



In Horiuti's footsteps: links between catalysis and electrocatalysis

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Abstract

The links between catalytic and electrocatalytic hydrogenation processes are analyzed starting from the fundamental principles outlined in almost all works by Horiuti and Polanyi 70 years ago. It has been shown that the mechanistic picture based on the role of protontransfer step in processes taking place at the aqueous phase/catalyst (electrode) interface can be extended to a great number of electrocatalytic reductive transformations. Illustrative examples are shown including the reductive splitting of C–OH and C–Cl bonds in allyl position, the transformation of $>C=O$ groups into $-CH_2-$ ones. The examples presented confirm the view that electrocatalytic studies, the application of electrochemical methods, constitute important contributions to the understanding of catalytic phenomena.

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1. Introduction

For a long period beginning from the fifties of the last century in the usual chemistry curriculum catalysis and electrochemistry were considered as subjects that are very far from each other.

Although the notion of electrocatalysis, considered as a combination of the two fields, nowadays is widely used by electrochemists the distance between the two disciplines the differences in the ways of thinking are changing only slowly. From historical point of view this situation is very curious as in the first fundamental works by Horiuti and Polanyi [1–5] the catalytic and electrochemical phenomena were considered as inseparable attributes of processes occurring with hydrogen in heterogeneous systems consisting of certain metals and aqueous solutions. In their paper entitled:

"A Catalyzed Reaction of Hydrogen with Water" [1] the following fundamental statements can be found:

It has been recently observed by M.L. Oliphant that, when hydrogen is kept in contact with water for a few months, an exchange of atoms occurs between the hydrogen and the water. We have now found that this reaction can be catalyzed by platinum black, such as is used in hydrogenation.

We suggest that the catalytic exchange of atoms between hydrogen and water caused by platinum black is due to the ionization of hydrogen corresponding to the electromotive process of the hydrogen electrode. When a hydrogen electrode is in equilibrium with an aqueous solution, it constantly produces ions from the hydrogen, while an equal amount of hydrogen is formed from the ions of the solution.

In a next paper they write [2]:

In the electrolytic formation of hydrogen from water an inertia is present, which has to be overcome

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by a certain amount of over-voltage. The nature of this inertia is still under discussion. It may either be ascribed to the process of the transition of the hydrogen ions from the water into the state of atoms adsorbed on the electrode, or to the process of formation of hydrogen molecules from the adsorbed atoms.

Our observations on the spontaneous transition of hydrogen from platinum into water seem to settle this question for the case of a platinum electrode. It appears that the rate at which the hydrogen is ionized strongly depends on the composition of the aqueous solution with which the platinum is in contact. This influence can scarcely be explained if one attributes the inertia of the process to the reaction of hydrogen with platinum, whereas its presence is easily understood if the inertia is attributed to the transition of the hydrogen atoms into the solution.

These statements laid down the theoretical basis for the understanding of the intrinsic links between electrocatalytic and catalytic reductions at the metal solution interface. The main element of this link is formulated by the



reactions.

It was analyzed and demonstrated in previous communications [6,7] that the difference in the approach of people involved in catalysis and electrochemistry can be conceived as a difference in the choice of thermodynamically independent components of a given system. The occurrence of the reactions described by Eqs. (1a) and (1b) gives us, at least to some extent, a free choice regarding the problem which species should be considered as thermodynamic components of the system. We have two options:

(i) H_2 and H^+ ions

or

(ii) H^+ ions and e^- (electrons)

This could be considered as components of the system. In the former case the pressure of H_2 and the activity of H^+ , in the latter case the activity of H^+ and the electrode potential define unambiguously the state of the system.

Bearing in the mind these options we are able to give a thermodynamic basis for the distinction and simultaneously for the link between catalytic and electrocatalytic approach to a given system.

In the case of catalytic hydrogenation H_2 and H^+ should be considered as components of the system. In contrast to this, treating the system in terms of electrocatalysis H^+ and electrons have to be considered as components.

The papers by Horiuti and Polanyi cited above contain tacitly the same message for these authors the catalytic and “electrochemical” properties of the systems considered are not separated from each other.

