V. E. WASSERBERG, Academician A. A. BALANDIN, and I. R. DAVYDOVA

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V. E. WASSERBERG, Academician A. A. BALANDIN, and I. R. DAVYDOVA

ON THE FORMATION OF SURFACE RADICAL-LIKE INTERMEDIATE FORMS IN HETEROGENEOUS CATALYSIS

The experimental material accumulated in the study of heterogeneous catalytic reactions long ago led many investigators to the supposition that these processes proceed through the intermediate formation of free radicals on the catalyst surface. This concept, one of the first to be advanced by N. D. Zelinskii and co-workers ([1,2]), was subsequently developed in the works of V. V. Voevodskii, F. F. Vol' kenshtein, and N. N. Semenov ([3]), Ya. T. Eidus ([4]), S. Z. Roginskii ([5]), M. I. Temkin ([6]), and other investigators (see, for example, ([7])). In the theory of catalytic hydrogenation proposed by one of us ([8]) and based on the multiplet theory, the probability of the existence on metal surfaces of weakly bound hydrogen atoms as intermediate forms in hydrogenation was shown on the basis of kinetic data.

However, up to the present time, despite numerous attempts, direct experimental proof of the existence of free radicals or similar formations under the conditions of heterogeneous catalysis has not been obtained; the arguments in favor of their existence are based on indirect data on the kinetics of the processes, the composition of the reaction products, and so forth.

In our investigation of the mechanism and elementary stages of the dehydration reaction of lower aliphatic alcohols in the adsorbed layer at low degrees of coverage on a series of catalysts (alumina prepared by various methods, $Al_2O_3 + ZnO$, $Al_2O_3 + Fe_2O_3$, WO_3, $MgSO_4$, etc.), numerous kinetic data were obtained ([9,10]) that could most readily be interpreted from the standpoint of ideas concerning the formation of surface radical-like complexes. In particular, we showed that the rate of dehydration of a given alcohol, for example isopropyl alcohol, in the adsorption layer on the catalyst surface at a coverage density of 2–4% of a monolayer can vary over wide limits (usually decreasing) if, on the surface, other alcohols (ethyl, methyl, etc.), ethers (ethyl, diisopropyl), or other substances (for example, acetone, acetoacetic ester, acetonitrile, dioxane, etc.) are also present in amounts of 2 to 10–15% of a monolayer, having been preadsorbed ([11,12]). It is significant here that different preadsorbed substances, at the same coverage density, affect the rate of decomposition of the initial alcohol to different extents. Another indirect confirmation of the formation of surface free

radical-like forms may be the fact established by us under conditions of dehydration catalysis: transfer of a label from dimethyl ether labeled with radioactive carbon C^{14} to unlabeled ethyl or isopropyl alcohol, and also to the products of their dehydration ([13,14]).

Since dehydration reactions in the adsorbed layer proceed at comparatively low temperatures (120-130° instead of 250-350° under ordinary conditions), when the lifetime of radical-like complexes on the surface should increase, we undertook an attempt

directly detect them by a physical property characteristic of a number of compounds with unpaired electrons, including free organic radicals—paramagnetism. The presence of paramagnetism can be detected, for example, from the acceleration of the para-ortho conversion of hydrogen in the presence of the given compound. For the first time, such a method for detecting (and even quantitatively estimating) the concentration of free organic radicals from the hydrogen para-ortho conversion catalyzed by them was proposed by Schwab ([15]). Unlike Schwab, we proposed to study in this way not heavy hydrocarbon radicals (of the triphenylmethyl type) in solutions, but light lower radical-like formations arising during the dehydration of isopropyl alcohol on the catalyst surface.

Initially we intended to use as catalyst one of the alumina preparations employed by us in studies ([9,10]). However, it turned out that this material itself is an active catalyst for the hydrogen para-ortho conversion reaction, not only at the temperatures at which the dehydration reaction is carried out in a monolayer (120-150°), but also at room temperature. We then selected magnesium sulfate, described as an active catalyst for the dehydration of secondary alcohols in work ([16]) and also investigated by us under conditions of reaction in an adsorbed layer. As it turned out, on this catalyst, which carries out the dehydration reaction of alcohols in an adsorbed layer sufficiently actively at 150-180°, the hydrogen para-ortho conversion reaction does not occur at all at temperatures up to 300°. However, it was found that under the conditions of the alcohol dehydration reaction, followed by regeneration in a hydrogen atmosphere at 300°, the catalyst is partially reduced with formation of hydrogen sulfide and loses activity. (We propose to investigate separately the question of the possible influence of H_2S or intermediate reduction products.) Therefore, subsequently we carried out each experiment with a fresh charge of catalyst, without regenerating it after experiments. The catalyst was prepared by the method described in work ([16]). The surface area of the catalyst, determined by the BET method from the isotherm of low-temperature nitrogen adsorption, was 10-15 m^2/g.

Fig. 1. Vessel for measuring thermal conductivity. 1 —body: glass tube ($d = 12$ mm, $l = 100$ mm); 2 —molybdenum-wire leads ($d = 0.5$ mm); 3 —platinum wire ($d = 0.3$ mm); 4 —tungsten spiral made of wire ($d = 20$ μ, resistance ~ 300 ohm); 5 —holder for the spiral, a piece of capillary with a T-shaped glass filament soldered to it; the filament is soldered to the bottom of the vessel; 6 —capillary

outlet tube.

