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PHYSICAL CHEMISTRY

M. E. MANZHELEI and A. F. SHOLIN

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

PHYSICAL CHEMISTRY

M. E. MANZHELEI and A. F. SHOLIN

ELECTROCHEMICAL HYDROGENATION OF ALLYL ALCOHOL

(Presented by Academician A. A. Balandin, July 3, 1961)

The present investigation was carried out in order to elucidate the mechanism of the cathodic reduction of allyl alcohol on platinized-platinum electrodes. This question was studied as early as 1906 by S. Fokin, who first pointed out the possibility of reducing allyl alcohol by means of an electric current. In his opinion, the reaction product was propyl alcohol ([1]).

Several methods were chosen for solving the problem posed. Polarization curves were recorded, i.e., the steady values of the potentials were determined while varying the strength of the polarizing current from 0.001 to 10 mA. These determinations were accompanied by measurement of the volume of the gas evolved and by its detailed analysis. The gas for analysis was directed into an ampoule (Fig. 1) (chromatographic method).

The interaction of allyl alcohol with the degassed surface of the electrode, i.e., its adsorption (potentiometric method), was investigated. The reaction in a layer of adsorbed hydrogen was also studied ([2,3]). The electrode material was a plate of platinized platinum ($S_{\text{vis}} = 2$ cm^2, $S_{\text{true}} = 3000$ cm^2) with a clean surface and with various additions of mercury and arsenic. The method of applying them to the electrode surface is described in ([4]). Charging curves of the electrodes used were recorded beforehand ([5]), in order to determine the change in the adsorbability of hydrogen and in the energy of its bond with the electrode surface under the influence of the indicated additives. The principal electrolyte was a 0.1 N solution of H_2SO_4. All measurements are given relative to the potential of the reversible hydrogen electrode in this solution.

Fig. 1

Electroreduction of allyl alcohol over the entire range of current densities ($3 \cdot 10^{-10}$—$3 \cdot 10^{-6}$ A/cm^2) occurs at potentials which, according to the charging curve, correspond to the presence of adsorbed hydrogen on the electrode sur-

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face. At the same time a characteristic phenomenon is observed—the evolution of gaseous products, beginning at a potential 150 mV more positive than the reversible value of the potential of the hydrogen electrode. The composition of these products, determined by gas chromatography, is given in Table 1 in mole percent, while the amounts of mercury and arsenic are given in percent of the total number of surface atoms of platinum. (In experiments Nos. 5 and 6 the electrode was a platinized platinum wire.)

From the data of Table 1 and from comparison of the volume of the gas evolved with the current consumption, it is seen that the process of reduction of allyl alcohol in an acid medium on a cathode of platinized platinum proceeds mainly with the formation of C_3H_8, C_3H_6, and small amounts of CH_4, C_2H_4, C_2H_6, and H_2.

When the electrode potential is shifted in the negative direction, the amount of propylene decreases owing to an increase in the amount of propane (experiments Nos. 1-3). At potentials in a more distant region of overvoltage, the reduction process ceases (experiment No. 4). In an alkaline medium the course of the process differs sharply; evolution of gaseous products takes place only at potentials corresponding to the hydrogen-

overvoltage. The bulk of them is hydrogen, for whose evolution initially (experiment No. 5) part of the supplied current is consumed, and then (experiment No. 6) the entire current. Thus, it may be concluded that in an alkaline medium the reduction of allyl alcohol proceeds through the formation of propyl alcohol.

Table 1

Experiment No.	φ, mV	C_3H_8	C_3H_6	$C_2H_4 + C_2H_6$	CH_4	H_2
Electrolyte H_2SO_4	**Electrolyte** H_2SO_4	**Electrolyte** H_2SO_4	**Electrolyte** H_2SO_4	**Electrolyte** H_2SO_4	**Electrolyte** H_2SO_4	**Electrolyte** H_2SO_4
1	80-50	29.8	66.3	1.3	1.2	1.4
2	40-20	32.5	62.4	1.8	1.3	2.0
3	–60	10.0	69.3	2.7	2.5	15.5
4	–260	2.7	10.8	–	–	86.5
Electrolyte NaOH	**Electrolyte NaOH**	**Electrolyte NaOH**	**Electrolyte NaOH**	**Electrolyte NaOH**	**Electrolyte NaOH**	**Electrolyte NaOH**
5	–70	4.1	1.4	–	–	94.5
6	–270	0.8	–	–	–	99.2
Electrolyte H_2SO_4, **electrode 20% Hg**	**Electrolyte** H_2SO_4, **electrode 20% Hg**	**Electrolyte** H_2SO_4, **electrode 20% Hg**	**Electrolyte** H_2SO_4, **electrode 20% Hg**	**Electrolyte** H_2SO_4, **electrode 20% Hg**	**Electrolyte** H_2SO_4, **electrode 20% Hg**	**Electrolyte** H_2SO_4, **electrode 20% Hg**
7	–60	0.4	10.2	–	–	89.4

