## THE CATALYTIC HYDROGENATION OF (+)-CARVONE ON PALLADIUM AND PLATINUM CATALYSTS

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In an investigation of the sequence of the hydrogenation of carvone on a Raney nickel catalyst [1], it was shown that hydrogenation proceeds through the formation of intermediate products: dihydrocarvone, isodihydrocarvone, carvotanacetone, which are hydrogenated to carvomenthone and isocarvomenthone; the final products of hydrogenation are isomeric carvomenthols.



Fig. 1. Change in the reaction rate (1-3) and potential of the catalyst (4-6) as a function of the degree of conversion (X, %) in the hydrogenation of (+)-carvone on Pd-black in ethanol at various reaction temperatures: 1, 5) 10°; 2,4) 20°; 3,6) 50°.

Fig. 2. Dependence of the composition of the catalyzate (A, %) on the degree of conversion in the hydrogenation of (+)-carvone on Pd-C (0.94 g of carvone, 20 ml abs. ethanol, 0.6 g 10% Pd/C): 1) carvone; 2) carvomenthone; 3) dihydrocarvone; 4) isohydrocarvone; 5) carvotanacetone; 6) carvacrol; 7) dihydrocarveol.

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Fig. 3. Dependence of the composition of the catalyzate (A, %) on the degree of hydrogenation (moles of absorbed hydrogen) in the hydrogenation of (+)-carvone on Pt-black: 1) carvone; 2) carvotanacetone; 3) carvomenthone; 4-7) stereoisomeric carvomenthols.

Fig. 4. Dependence of the rate constant of hydrogenation of carvone on the amount of Pt-black (0.67 g carvone, 15 ml abs. ethanol,  $20^{\circ}$ ).

Fig. 5. Change in the reaction rate and potential of the catalyst as a function of the degree of conversion, % in the hydrogenation of carvone on Pt-black at various reaction temperatures (0.48 g of carvone, 0.05 g Pt-black, 10 ml abs. ethanol): I, VII) 5°; II) 12°; III, IX) 20°; IV, VIII) 30°; V) 40°; VI, X) 50°.

The purpose of this work was to study the hydrogenation of (+)-carvone on palladium and platinum catalysts. There are a number of indications in the literature of the hydrogenation of carvone on Pd- and Pt-catalysts. The hydrogenation on Pd [2-4] proceeds with the formation of carvomenthone and carvacrol, arising as a result of the isomerization of carvone. After the absorption of one mole of hydrogen, a difficult-to-separate mixture of ketones is obtained. In this case of hydrogenation on Pd under pressure [5], up to 60% of the theoretical amount of hydrogen is absorbed. The carvomenthone formed does not undergo an optical inversion. In the hydrogenation of carvone on Pt-black in ethanol medium or without a solvent, carvotanacetone is formed, the hydrogenation of s% HCl, the reaction does not stop at the absorption of two moles of hydrogen, in contrast to hydrogenation in ethanol [7]. On platinum carvone can be selectively hydrogenated to (+)-carvotanacetone, (-)-carvomenthone, or (-)-carvomenthol [8]. The rate of absorption of hydrogen in the hydrogenation of the isopropenyl group is almost constant; the rate of hydrogenation of the C=O bond is very low, and its reduction requires a very active catalyst.

As can be seen from the literature data cited, it remains unclear whether hydrogenation on Pt in ethanol medium proceeds only to carvomenthone, as is indicated in [6, 7], or whether the final product of the reaction is carvomenthol [8]. In the case of hydrogenation on a Pd-catalyst it is unclear what intermediate products are obtained. In the studies under consideration, the products were identified only through their derivatives, and the quantitative composition of the catalyzate was not determined.

In this work we investigated the sequence of hydrogenation of (+)-carvone on Pd- and Pt-catalysts, using gas chromatographic and polarimetric analysis of the reaction product and with a measurement of the potential of the catalyst in the course of the reaction. The experimental procedure was described earlier [1].

Experiments on the hydrogenation on Pt-, Pd-, and Pd/C-catalysts, prepared according to [9, 10], were conducted in abs. ethanol at atmospheric pressure and under a pressure of 100-120 atm. The dependence of the reaction rate and composition of the catalyzate on the reaction temperature (2-50°) concentration of the initial carvone (0.1-3g in 10 ml of solvent), and amount of the catalyst (0.002-0.1g Pt black was investigated.