This unifying approach was lost for a long period in the general literature although researchers from Horiuti’s school made significant efforts to continue his work (see, for instance, [6–8]). In the following an attempt will be made in the spirit of this heritage to reconsider the link between heterogeneous catalytic and electrocatalytic hydrogenation processes occurring at the aqueous phase/metal interface.

2. Mechanistic considerations

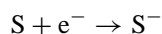
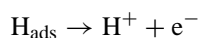
The mechanism of hydrogenation of ethylene and benzene suggested in the classical work by Horiuti and Polanyi was based on their results concerning the interchange of hydrogen between water and ethylene and benzene. They postulated the following main steps:

1. The chemisorption (activated adsorption) of the hydrogen producing adsorbed hydrogen atoms.
2. The chemisorption (activated adsorption) of the double bond compound on the surface accompanied by an opening of the double bond and the formation of two new links with the catalyst.
3. The transfer of a hydrogen atom to one of the carbon atoms of the adsorbed hydrocarbon thus forming the half hydrogenated state; a process which may be followed by
 - (a) the removal of a hydrogen atom from the carbon atom in the half hydrogenated state leading to replacement;
 - (b) the subsequent attachment of a hydrogen atom to another carbon atom, giving rise to hydrogenation.

This mechanistic picture did not change significantly during the last almost 70 years. Although from

the exchange experiments it followed clearly that protons in the liquid phase could and should be in equilibrium with adsorbed hydrogen creating equilibrium electrode potential no attention was paid to this parameter. Thus, the very principle that heterogeneous aqueous phase hydrogenation processes at noble metal catalysts can be monitored by measurement of the potential of the catalyst was left out of consideration for a long period of time.

The mechanism discussed above is only one of the two mechanism types for the involvement of hydrogen in the catalytic reduction [9,10]. The other mechanism is the electrochemical or ionic mechanism where the adsorbed hydrogen serves only as an electron source for the reduction process. This type of reaction is formulated by the following reaction steps:

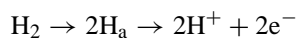
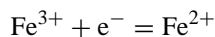


From electrochemical point of view this type of catalytic reduction can be conceived as two coupled electrode processes.

The typical representative of this group is the catalytic reduction of various nitrocompounds. The simplest models illustrating the peculiarities of such reactions are the reduction of ionic redox species, both cations and anions.

For instance, the catalytic reduction of Fe^{3+} ions by molecular hydrogen in the presence of a platinum black catalyst or at a platinized platinum electrode (under open circuit condition) is one of the simplest cases reflecting the behavior of such a system.

The coupled processes are



In this case only the adsorption and ionization of H^+ requires the catalyst in contrast to the saturation of double bonds where both the organic species and H_2 should be activated.

In the case of compounds containing two reducible groups reacting via different mechanisms (for instance, double bond (or aromatic nucleus) and nitro

group) there is a possibility of achieving selective reduction of the nitro group using a catalyst activating only the H_2 molecules.

Tungsten carbide was found to fulfill such requirements. The suggestion to use tungsten carbide as catalyst in liquid-phase hydrogenation was prompted from electrocatalytic studies. During the second half of the last century several studies involved in fuel cell research were devoted to the problems of the oxidation of hydrogen and other, carbonaceous, fuels at tungsten carbide electrodes [11–18].

As a result of the fuel cell research oriented interest the study of other aspects of the catalytic electrocatalytic behavior of tungsten carbide has been neglected. It was found that WC promotes the anodic oxidation of hydrogen, i.e. it acts as a catalyst for the $\text{H}_2 \rightarrow 2\text{H}_{\text{ads}} \rightarrow 2\text{H}^+ + 2\text{e}^-$ reaction. On the other hand, no significant adsorption of organic species on WC surfaces was observed.

From these facts the conclusion could be drawn that WC should be a catalyst for hydrogenation processes taking place via ionic mechanism. This was demonstrated by a series of studies [19–23].

