INFLUENCE OF AMINES ON THE ACTIVITY AND SELECTIVITY OF A SKELETAL NICKEL CATALYST

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The Lindlar catalyst - palladium on calcium carbonate, deactivated by lead [1], has found the most widespread use in the practice of organic synthesis for the partial hydrogenation of the triple bond. Of no less interest for the selective hydrogenation of unsaturated bonds may be the method of hydrogenation in the presence of nitrogen-containing compounds [2]. It was recently shown that in the presence of pyridine, quinoline, or piperidine, cyclopentadiene, tolane [3], cyclohexadiene [4], isoprene [5], and butynediol [6] are selectively hydrogenated on a skeletal nickel catalyst to the corresponding monoolefinic compounds. It is interesting to note that the amount of pyridine required for the selective hydrogenation, as was shown by a potentiometric investigation of the hydrogenation of cyclopentadiene, depends to a great degree on the nature of the solvent [7].

The hydrogenation of the quinone ring [8] or the anthraquinone ring [9] may be prevented by treating skeletal nickel with certain amines. Amines suppress hydrogenolysis of alkylphenols on a nickel catalyst or on platinum applied on aluminum oxide, at the same time, without reducing the hydrogenating activity of the catalyst [10]. On the other hand, the addition of alicyclic amines exerts a considerably greater inhibiting effect upon the hydrogenation of chlorobenzene than on its hydrogenolysis on an Adams catalyst [11]. In a number of studies of Japanese researchers, a decelerating effect of the NH₂ groups on the hydrogenation of the C≡N bond is also noted [12, 13]. The Japanese patent [14] describes a method of producing unsaturated aliphatic amines by the hydrogenation of unsaturated aliphatic nitriles in the presence of Raney nickel, treated with an amide (RCONHR') or an amine (RCH₂NHR'), where R represents C₇-C₁₇ alkyl, while R' represents H or C₈-C₁₈ alkyl.

In this work we studied the influence of a number of nitrogen-containing compounds on the activity and selectivity of the action of a skeletal nickel catalyst in reactions of hydrogenation of the triple bond -C≡C−(tolane), systems of conjugated bonds -C=C−C=C−(cyclopentadiene) and -C≡C−C≡C−(dimethylvinylethynylcarbinol).

EXPERIMENTAL

Hydrogenation was conducted with electrolytic hydrogen in alcohol medium at 25° in a glass long-necked hydrogenation flask, the rate of shaking of which was 700 oscillations per minute. Each time freshly prepared cyclopentadiene (b. p. 41-42°, nD₂₀ 1.4442-1.4446), produced by depolymerization of the dimer, and freshly distilled dimethylvinylethynylcarbinol (b. p. 53° (9 mm), nD₂₀ 1.4778) were used in the reaction. Tolane possessed m. p. 60-61° after recrystallization from alcohol. Methylamine (25% aqueous solution), diethylamine, butylamine, ethylenediamine (20% aqueous solution), hexamethylenediamine, diphenylamine, α-naphthylamine, piperidine, α-picoline, 2- and 4-ethylpyridines, benzotriazole, and quinoline methiodide were used as the amines.

Skeletal nickel was produced by leaching out a Ni-Al alloy (1:1) with 20% sodium hydroxide for 2 h at 100°. After complete saturation of the catalyst with hydrogen (0.3 g), an alcoholic or aqueous solution of the amine was introduced, and then a weighed sample of the compound to be hydrogenated was added. Moreover, after preliminary decanting of the solution and washing of the catalyst with 10 ml of alcohol, repeated experiments were conducted on the same portion of catalyst with fresh portions of the compound to be hydrogenated.
Fig. 1. Hydrogenation of cyclopentadiene (experiments 1-2), tolane (experiment 27), and dimethylvinylethylnylcarbinol (experiments 41-42) on skeletal nickel. Experiments 1 and 41 - 10 ml of 96% C₂H₅OH; experiment 27 - in 20 ml of CH₃OH; experiments 2 and 42 - in 10 ml of 96% C₂H₅OH + 5 ml H₂O. Here and henceforth the numbers on the curves correspond to the numbers of the experiments.

Fig. 2. Hydrogenation of cyclopentadiene (experiments 3-4), tolane (experiment 28), and dimethylvinylethylnylcarbinol (experiments 43-44) on skeletal nickel in the presence of methylamine.

We judged the activity of the catalyst according to the rate of absorption of hydrogen. The results obtained are depicted on kinetic curves characterizing the dependence of the rate of absorption of hydrogen (ΔV/Δt) on the summary volume of hydrogen consumed (ΣV/2). The selectivity of the hydrogenation was determined by chemical analysis of the catalyzate.

Results of the measurements. The results obtained are presented in the table and in Figs. 1-7. Figure 1 presents the kinetic curves of the hydrogenation of cyclopentadiene (experiment 1), tolane (experiment 27), and dimethylvinylethylnylcarbinol (experiment 41), which will henceforth be referred to as the carbinol. As can be seen from Fig. 1 and the table data, all the compounds investigated are hydrogenated at a great rate, forming completely hydrogenated compounds. On the kinetic curves of the hydrogenation of cyclopentadiene and the carbinol, there are two clearly pronounced portions, the break between which corresponds to the addition of approximately one and two moles of hydrogen, respectively. The portion of the kinetic curve before the break, as was established earlier, reflects the hydrogenation of cyclopentadiene to cyclopentene [15] or the carbinol to dimethylbuenylnylnylcarbinol [16], while the portion after the break renders the rate of the second step of the process, i.e., hydrogenation