## DISCUSSION OF RESULTS

Hydrogenation on Pd-Black. In the case of hydrogenation on Pd-black the reaction proceeds through the formation of an intermediate compound, carvotanacetone (scheme); isomeric dihydrocarvones are not formed. Simultaneously with carvotanacetone, carvomenthone and carvacrol are detected in the catalyzate. The reduced amount of absorbed hydrogen in comparison with the theoretically calculated amount is explained by the presence of carvacrol. The formation of the latter is due not only to isomerization of carvone, as was suggested in [2-5], but also to the occurrence of irreversible catalysis of carvotanacetone, formed as a result of the hydrogenation of carvone. The formation of carvacrol as a result of the occurrence of irreversible catalysis was confirmed by our special experiments on the hydrogenation of carvotanacetone on a Pd-catalyst. In this case the formation of carvacrol cannot be explained by isomerization. The stoichiometric ratios of the components formed show that carvomenthone is formed both as a result of the occurrence of irreversible catalysis and in direct hydrogenation of carvotanacetone at the 1,6-bond. We should note that only in the initial stage is carvomenthone formed by parallel pathways (2-4 and 2-3, see Scheme 1),



while its subsequent formation is due primarily to hydrogenation of carvotanacetone (pathway 2-4). The further hydrogenation of carvomenthone to carvomenthols does not occur either when a new portion of catalyst is added or in hydrogenation under pressure.

Raising the reaction temperature from 10 to 50° leads to an increase in the amounts of carvacrol from 19 to 38%. However, when the reaction temperature is raised from 10 to 20° the content of carvomenthone in the catalyzate in the initial stage decreases, while when the process is conducted at 50°, no carvomenthone is formed in the catalyzate at all in the presence of 0.5 mole of absorbed hydrogen, whereas carvacrol is present in substantial amounts. This fact indicates that an increase in the reaction temperature promotes the formation of carvacrol as a result of the isomerization of carvone, while the fraction of carvacrol formed on account of the occurrence of irreversible catalysis is reduced.

The rate of hydrogenation of carvone increases substantially with increasing temperature (Fig. 1, curve 1, 2, 3). From the curves of the change in the potential of the catalyst (4-6), the nature of which is identical with the nature of the kinetic curves, it is evident that the reaction products are weakly adsorbed on the surface of a palladium catalyst: the value of the shift of the potential of the catalyst decreases rapidly during the reaction, approaching the potential of the reversible hydrogen electrode. A Pd-catalyst, in contrast to Pt and Ni, proved incapable of reduction of the carbonyl group.

<u>Hydrogenation on a 5% Pd/C-Catalyst</u>. To detect the influence of the carrier on the process of hydrogenation we investigated a Pd/C-catalyst. The hydrogenation of carvone on a Pd/C-catalyst (Fig. 2) differs substantially from the process on Pd-black and proceeds analogously to the reaction on Ni [1], through the intermediate formation of dihydrocarvone, isodihydrocarvone, carvotanacetone, which are then hydrogenated to carvomenthone. But in contrast to Raney nickel, on a Pd/C-catalyst after the absorption of one mole of hydrogen, a new component is formed – dihydrocarveol (see Fig. 2), the amount of which reaches 15% after the absorption of 1.5 moles of hydrogen. Further hydrogenation of carvomenthone to carvomenthols, just as on Pd-black, does not occur. The isomerization of carvone to carvacrol is observed to a negligible degree (up to 6%).

<u>Hydrogenation of Carvone on Pt-Black</u>. From the dependence of the composition of the catalyzate on the number of moles of absorbed hydrogen, it is evident that in contrast to hydrogenation on Raney nickel, the hydrogenation of carvone on Pt-black proceeds selectively. First the C = C bond in the

isopropenyl group is hydrogenated, and after the absorption of one mole of hydrogen, practically only carvotanacetone is detected in the reaction products, then the unsaturated bond in the ring is hydrogenated, which leads to the formation of isomeric carvomenthones; the latter are hydrogenated to isomeric carvomenthols (Fig. 3).

The rate of hydrogenation of carvone in the initial stage of the reaction (the hydrogenation of carvone to carvotanacetone) is constant, but then it gradually drops. A 10-fold change in the initial concentrations of carvone practically does not change the initial rate of hydrogenation, which permits the reaction order to be considered as zero and the rate of absorption of hydrogen corresponding to 10% conversion should be taken as the rate constant. From the graph (Fig. 4) it is evident that the rate of hydrogenation of carvone increases in proportion to the increase in the amount of Pt-black, and a threshold concentration of the catalyst is detected.

The selectivity of the hydrogenation of carvone on Pt-black is maintained within the temperature interval studied. Figure 5 presents the kinetic curves and the curves of the change in the potential of the catalyst in hydrogenation at various temperatures. The total rate of hydrogenation of carvone increases with increasing temperature, while the hydrogenation of the C = C bond in the aliphatic chain (i.e., the hydrogenation of carvone to carvotanacetone) proceeds at a rather high rate, whereas the rate of hydrogenation in the ring (hydrogenation of carvotanacetone to carvomenthone) is substantially lower.