3. Electrochemical methods for elucidation of the mechanism of catalytic hydrogenation

The overall catalytic hydrogenation process involves the transport of molecular hydrogen through the gas/liquid and liquid/solid interfaces. This means that in most cases the overall reaction rate is determined by the transport rate of hydrogen. Thus, it is not easy to get reliable information on the parameters determining the rate of the processes taking place on the surface of the catalyst. On the other hand, under conditions of usual hydrogenation procedure it is very difficult to obtain in situ information on the adsorption of reacting species on the surface of the catalyst. However, bearing in mind the equivalency of catalytic and electrocatalytic processes, by the transformation of the mostly powdered catalyst into an electrode with high real surface area most of the complications can be avoided by the application of polarization measurements coupled with optical spectroscopic radiotracer, analytical and other methods for the investigation of the reactions occurring on the surface of the electrode/catalyst [9,10].

A classical example for this approach is the platinized platinum and platinum black pair. The platinum black layer of platinized electrode is composed of nano-scale particles similarly to platinum black powder.

The specific surface area of platinum black used to be about $10^5 \text{ cm}^2 \text{ g}^{-1}$ that corresponds to an average particle size of about 10–20 nm. Roughness factor values of platinized electrodes corresponding to 300–1000 can be obtained with a layer structure composed of the similar particle dimension. Studying the electrocatalytic reduction of various compounds by polarization measurements at potentials more positive than that of the hydrogen electrode in the same solution the reduction rate versus potential relationship can be obtained without the interference of other side processes. The simultaneous in situ adsorption measurements could furnish data to find the relationship between reaction rate and coverage with respect to adsorbed reacting species. The product analysis carried out at different potentials may contribute to formulate the reaction scheme in the case of multistep reactions and to find the way for changing the selectivity with respect to certain products by controlling the potential of the electrode/catalyst.

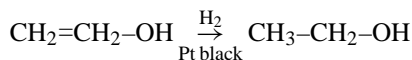
In some cases of electrocatalytic, electrochemical studies led to results that were not expected on the basis of classical views concerning the catalytic transformations of certain compounds. Two illustrative examples will be discussed in the next section.

4. The reductive splitting of C–OH bonds in allyl position [24–28]

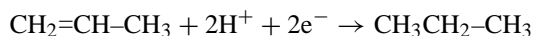
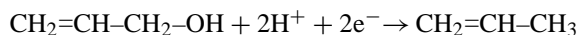
According to the classical views in catalysis noble metals, especially platinum, palladium and rhodium are very active catalysts in the hydrogenation, saturation of $\text{C}=\text{C}$ bonds. In a series of papers by researchers from Horiuti's school the electrocatalytic reduction of olefins was investigated in detail. These studies confirmed the occurrence of Horiuti–Polanyi type reaction paths [6–8].

For a long period it was generally accepted view that noble metal catalysts are unable to catalyze the reductive splitting of the C–OH bonds in simple aliphatic alcohols, for instance in ethanol and propanol, under mild conditions (room temperature, atmospheric pres-

sure). Thus, on the basis of the classical approach the catalytic hydrogenation of allyl alcohol in aqueous solution in the presence of Pt black catalyst should follow the equation:



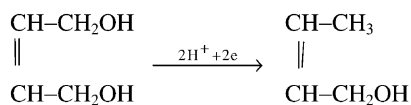
However, in an electrocatalytic procedure using platinized platinum electrode immersed in an acidic solution containing dissolved allyl alcohol and polarizing the electrode in a potential region of potentials where no H_2 evolution occurs formation of gas bubbles on the electrode can be observed [21]. An analysis of the gaseous product shows that it contains $\text{CH}=\text{CH}-\text{CH}_3$ and $\text{CH}_3-\text{CH}_2-\text{CH}_3$. This means that the reactions