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Fig. 2

Figure 2: Fig. 2

Experiment No.	φ, mV	C_3H_8	C_3H_6	$C_2H_4 + C_2H_6$	CH_4	H_2
Electrolyte H_2SO_4, electrode 10% As	**Electrolyte H_2SO_4, electrode 10% As**	**Electrolyte H_2SO_4, electrode 10% As**	**Electrolyte H_2SO_4, electrode 10% As**	**Electrolyte H_2SO_4, electrode 10% As**	**Electrolyte H_2SO_4, electrode 10% As**	**Electrolyte H_2SO_4, electrode 10% As**
8	−150	–	–	–	–	100

Adsorption measurements in both acidic and alkaline media showed that $H_2C = CH—CH_2OH$, just like CH_3OH, C_2H_5OH, and C_3H_7OH, is adsorbed on the electrode with a sharp shift of its potential in the negative direction (Fig. 2, 1). It may be assumed that the molecules of $H_2C = CH—CH_2OH$ are arranged horizontally during adsorption. Apparently, vertical orientation is also possible; in favor of this is the fact that larger amounts of propylene are formed.

The interactions of allyl alcohol with hydrogen adsorbed on platinum in acidic and alkaline media also differ sharply. In an acidic medium, simultaneously with the shift of the potential in the positive direction, gas bubbles are released from the electrode; its chromatogram has a single peak corresponding to propane.

In the presence of small amounts of mercury on the electrode, the processes of hydrogenation by preadsorbed hydrogen and electrohydrogenation proceed in the same direction as on a clean platinum surface, but at a lower rate. Both processes cease at such amounts of mercury when, according to the charging curves, platinum loses its ability to adsorb hydrogen. The potential shift upon adsorption of allyl alcohol gradually decreases and, at high coverages, becomes equal to zero (Fig. 2, 2, 3). Thus, on a mercury electrode allyl alcohol is not reduced, which agrees with polarographic data (6). Arsenic, which strengthens the bond of hydrogen adsorbed on platinum and greatly lowers the rate of adsorption of allyl alcohol (Fig. 2, 4), causes a sharp decrease in the rate of both hydrogenation processes and, to an even greater extent, the process of hydrocarbon formation. Already at approximately 4% coverage with arsenic, polarization curves at current densities of $1 \cdot 10^{-8}$ A/cm^2 pass into the overvoltage region and reproduce the curves for hydrogen overvoltage.

Fig. 2

The data presented indicate a far-reaching similarity between the processes of hydrogenation in a layer of adsorbed hydrogen and electrohydrogenation. Both

these processes have a catalytic character and occur through interaction of adsorbed molecules of allyl alcohol with adsorbed hydrogen.

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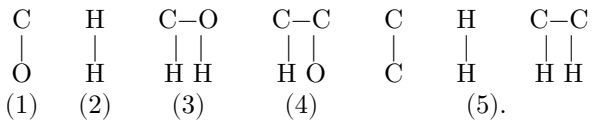
Data on the composition of the products of the hydrogenation process of allyl alcohol on a platinum electrode-catalyst make it possible to put forward a hypothesis concerning the scheme of the process. For its theoretical substantiation one should take as a basis the calculations carried out by A. A. Balandin using the energetic aspect of the multiplet theory of catalysis. A. A. Balandin [7] showed, for a nickel catalyst, the sequence of possible reactions with alcohols, the indices of which may be written in order of increasing energy barriers:



(1) (2) (3) (4) (5).

For unsaturated alcohols there must be an antecedent index corresponding to the reaction of saturation of the multiple bond. Quite possibly the same sequence of reactions also holds on a platinum catalyst, since it has been shown [8] that the bond energies of the atoms in the indices with the surface of catalysts change little on passing from metal to metal in the group Ni, Pt, Pd. Under the conditions of the present experiment, i.e., in the presence of adsorbed hydrogen on the electrode surface, reactions with indices (1) and (4) are the most probable. It is known that for the reaction with index (3), platinum is not a catalyst.

Moreover, in view of the fact that a large amount of propylene was found among the reaction products, the indicated reactions are possible without preliminary hydrogenation of the double bond. In this case hydrogenolysis of the C–O bond should be facilitated because of the presence in the allyl alcohol molecule of a double bond in the α–β-position, which leads to lability of the OH group. Additional experiments showed that CH_3OH, C_2H_5OH, and C_3H_7OH are not reduced. This confirms what has been stated above. In addition, polarized adsorbed hydrogen atoms H^+_{ads} should cause polarization of the alcohol molecule at the site of the C–OH bond, while hydrogen ions located in the electrical double layer of the electrode should shift the equilibrium toward the formation of water. The latter assumption is based on experimental data in alkaline medium, where H^+ ions in the electrical double layer are replaced by Na^+ ions and hydrocarbon formation does not occur.

All that has been said leads to the following scheme of the process:

$$H_2C{=}CH{-}CH_2OH + H^+_{ads} = H_2C{=}CH{-}CH^+_2 + H_2O;$$

$$H_2C{=}CH{-}CH^+_2 + H^-_{ads} = H_2C{=}CH{-}CH_3.$$

The existence on the surface of metallic adsorbents of two oppositely charged hydrogen ions is assumed by many investigators in the field of adsorption and catalysis [9].

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In addition to the main reaction, saturation of the double bond takes place as a parallel or successive stage, and partial hydrogenolysis of the C—C bond occurs with formation of hydrocarbons of lower molecular weight.

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