The carbonyl group in carvomenthone is hydrogenated only 17-25% in the interval  $12-30^{\circ}$ , at a low rate; lowering the temperature to 5° promotes a more profound hydrogenation (60%). When the temperature is raised (50°), a cessation of the hydrogenation of the C=O bond is observed, whereas in the case of repeated introduction of a new portion of carvone into the reaction mixture under these conditions, hydrogenation of the C=C bond occurs to a substantial degree. This fact is probably due to the substantial decrease in the adsorbability of the C=O bond in carvone with increasing temperature. The hydrogenation of carvomenthone under a pressure of 116 atm for 2 h led to an almost total (98%) hydrogenation of the carbonyl group.

The activation energy of the hydrogenation of carvone to carvotanacetone, calculated according to the Arrhenius equation, is 3.7 kcal/mole.

The potential of the catalyst at various temperatures (see Fig. 5, curves 7-10) in the first moment is displaced by 180-200 mV in the anodic direction, and then, at the stage of hydrogenation of carvone to carvotanacetone, is displaced into the cathodic region, gradually returning to the potential of the reversible hydrogen electrode (RHE). The hydrogenation of carvotanacetone to carvomenthone occurs at a potential close to the potential of the RHE, which indicates a weaker adsorption of carvotanacetone and carvomenthone on the surface of a Pt-catalyst, in contrast to carvone; the reaction proceeds at a substantial degree of coverage of the catalyst surface by hydrogen.

Quantitatively the adsorption capacity of the components of the reaction can be estimated on the basis of the ratios of their adsorption coefficients, obtained from experiments on the successive hydrogenation of several weighed samples of the initial carvone on one sample of the catalyst. A series of experiments conducted at different temperatures showed that when new portions of carvone are added to a reaction mixture containing carvone, carvotanacetone, and a small amount of carvomenthone, the carvone immediately begins to be hydrogenated to carvotanacetone, whereas the content of carvomenthone changes negligibly. This fact indicates that actually the adsorption coefficient of carvone is substantially higher than the adsorption coefficient of carvotanacetone, and therefore the latter is displaced into the volume by carvone. The adsorption coefficients were calculated according to the formula [11]:

$$b_2/b_1 = (W_1 - W_2)/(3W_2 - W_1)$$

where  $W_1$  and  $W_2$  are the rates of successive hydrogenation of carvone at 50% conversion;  $b_1$  and  $b_2$  are the adsorption coefficients of the initial and final products of the reaction, respectively. When the temperature is increased from 0 to 30°, the ratio  $b_2/b_1$  drops from 0.25 to 0.04, i.e., carvone displaces the reaction product, carvotanacetone, from the surface of the catalyst into the volume to a greater degree, and is hydrogenated at a higher rate.

A comparison of the results of the hydrogenation of carvone on three catalysts in neutral medium in the temperature interval 2-50° showed that Pd- and especially Pt-catalysts are more selective in this

reaction with respect to the sequence of hydrogenation of C = C bonds than a nickel catalyst [1]. In the presence of Pt- and Pd-black, hydrogen is first added at the C = C bond in the isopropenyl group, i.e., predominant adsorption of the carvone molecule on the surface of these catalysts with the  $C_8 - C_{10}$  bond is observed.

A comparison of the energy barriers for the hydrogenation of C = C calculated according to the known values of the bond energies [12] (-E; for Ni = 3.4; Pd = 13.8; Pt = 14.4 kcal/mole) and the energy barriers for the hydrogenation of C = O (-E; for Ni = 10.7; Pd = 22; Pt = 31.2 kcal), it is evident that -E for C = C bonds on all three catalysts is lower than for the hydrogenation of the C = O bond. Consequently, the C = C bond should be hydrogenated first, and then C = O, which is also observed in the hydrogenation of carvone on the catalysts that we investigated. The energy barriers of the isomerization of carvone on a Ni-catalyst with respect to the bonds C = C (I) and C = O (II) (I: 25.9; II: 33.2 kcal) are lower than on Pd- (I: 38.1; II: 46.3 kcal) and Pt-catalysts (I: 40.8; II: 53.6 kcal)., and consequently, nickel should cause a greater isomerization of carvone. However, it was shown experimentally that of all three catalysts, only palladium catalyzes the isomerization of carvone. Thus, the data obtained indicate a complex nature of the occurrence of heterogeneous processes, which depends to a substantial degree on the conditions of the reaction.

## CONCLUSIONS

1. The sequence of hydrogenation of carvone on platinum and palladium catalysts was investigated.

2. The hydrogenation of carvone on Pd-black proceeds nonselectively with the formation of carvotanacetone and carvomenthone. As a result of parallel reactions of isomerization and irreversible catalysis, carvacrol is formed. Palladium on carbon catalyzes the process differently from Pd-black.

3. Hydrogenation of carvone on Pt-black proceeds selectively through the successive formation of carvotanacetone, isomeric carvomenthones, and isomeric carvomenthols.

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