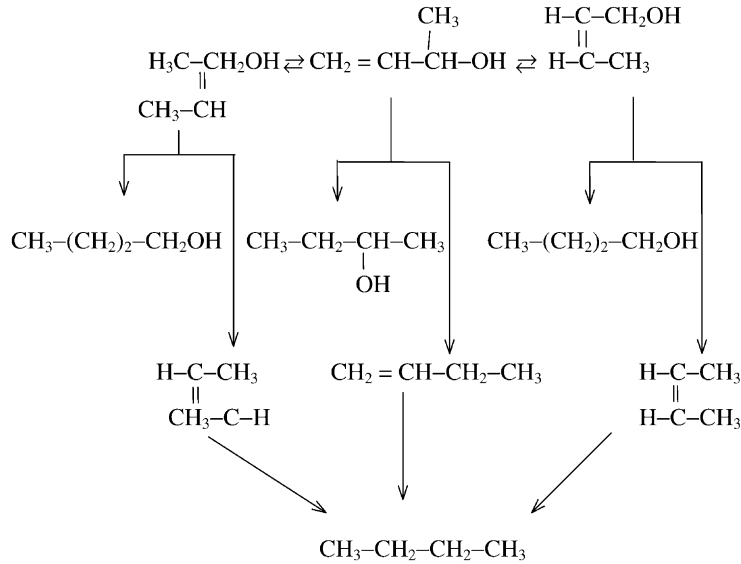
took place.

The composition of the gaseous product, the ratio of unsaturated component to the saturated one depends on the potential of the electrode/catalyst thus the selectivity of the hydrogenation can be controlled by electrochemical means. For instance, carrying out the electrocatalytic process under potentiostatic control and shifting the potential (measured against the hydrogen electrode in the same supporting electrolyte) from 80 to 100 mV the propane content of the propane/propene mixture changes from 20 to 29%. Similar behavior was found in the case of crotyl alcohol, however, in this case the isomers of butene appear in the product (1-butene, *cis*-2-butene, *trans*-2-butene). The main steps involved in the electrocatalytic reduction of crotyl alcohol are shown in Scheme 1.

It is interesting to mention that the reduction of 2-butene-1,4-diol leads to the same gaseous products. Thus, the first step of the reduction is the formation of crotyl alcohol:

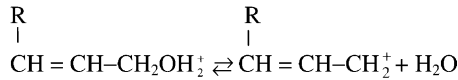


The splitting of a C–OH bond situated in allyl position can be interpreted by a mechanism involving the formation of the protonated alcohol. According to



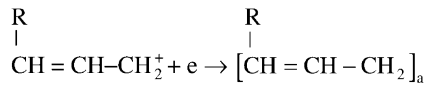
Scheme 1.

the literature [28] in acid media there is equilibrium between protonated alcohol and a carbonium cation:

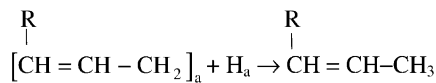


R = H, CH₃, CH₂OH.

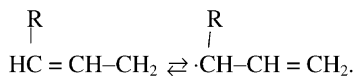
Discharge of this cation yields a radical:



On platinum the equilibrium 1/b exists simultaneously and with H_a the reaction

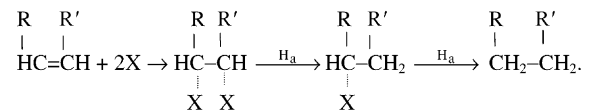


takes place. The formation of isomers may be explained on the basis of this mechanism. The real structure of the allyl and substituted allyl cations and radicals does not correspond to the formulae given above as there is no difference between the two terminal carbon atoms:



Thus, the very fact that the gaseous product of the reduction of crotyl alcohol contains a significant amount of 1-butene may be ascribed to this property of the cation and radical.

In accordance with the model suggested by Horvati and Polanyi the saturation of the double bond occurs *via* chemisorbed particles occupying at least two surface sites of platinum. Denoting by X the surface sites the reaction steps may be formulated as follows:



This means that for the saturation reaction at least two neighboring free sites should be available on the surface while for the splitting of the C–OH bonds such a stringent requirement is not expected.

This mechanistic difference could be well demonstrated if we find a tool to decrease the number of neighboring sites inhibiting the saturation of the double bonds. As a result of such a procedure an increase in the ratio of unsaturated compound to the saturated one should be expected.

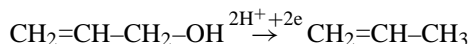
By chemisorption of methanol there is a possibility of obtaining a relatively well-defined organic chemisorbed layer on the electrode. Starting from this

possibility, the study of the influence of chemisorbed methanol on the product composition may be proposed in the case of reduction processes composed of several steps of different kinds of mechanism.

