] Hanzlík J., *Chemicke Listy* 65, 454 (1971)
[18] Boreskov G.K., *Geterogennyi kataliz v khimicheskoi promyshlennosti*, Goskhizdat Moskva 1955, p. 7
[19] Gostunskaya I.V., Trinko A.I., Dobroserdova N.S., Kazanskiy S.A., *Neftekhimia* 11, 326 (1971)
[20] Fasmah A.S., Ishanov Zh.A., *Kinetika i Kataliz* 8, 66 (1967)
[21] Bond C.C., Wells P.B., *Advances in Catalysis* 15, 91 (1964)
[22] Sokolskiy D.V., *Gidrirovanie v rastvorach*, Alma-Ata 1962
[23] Freidlin L.Kh., Kaup Yu.Yu., Litvin E.F., Ilomets T. I., *Dokl.AN SSSR* 143,883 (1962)
[24] Siegel S., Smith G.V., *J.Am.Chem.Soc.* 82, 6087 (1960)
[25] Young W.C., Weir R.S., Bollinger H., Kaplan L., Linder S.L., *J.Am.Chem.Soc.* 69, 2046 (1947)
[26] Taylor T.I., Dibeler V.H., *J.Phys.Chem.* 55, 1036 (1951)
[27] Burwell R.L.Jr., *Chem.Rev.* 57, 895 (1957)
[28] Smith V., J., *Catalysis* 5, 152 (1966)
[29] Loewental H.J.E., *Tetrahedron* 6, 269 (1958), quoted in Siegel S., *Advances in Catalysis* 16, 123 (1966)