

# LIQUID-PHASE ELECTROCATALYTIC HYDROGENATION\*

D. V. SOKOLSKY

Institute of Organic Catalysis and Electrochemistry,  
Alma-Ata, S.S.S.R.

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Presented by Prof. Dr. J. PETRÓ

## Summary

Catalytic and electrocatalytic hydrogenation mechanisms of various compounds have been investigated. Three main types of mechanisms were found to occur indicated also by the different shift of the reversible hydrogen potential of the catalyst. It has been stated that the selectivity and reaction rate can be controlled by adjusting an appropriate potential.

In catalytic hydrogenation hydrogen and an unsaturated compound are, as a rule, activated on the surface of the catalyst. The degree of activation of the components depends on the potential of the catalyst, on its nature and on the structure of the unsaturated compound. Four main types of catalytic hydrogenation mechanisms occur, defined by the degree and form of the interaction of the catalyst and the unsaturated compound during the period of the reaction [1].

In the case of electrohydrogenation, the charge of the surface and hence the chemical composition of the catalyst will, above all, change during the reaction. As a rule the reaction will not be confined to the activation of hydrogen; the major forms of reactive hydrogen are atomic and molecular hydrogen with positive charge:



Consequently the rate of reaction, its selectivity and its mechanism will change. Hence the hydrogenation of one and the same compound will take place according to different mechanisms. The study of electrohydrogenation at intense agitation in hydrogen atmosphere is particularly interesting. In this case, hydrogen supply to the surface will come from two sources:

1.  $H^+ + e + K \rightarrow K-H$ ,      and
2.  $H_2 + 2 K \rightarrow 2 K-H$ .

\* Lecture delivered at the Department of Organic Chemical Technology, Technical University Budapest, 1981.

In case 1, it is not necessary to consider structural correspondence (lattice parameters of the catalyst), in case 2 structural correspondence will come to the fore as a factor of major importance.

It may be assumed that the bond energy of hydrogen to the catalyst surface is different in the two cases. In normal hydrogenation, hydrogen and acetylene derivatives will be activated on one type of centres (2 K), hydrogen and ethylene derivatives, on others. In electrohydrogenation, competitiveness will appear in both cases. At hydrogenation in solutions, the rate of reaction frequently depends on the solubility of hydrogen, at electrohydrogenation such dependence does not occur. Hence the difference does not only appear in the mechanism of the elementary process, but also in the macroscopic stages.

Joint catalytic and electrocatalytic hydrogenation allows optimization of the process by using conditions at which one or the other will be more emphasized.

By way of example, let us consider electrohydrogenation of nitrobenzene in a hydrogen atmosphere. The kinetic and potentiometric curves for the electrocatalytic hydrogenation of nitrobenzene dissolved in 0.5 mol  $H_2SO_4$ /litre 50% ethanol are presented in Fig. 1. Curve 1 reflects the kinetics of the process without applying a polarizing current. The order of the reaction is zero relative to nitrobenzene. The amount of hydrogen consumed corresponds to the theoretically required amount for reducing the nitrobenzene sample into aniline. When current is applied to the catalyst electrode, hydrogen uptake rate from the gas phase first slightly increases and subsequently systematically decreases with rising current density (curves 2, 3, 4). The value of the potential shift systematically decreases, and the hydrogen volume uptake from the gas phase also decreases. The total volume of hydrogen, evolved in electrolysis plus

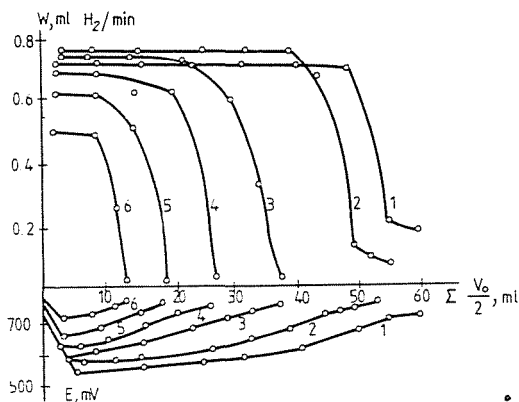


Fig. 1. Electrohydrogenation and hydrogenation of nitrobenzene. Pd-Pt electrode, cathodic polarization, solvent: 0.5 mol  $H_2SO_4$ /litre 50% ethanol

consumed from the gas phase is practically equal to the hydrogen amount theoretically required to reduce the nitrobenzene sample into aniline (Table 1). The analysis of the reaction product demonstrated that aniline yield was 100%. The period required for complete hydrogenation was reduced from 105 min to 75 min by applying the polarizing current.