It is well known that methanol chemisorbed at potentials of 300–400 mV remains on the surface of platinum at lower potentials, and that no desorption or transformation of chemisorbed particles has to be considered in the potential range corresponding to the hydrogen adsorption. This means that the chemisorbed species remains on the surface of the electrode under the usual conditions of electroreduction.

It was of interest to demonstrate the influence of chemisorbed methanol on the rate of a simple electroreduction reaction. As a model reaction the saturation of the double bond of maleic acid was taken. Chemisorption of methanol resulted in a dramatic change in the electroreduction rate of maleic acid as is shown by the polarization curves presented in Fig. 1. In the presence of chemisorbed methanol the reduction of maleic acid is almost completely inhibited. In contrast to this, significant reduction rates may be observed in the case of the reduction of allyl and crotyl alcohols. The volume of the gas evolved was measured at a given potential and plotted against the

charge passed through the system, as shown by Fig. 2 in the case of allyl alcohols using an electrode covered by chemisorbed methanol. Curve 1 is obtained from the experimental results, Curve 2 is calculated assuming that the



process is the only reaction in the system, whereas Curve 3 is calculated on the basis of the assumption that the only product of the reduction is propane. It may be concluded from comparison of the curves that the main component of the reduction product should be propene. This expectation was confirmed by the gas chromatographic analysis of the gases. Comparison of the results obtained with and without chemisorbed methanol in Table 1 proves that the presence of chemisorbed methanol results in a significant change in the selectivity of the reduction process. Moreover, from the volumetric and analysis data it may be stated that the Faradaic yield with respect to the gaseous products is practically equal to 100%, i.e. the role of the reaction leading to propanol ($\text{CH}_2=\text{CH}-\text{CH}_2\text{OH} + 2\text{H}^+ + 2\text{e} \rightarrow \text{CH}_3-\text{CH}_2-\text{CH}_2(\text{OH})$) can be neglected.

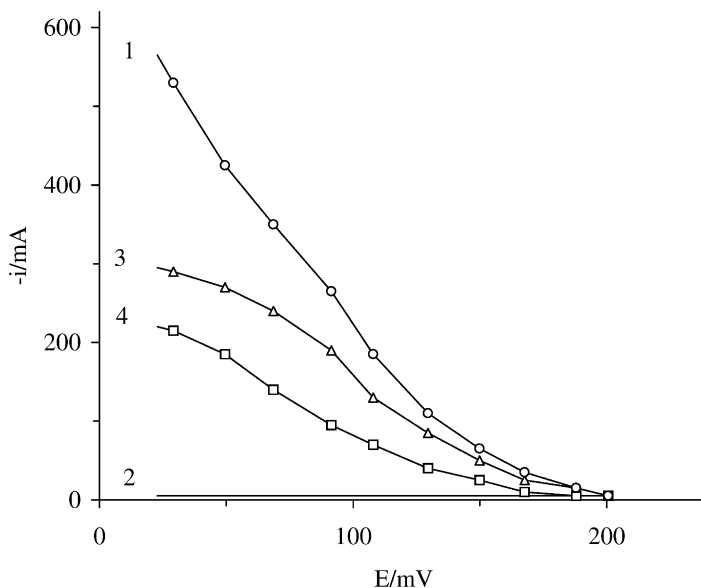


Fig. 1. Effect of chemisorbed methanol on the polarization behavior of different compounds. (Curve 1) Maleic acid without pretreatment of the electrode; (Curve 2) maleic acid after chemisorption of methanol; (Curves 3 and 4) allyl and crotyl alcohols in the presence of a chemisorbed methanol layer (concentration in all cases $1 \times 10^{-1} \text{ mol dm}^{-3}$).

