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Abstract

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ON THE HYDROGENIZATION OF α-KETO ACIDS OVER A COLLOIDAL PALLADIUM CATALYST

The study of asymmetric catalysis using catalysts based on optically active supports makes it possible to reveal the correspondence between the configuration of the dissymmetric molecule formed in the reaction and the structure of the optically active compound used as the catalyst support. The previously established fact of asymmetric catalysis (^{1}) with Skita catalysts also makes it possible to judge the nature of the spatial interaction of the colloidal particles of the catalyst metal with the molecules of the lyophilic protective colloid. An essential factor in the creation of such colloidal dissymmetric catalysts is the presence of structural formations of molecules of the optically active protective colloid with the particle of the metallic catalyst, on the one hand, and with the reacting molecule, on the other. The protective colloid thus exhibits the functions of a dissymmetric support that determines the course of asymmetric catalysis (^{2}). This follows both from the fact that asymmetric catalysis (^{1}) occurs on such a catalyst and from the fact that the hydrogenation of α-keto acids with formation of dissymmetric α-hydroxy acids proceeds, in the initial stage, in the kinetic region. If the determining factor in the structure of the colloidal particles of the catalyst were the protective layer of the lyophilic colloid on the surface of the Pd particles, and not the structural spatial network of the macromolecules of the support connected with the colloidal metal particles (^{3}), then diffusion factors would play the decisive role in the kinetics.

We studied the kinetics of the hydrogenation of α-keto acids. Until now, little attention has been paid to the catalytic hydrogenation of α-keto acids. The work of Kindler et al. (^{4}) is known; they hydrogenated phenylglyoxylic acid and its esters over palladium black for preparative purposes.

The hydrogenization of keto acids was carried out by us in an alcohol-water medium at atmospheric pressure in the range 5-40° in a thermostated duck ($\pm 0.1^\circ$) in the presence of a colloidal palladium catalyst with gum arabic as protective colloid, at a palladium-colloid ratio of 1 : 2.3 (by weight). To free it from salts, the gum arabic was first subjected to electrodialysis (1000 V, 100 mA) for 48 hours and dried in vacuo: $[\alpha]_D^{20} = -29.9^\circ$ ($\alpha_D^{20} = -1.67^\circ$, $c = 2.866$, $l = 1.9009$, water). The catalyst was prepared according to ($^{5-7}$).

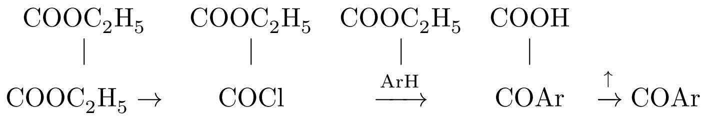
Fig. 1 and Fig. 2 graphs

Figure 1: Fig. 1 and Fig. 2 graphs

Fig. 3 graph

Figure 2: Fig. 3 graph

The initial α-keto acids were prepared according to the scheme (^{8}):



$$\begin{array}{ccccccc} \mathrm{COOC_2H_5} & & \mathrm{COOC_2H_5} & & \mathrm{COOC_2H_5} & & \mathrm{COOH} & & \\ | & & | & & | & & | & & \\ \mathrm{COOC_2H_5} & \rightarrow & \mathrm{COCl} & & \xrightarrow{\mathrm{ArH}} & & \mathrm{COAr} & \overset{\uparrow}{\rightarrow} & \mathrm{COAr} \end{array}$$

The α-keto acids obtained were purified from possible catalytic poisons by shaking their alcoholic solutions with a skeletal nickel catalyst (1 hour, 10°, 10% Ni based on the acid taken) and were recrystallized. Phenylglyoxylic acid had m.p. 64° (CCl_4, xylene); α-naphthyl-

glyoxylic acid (separated from the β-isomer through the picrate) had m.p. 112–113° (xylol).

Phenylglyoxylic acid was hydrogenated in an alcohol-water medium in a ratio of 1 : 2; β-naphthylglyoxylic acid, in an alcohol-water medium (1 : 1).

Fig. 1. Dependence of the rate of hydrogenation of phenylglyoxylic acid on the degree of conversion in the range 5–35° (10 mg palladium; 5 mmoles acid) (Curve A—hydrogenation of cinnamic acid (25°))

Fig. 2. Dependence of the rate of hydrogenation of α-naphthylglyoxylic acid on the degree of conversion in the range 10–40°

The amount of starting acid used was 0.005 mole. Hydrogenation was carried out at 800 oscillations per minute (shaker stroke length 20 cm). Special experiments established that the rate of hydrogenation does not increase when the number of oscillations is raised above 600 per minute.