Electrocatalytic hydrogenation of quinone was fully similar to that of nitrobenzene. However, hydrogenation of maleic acid at analogous conditions proceeds somewhat differently (Fig. 2). Similarly to the experiments with nitrobenzene and quinone, the application and raise of current from  $4 \cdot 10^{-4}$  to  $16 \cdot 10^{-4}$  A/cm<sup>2</sup> lowers the hydrogen uptake from the gas phase, by reason of increasing participation of electrohydrogenation in the overall process. The rate of hydrogen uptake from the gas phase sharply decreases already at very low current densities, while the overall rate of the process remains constant over the total range of studied current densities. This finding indicates that polarization does not promote activation of maleic acid on the surface of the

**Table 1**  
Electrolytic reduction of nitrobenzene in hydrogen gas

Density $\cdot 10^{-4}$ A/cm <sup>2</sup>	Time of experiment, min	Hydrogen quantity, cm <sup>3</sup>		
		evolved in electrolysis	taken up from the gas phase	total
0	105	—	54.5	54.5
4	90	12.6	43.0	55.6
8	80	22.5	33.5	56.0
12	75	31.0	23.0	54.0
16	75	43.0	10.6	53.6

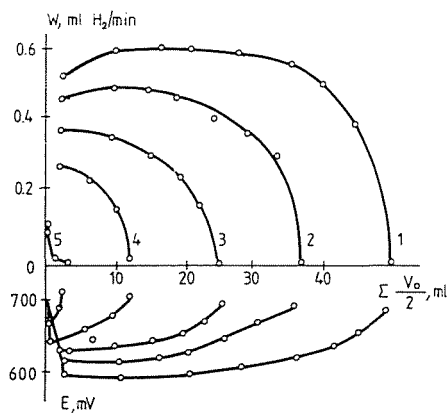


Fig. 2. Electrohydrogenation and hydrogenation of maleic acid. Pt—Pt electrode, cathodic polarization

catalyst, but that the active forms of hydrogen are equivalent for both catalytic hydrogenation and electrohydrogenation of maleic acid.

Relying on the above findings, one may conclude that the reduction processes of nitrobenzene and quinone proceed according to the scheme

1.  $R + e \rightarrow R^-$
2.  $H - e \rightarrow H^+$
3.  $R^- + H^+ \rightarrow RH$ ,

and the application of the polarizing current accelerates process 1, slightly decelerates process 2 and provides protons ( $H^+$ ) indispensable for process 3.

In the case of maleic acid, hydrogenation proceeds according to the radical mechanism

4.  $R + H \rightarrow RH$ ,

and by applying the polarizing current, the protons of the solvent will turn into an additional source of atomic hydrogen:

5.  $H^+ + e \rightarrow H$

complementing the supply from the gas phase.

The effect of the polarizing current is very interesting in multistage processes. Let us consider, for instance, the hydrogenation of 1,1-dimethyl-2-propyne-1-ol (Fig. 3).

Without the polarizing current (curve 1) the rate of hydrogenation is constant up to the end of the reaction. The cathodic current acts in a different manner on the hydrogenation kinetics of triple and double bonds (curves 2, 3, 4). Pronounced maxima appear on each kinetic curve, followed by a sharp decrease in the rate of hydrogen uptake from the gas phase, and subsequently the rate remains constant till the end of the experiment. The analysis of the reaction products indicates the selective course of the process; hydrogenation and electrohydrogenation kinetics of the triple bond are similar to the kinetics of nitrobenzene reduction, those of the double bond to those of maleic acid. By studying the hydrogenation rates of the individual stages and the overall reaction rate, it could be demonstrated that the polarization of the electrode-catalyst significantly lowers the time required for complete hydrogenation, by virtue of lowering the time for the uptake of the first mole of hydrogen. The time required for the second stage is independent of the presence and density of polarizing current.

The rate of hydrogenation, and in some cases its selectivity can be increased by using cathodes activated with powder-form catalysts. These catalysts are held on the surface of the cathode by means of a magnetic field. The electrode type proposed by I. V. Kirilyus [1] is characterized by its high performance, high selectivity, high yield (up to 98%) relative to current and easy

changing of the active layer. Depending on the nature of the catalyst, of the unsaturated compound, of the solvent, respectively, and on hydrogen pressure, hydrogenation and electrohydrogenation may proceed according to three main mechanisms:

(i) In the course of the reaction, the potential of the electrode-catalyst is equal to or rather more negative than the reversible potential in the solution

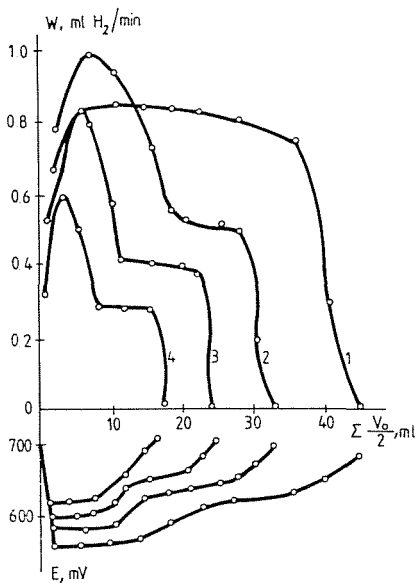


Fig. 3. Electrohydrogenation and hydrogenation of 1,1-dimethyl-2-propyne-1-ol. Pd-Pt electrode, cathodic polarization, solvent: 0.5 mol  $H_2SO_4$ /litre 50% ethanol

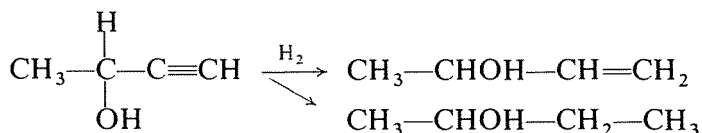
being tested. The surface is saturated with hydrogen, and the order of the reaction relative to the unsaturated compound is close to 1 (substituted olefins).