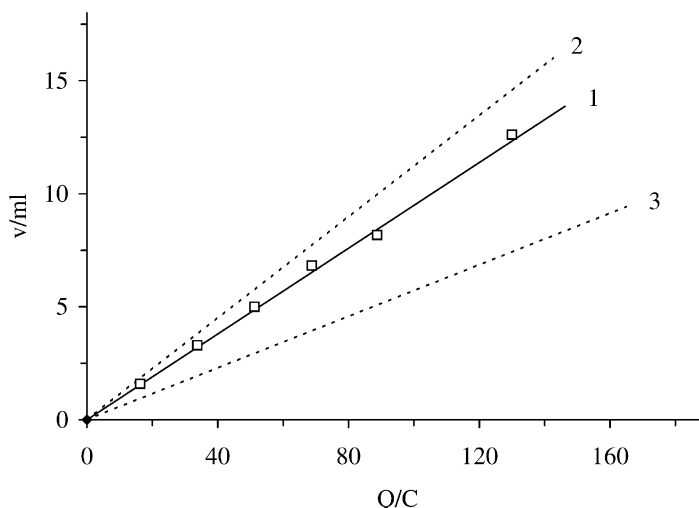
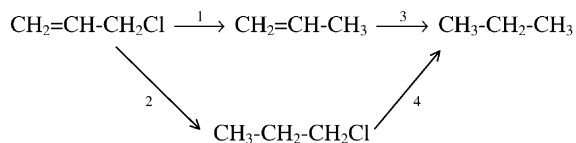


Fig. 2. (Curve 1) Volume of gas evolved as a function of the charge passed through the system in the course of the electroreduction of allyl alcohol at 100 mV in the presence of chemisorbed methanol ($c_{\text{allyl alcohol}} = 0.1 \text{ mol dm}^{-3}$). Curves 2 and 3 are calculated ones.

5. Electrocatalytic reduction of allyl chloride [29]

The mechanism of the electrocatalytic splitting of C–Cl bond in allyl position is very similar to that of C–OH bond. Results of experiments carried out with allyl chloride confirm the mechanistic considerations made in connection with allyl alcohol.

In principle the transformations given by the following scheme may be expected in the case of the electrocatalytic reduction of allyl chloride at a platinum electrode in acidic medium.



Both the double bond and the C–Cl bond may be the subject of a reductive attack. However, depending on the rate of the different reaction paths figuring in the scheme, the products and intermediates detectable in the course of the reduction may be very different. For instance, if the rate of step 2 is much higher than that of step 1, no significant amount of propene may be found among the gaseous products. In the opposite case the propene/propane ratio would depend on the rate of steps 1 and 3.

Table 1

Gaseous products of the electroreduction of allyl alcohol

Potential, E (mV)	Without chemisorbed methanol		In the presence of chemisorbed methanol	
	Propane (%)	Propene (%)	Propane (%)	Propene (%)
100	70	29	12	87
80	79	20	14	85

In the course of the electroreduction formation of gaseous products can be observed. This observation is in accordance with the expectations. Table 2 show the composition of the gases evolved at different potentials. The occurrence of propene in the gas phase confirms the assumption that the splitting of the C–Cl bond plays a significant role in the overall process. It should be assumed that propane is formed via the

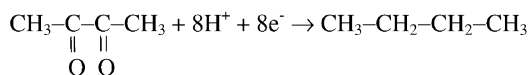
Table 2

Composition of gaseous products formed in the course of the reduction of allyl chloride at different potentials

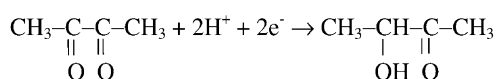
Potential, E (mV)	Composition (%)	
	C_3H_8	C_3H_6
30	92	7
40	82	17
60	71	28
100	49	50

and the mechanism of the process is similar to that of the chemical Clemmensen reduction with the exception of the role of adsorbed hydrogen.

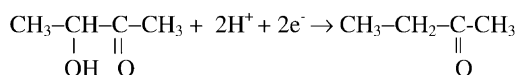
The behavior of α , β and γ aliphatic diketones was also studied [28,37]. The simplest α diketone is biacetyl. Its behavior is determined by the very fact that the carbonyl groups are in the α -position. The overall process resulting in hydrocarbon is:



The first step of the reduction is the formation of acetoin according to the reaction:



The next step is the formation of 2-butanone by reductive splitting of the C–OH bond:

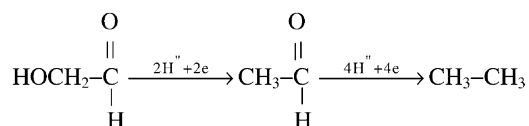


The gaseous end product, butane, is formed from 2-butanone. It is of interest that the splitting of C–OH bond shown above is very similar to the phenomenon observed in the case of C–OH bonds in allyl position. However, if we consider the section HO–C–C=O we can see the structural analogy with compounds containing allyl entities.