Fig. 3. Dependence of the rate of hydrogenation on the initial acid concentration, 25°, 10 mg Pd: I—phenylglyoxylic acid, II—α-naphthylglyoxylic acid

The results obtained for the hydrogenation of α-keto acids are presented in the figures. Figures 1 and 2 show the course of hydrogenation of phenylglyoxylic, α-naphthylglyoxylic, and, for comparison, cinnamic acids in coordinates: rate (milliliters of absorbed H_2 (N.T.P.) per 1 min.)—degree of conversion (in percent).

As is evident from Figs. 1 and 2, the hydrogenation reaction of keto acids proceeds with zero order up to 30–60%, and then the reaction rate decreases. The change in reaction order from zero to first is in agreement with the theory

Fig. 4

Figure 3: Fig. 4

of hydrogenation (9). The fact that such a change occurs at a low degree of conversion is due to the strong adsorption of the reaction product formed (α-hydroxy acid), which is not observed, for example, in the hydrogenation over colloidal palladium of ethylenic and acetylenic compounds (6).

Taking as the rate constant the rate of hydrogen uptake over the course of 30–50% hydrogenation, and varying, at constant temperatures (25°) and catalyst amount (10 mg Pd), the amount of starting substance (by a factor of 6–8), straight lines were obtained, shown in Fig. 3, in the coordinates: rate (milliliters of H_2 (N.T.P.) per min.)—amount of compound being hydrogenated (in millimoles). The data obtained confirm zero order with respect to the substance being hydrogenated for the α-keto acids studied. Investigation of the dependence of the rate of acid hydrogenation on the amount of catalyst (variation of the catalyst amount by a factor of 8–10) showed that the reaction is first order with respect to catalyst, which indicates that the reaction proceeds in the kinetic, and not in the external-diffusion, region.

Fig. 4. Dependence of the rate of hydrogenation of α-keto acids on the amount of catalyst.
I—α-naphthylglyoxylic acid (25°, 5 mmol), *II*—α-naphthylglyoxylic acid not purified with Norit (25°, 3 mmol), *III*—α-naphthylglyoxylic acid (40°, 3 mmol), *IV* —phenylglyoxylic acid (25°, 5 mmol)

In Fig. 4 the dependence is shown of the hydrogenation rate of phenylglyoxylic and α-naphthylglyoxylic acids on the amount of catalyst (from 2 to 10 mg Pd) at a constant concentration of the starting compound. It should be noted that for acids not purified with Norit there exists a minimum limiting catalyst concentration (0.8-1.0 mg Pd per 0.003–0.005 mole of acid), below which the reaction does not proceed. This is explained by poisoning[11] of small amounts of catalyst. For acids purified with Norit, the straight-line dependence of the rate on the amount of catalyst begins at the origin (straight lines *I* and *II*, Fig. 4). First order with respect to catalyst and zero order with respect to the substance being hydrogenated were found for the hydrogenation of nitro compounds on colloidal palladium.[12]

The temperature dependence of the rate of hydrogenation of α-keto acids is presented in Figs. 1 and 2. As the rate constants, the hydrogen uptake rate was taken that corresponded to portions with zero order. From the data obtained, Arrhenius straight lines were constructed and activation energies were calculated, equal to 9.0 kcal/mol ($\varepsilon / \lg k_0 = 1.17 \cdot 10^3$) for phenylglyoxylic acid and 14.0 kcal/mol ($\varepsilon / \lg k_0 = 1.99 \cdot 10^3$) for α-naphthylglyoxylic acid.

The data obtained on the kinetics of hydrogenation of α-keto acids are of interest for understanding the fine structure of the colloidal catalyst. The mechanism of protection of metal sols is explained to a considerable extent by the presence of structural networks formed between hydrophobic and hydrophilic sols.[3] [13] On the surface of the metal particles, individual segments (predominantly functional groups) of the macromolecules of the protective colloid are adsorbed, with their orientation—intermediate between a "Langmuir palisade" and a planar arrangement—approaching W-shaped.[14] Owing to this, part of the catalyst surface remains free, and on these regions, more precisely at the zones of separation between the metal and the carrier, the catalytic reaction takes place. The presence of such regions on the catalyst surface accounts for the occurrence of the hydrogenation reaction in the kinetic region; moreover, even at elevated temperature (40°) and a high rate of hydrogen uptake (hydrogenation of phenylglyoxylic acid), no transition to the external-diffusion region was observed.

An increase in temperature promotes rupture of the structural networks, in-

thereby causing coagulation of the colloidal metal. In the case of colloidal catalysts this should be accompanied by a decrease in the reaction rate and by an increased role of diffusion factors in the kinetics of the reaction. In the temperature range investigated (up to 40°), we did not observe a decrease in the rate due to diffusion factors, as is evident from the curve for the dependence of the reaction rate on the amount of catalyst at 40° (curve *III* in Fig. 4). Consequently, during the experiments coagulation of the catalyst did not occur to any appreciable extent.

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