(ii) In the course of the reaction the potential is shifted towards the anodic range by 0.1 . . . 0.2 V, that is, the reaction proceeds at maximum adsorption of the unsaturated compound, at the most favourable ratio of the reactants on the surface of the catalyst (substituted enins).

(iii) In the course of the reaction the potential is shifted by more than 0.36 V and the surface contains practically no adsorbed hydrogen (nitrobenzene, quinone). In the kinetic range the activation energy of the reaction for both components can be calculated by means of the formula

$$E_a = \Delta\varphi \cdot 94 \pm 16 \text{ kJ/mol } (\Delta\varphi \cdot 23 \pm 4 \text{ kcal/mol}).$$

For any given compound one may, by anodic or cathodic polarization, choose the optimum potential of the electrode-catalyst at which the reaction will proceed at highest rate or highest selectivity. G. D. Zakumbaeva and co-workers [4] investigated the hydrogenation of 1-butyne-3-ol on a Pd/Pt electrode in 0.05 mol/l  $\text{Na}_2\text{SO}_4$  at given potentials. They found that at all potentials more positive than the reversible potential the triple bond will be hydrogenated more slowly than the double bond. In usual hydrogenation the potential shift is 0.075 . . . 0.080 V. Hydrogenation at more positive potentials will increase the difference between the hydrogenation rates of triple and double bonds, resp., and by reason of insufficient hydrogen on the surface, selectivity of hydrogenation will increase:



Under ordinary conditions, hydrogenation will yield, besides the main reaction product 1-butene-3-ol, substantial amounts of butane-2-ol and some decomposition products.

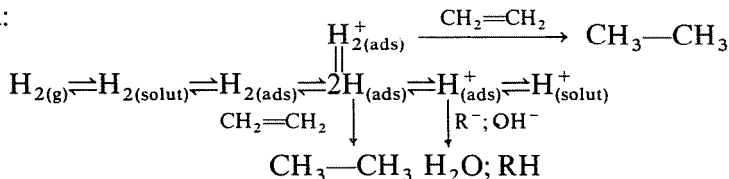
Full selectivity of the process was attained in 0.05 mol/l  $\text{H}_2\text{SO}_4$  by shifting the potential towards the anodic range by 0.1 V, in 0.05 mol/l  $\text{Na}_2\text{SO}_4$  by 0.3 V and in 0.1 mol/l NaOH by 0.4 V.

Relying on these findings, one may conclude that full selectivity of the process may be attained by means of regulating the potential. Selectivity of hydrogenation is achieved at a strictly defined potential, that is, at a defined degree of hydrogen deficiency on the surface and a given bond energy between hydrogen and surface.

In some cases the required potential will be established by binding the organic compound on the surface. Usually, however, external potential readjustment will be required. In hydrogenation of mixtures of organic compounds the optimum catalyst potential for one of the compounds can presumably be achieved at the expense of the other compound only.

Maximum rate of hydrogenation was achieved in all of the listed media at potentials more positive by 0.1 . . . 0.2 V than the reversible potential in the given medium, that is, at conditions where atomic hydrogen will still be present on the surface. The rate optimum is at potentials somewhat more negative than the potential corresponding to the selectivity optimum. It should, however, be considered that substantial shifts of the potential into the anodic range enhance the decomposition and oxidation of organic compounds and shorten the life of the catalyst. These effects are so considerable that in the case of hydrogenating triple bonds, the rate may increase at lower temperatures.

In analyzing all possible cases of hydrogenation and electrohydrogenation, the presence of the following equilibria on the surface of the catalyst must be considered:



In the solution, ionic and radical reactions proceed on the surface of the electrode-catalyst, and adsorbed hydrogen will usually be positively charged, while the unsaturated compound can be either positively or negatively charged. The main advantage of electrohydrogenation consists in the feasibility of maintaining the activity of the catalyst for long periods. Catalytic hydrogenation, on the other hand, provides high rates and selectivity. By uniting the advantages of the two methods, that is, by hydrogenating at relatively low cathodic or anodic polarization, high activity and selectivity of the electrode-catalyst will be attained jointly with long catalyst life at optimum conditions. Depending on the potential, the chemical composition will vary for each case.

It may be observed that electrocatalytic hydrogenation involves the main features of catalytic hydrogenation: the necessity to establish the system as a whole for the period of the reaction. The effect of applying external polarizing current must be studied taking into account the nature of the catalyst, the nature of the unsaturated compound and the nature of the solvent. In addition, it is obviously necessary to consider the effect of external current on the rate of hydrogen evolution and its forms on the surface as well as its effect on the activation of the unsaturated compound.

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\* In Russian.

Dr. Dimitrii V. SOKOLSKY Institute of Organic Catalysis and  
Electrochemistry, Alma-Ata, S.S.S.R.