The formation of 2-butanone from acetoin, the reductive cleavage of a C–OH bond situated in α -position with respect to a carbonyl group is not an exception.

The simplest example for this type of reaction is the transformation of glycolaldehyde into ethane [37].

The first step of the reduction process is the formation of acetaldehyde:



The second step, the transformation of an aldehyde group into methyl group, is known from studies of the electrocatalytic reduction of acetaldehyde and propionaldehyde carried out in acid medium at

Table 4

Composition of gaseous products formed at 60 mV during the electrocatalytic reduction of acrolein and croton aldehyde

Compound	Composition (%)	
	Acrolein	Croton aldehyde
C ₂ H ₆	4.8	–
C ₃ H ₆	61.8	–
C ₃ H ₈	33.3	10.1
C ₄ H ₁₀		86.2
<i>trans</i> -2-Butene		3.4

platinized platinum electrodes. The transformation of acrolein and crotonaldehyde is an interesting example for the demonstration of the behavior of α – β unsaturated aldehydes [38].

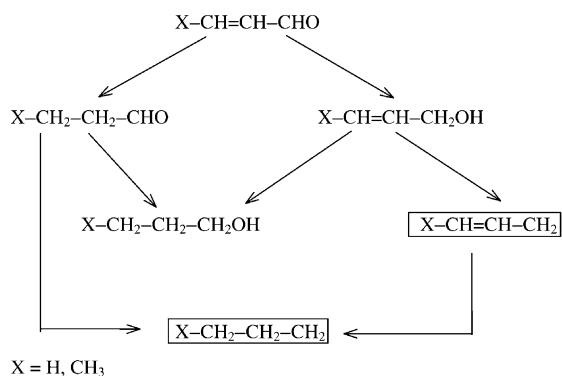
In both cases, formation of hydrocarbons was observed, however, the transformation of the aldehyde group was accompanied by the saturation of the double bond and by some rupture of C–C bonds. The composition of gaseous products observed following a prolonged polarization is shown in Table 4.

The current efficiency with respect to gaseous products was about 30%. It follows from the product composition that there is a splitting of the C–C bonds. However, the lack of methane suggests the assumption that a species containing one carbon atom remains in the solution phase and the splitting of the C–C bond occurs between the α carbon atom and the $-\overset{\text{H}}{\text{C}}=\overset{\text{O}}{\text{C}}$ group. The formation of unsaturated hydrocarbons proves that the saturation of the double bonds is preceded by the reductive transformation of the –CHO group into –CH₃. (The corresponding saturated alcohols cannot be reduced under the experimental conditions considered.)

The formation of main hydrocarbon products may be formulated as in Scheme 3.

7. Mechanistic approach in terms of proton transfer formulated by Horiuti and Polanyi

The splitting of C–OH in allyl position and the transformation of C=O groups into –CH₂– groups are processes occurring mainly or only in strong acid medium. This means that a great excess of H⁺



Scheme 3.

(H₃O⁺) ions is required for these processes and the reduction process presumably takes place with the protonated form of the organic species under consideration.

The role of such proton transfer in catalytic processes was analyzed in the fundamental work “Grundlinien einer Theorie der Protonübertragung” by Horiuti and Polanyi [5] for electrolytic dissociation, the catalytic hydrolysis of esters, electrode processes and tautomer transformations. In all cases presented above the occurrence of the transformations leading to hydrocarbons cannot be conceived without the assumption of the protonation of the reacting species.

The discharge of this positively charged species should be the first step in the reaction on a catalytic surface similarly to the evolution of hydrogen where H₃O⁺, protonated water, can be considered as the reacting molecule in acid medium.

In accordance with this similarity of the behavior the role of the electrode potential in the activation processes is similar in both cases and this is well reflected by the shape of the polarization curves and by the similarity in the so called Tafel behavior. Thus, it can be stated that the Horiuti and Polanyi approach can be applied without any problem in the processes leading to the formation of hydrocarbons.

Acknowledgements

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