The work was carried out as follows. Into a glass high-vacuum circulation apparatus (the apparatus had been designed and assembled by S. L. Kiperman and I. R. Davydova and used by them in work on the investigation of the hydrogen para–ortho conversion reaction on nickel ([17])), a sample of the catalyst was placed and carefully trained for 3 h at 300° and at a pressure of about $1 \cdot 10^{-5}$ mm Hg. Before each experiment, the absence of conversion of parahydrogen on the given catalyst sample was checked. For this purpose, over the preliminarily trained catalyst, cooled to the temperature of the experiment, a 50% mixture of para- + orthohydrogen was circulated (obtained by the usual method, by desorption from activated carbon after holding at the temperature of liquid nitrogen ···

over the course of several hours), periodically taking samples for control into the vessel for measuring thermal conductivity.

Unlike the apparatus used in work ([14]), in the present case the vessel (Fig. 1) was a test tube made of molybdenum glass, in which a coil of tungsten wire, $d = 20\,\mu$, with a resistance (at room temperature) of 300 ohms, was placed.

After it had been established that no ortho–para conversion occurred on the catalyst under the experimental conditions, the catalyst was again evacuated to a vacuum of $1 \cdot 10^{-5}$ mm Hg, and vapors of isopropyl alcohol were admitted by breaking, with the aid of an electromagnet, an ampoule containing iso-C_3H_7OH, which had been placed in the apparatus beforehand. The ampoule was filled with alcohol in another apparatus, likewise under high-vacuum conditions, in order to prevent the entry of O_2, which also possesses paramagnetic properties. When the alcohol from the broken ampoule evaporated and its vapors were adsorbed by the catalyst, i.e., 20–30 sec after breaking the ampoule, a 50% mixture of para- + ortho-hydrogen was admitted into the system, and after 10–15 min a sample was taken for thermal-conductivity analysis. The duration of exposure before sampling was chosen on the basis that the half-decomposition period of isopropyl alcohol in the adsorption layer, determined in the apparatus ([9]), under these conditions was 5–10 min.

Table 1

Effect of the surface catalytic reaction on the para–ortho conversion of hydrogen

Experiment No.	Amount of catalyst, g	Temp., °C	Amount of alcohol, ml	Time of circulation, min	Degree of conversion, %
1	0	180	0.2	indef.	0
2	0	200	0.4	»	0
3	3.3	156	0.0	»	0

Experiment No.	Amount of catalyst, g	Temp., °C	Amount of alcohol, ml	Time of circulation, min	Degree of conversion, %
3	3.3	156	0.05	15	13.3
3	3.3	156	0.05	indef.	13.3
4	10.7	185	0.0	»	0
4	10.7	185	0.4	15	13.5
4	10.7	185	0.4	indef.	13.5
5	11.0	187	0.0	»	0
5	11.0	187	0.2	15	5.3
5	11.0	187	0.2	indef.	5.3
6	11.0	183	0	»	0
6	11.0	183	0.4	15	13.2
6	11.0	183	0.4	indef.	13.2

After completion of the experiment, the reaction products were pumped off until a vacuum of the order of $1 \cdot 10^{-5}$ mm Hg was established over the catalyst; the apparatus was again filled with a 50% mixture of para- + ortho-hydrogen, and after 5–10 minutes of circulation over the catalyst the thermal conductivity of the gas was again determined. It practically did not differ from the initial value, which served as a check on reproducibility.

In some experiments, in order to make certain that no catalytic effect of extraneous substances on the para–ortho conversion reaction of hydrogen was present, the reaction products, previously frozen out in a special trap, were added to the parahydrogen introduced after the reaction had been carried out, and this mixture was circulated over the catalyst. Special experiments also showed the absence of any effect of vapors of the initial alcohol (in the absence of catalyst) on the para–ortho conversion reaction.

A summary of the experimental data obtained is given in Table 1. As is seen from Table 1 and from what has been said above, a 50% mixture of para- + ortho-hydrogen, which undergoes no change whatever under the experimental conditions in contact with the catalyst and with vapors of the reaction products, as well as with alcohol vapors in the absence of catalyst, undergoes a noticeable conversion only in contact with the catalyst on which, at that time, the catalytic reaction of alcohol dehydration is proceeding. The extent of the para–ortho conversion reaction of hydrogen amounts to as much as 13.5% of the theoretically possible value, and the observed values of the change in resistance of the measuring wire lie far beyond the limits of possible experimental error. After completion of the reaction, with all other conditions maintained, the process of para–ortho conversion of hydrogen no longer occurs.

Thus, the results of our experiments may be interpreted as direct experimental confirmation of the reality of the occurrence under conditions—

under conditions of heterogeneous catalysis, of such intermediate compounds—multiplet complexes—which possess the paramagnetic properties characteristic of free radicals. This also confirms the validity of the ideas concerning the formation of surface free radical-like species, which we used earlier to explain a number of features of the kinetics of elementary processes in the dehydration reaction of alcohols and ethers in the adsorbed layer.

Similar species of the free-radical type apparently also arise in other heterogeneous-catalytic processes, but their detection by means of the method we used proved possible only as a result of a fortunate combination of catalyst and reaction character. Application of this method to other processes would encounter greater difficulties, since, for example, all catalysts of hydrogenation and dehydrogenation reactions should themselves actively catalyze the para-ortho conversion of hydrogen; investigation of catalytic oxidation reactions is impossible because of the distorting influence of oxygen, etc.

N. D. Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.