Reports of the Academy of Sciences of the USSR

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1965

SovietRxiv

reaction scheme

Figure 1: reaction scheme

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1965. Vol. 163, No. 5

CHEMISTRY

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CHANGE IN THE SELECTIVITY OF THE ACTION OF NICKEL AND COBALT CATALYSTS BY MODIFICATION DURING THE HYDROGENATION OF A DIENONE GROUP

(Presented by Academician A. A. Balandin, 15 II 1965)

Selective hydrogenation of one C=C bond in 6-methylheptadien-3,5-one-2 (dienone)

is a difficult problem. It is known that hydrogen usually adds to a system of conjugated double bonds in all possible directions.

Studying the hydrogenation of dienone (1) in the presence of skeletal nickel and nickel catalysts on supports (20 : 80 wt.), we found that from the very beginning the process proceeds in two directions: hydrogen adds

Table 1

Support	Without pyridine: dienone	Without pyridine: methylheptenone	Without pyridine: isomeric ketone	Without pyridine: methylheptanone	In the presence of pyridine (7%): dienone	In the presence of pyridine (7%): methylheptenone	In the presence of pyridine (7%): isomeric ketone	In the presence of pyridine (7%): methylheptanone
MgO				Poisoning				
Al_2O_3	16.3	6.2	5.0	72.5	56.0	10.3	10.4	23.3
$Al_2O_3 \cdot SiO_2$	15.0	7.0	5.4	72.6	49.2	7.0	19.4	24.4
V_2O_5	15.6	6.6	11.7	66.1	20.0	3.5	25.5	51.0
$Ca_3(PO_4)_2$	30.8	3.0	15.4	50.8	19.5	5.5	30.0	45.0
ZnO	24.0	12.5	0.0	63.5	21.0	30.0	0.0	49.0

both at the 3,4 double bond and at the 5,6 bond, with formation respectively of 6-methylhepten-5-one-2 (methylheptenone) and 6-methylhepten-3-one-2 (isomeric ketone), Table 1. Migration of the 3,4 or 5,6 double bond of the unsaturated ketones does not occur under analogous conditions. Consequently, the formation of two unsaturated ketones at the stage of uptake of the first mole of hydrogen is due to the mechanism of addition of hydrogen to the dienone, and not to isomeric conversion of one of them.

Hydrogenation of the dienone proceeds nonselectively: in the course of uptake of the first mole of hydrogen, together with the unsaturated ketones there is formed

a large amount of the saturated ketone (Table 1). This did not make it possible to determine the direction of preferential addition of hydrogen, since methylheptanone could be formed through the stage of hydrogenation of both unsaturated ketones, and also directly from the dienone—by addition of two molecules of hydrogen without desorption of the intermediate product from the catalyst surface. The difficulty that arose was partly overcome by the use of an extraneous displacing component—pyridine. Pyridine has no substantial effect on the direction of addition of the first mole of hydrogen, but it lowers the rate of hydrogenation of the unsaturated ketone formed, partially displacing it from the catalyst surface (^{2}).

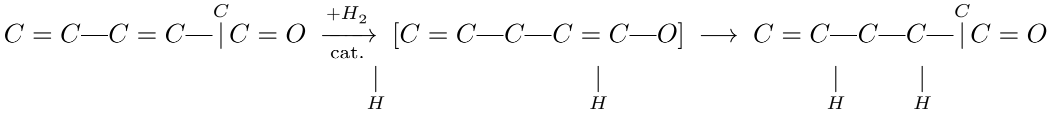
The experiments carried out showed that in the presence of pyridine the total yield of unsaturated ketones increases, while the yield of the saturated ketone decreases (Table 1). It follows from this that methylheptanone is formed mainly through unsaturated ketones. The isomeric ketone is hydrogenated at approximately the same rate as the dienone and considerably more rapidly than methylheptenone (1), and it may be assumed that the saturated ketone is formed mainly from the isomeric ketone. This is consistent with the fact that, in the presence of pyridine, on all catalysts the yield of the isomeric ketone increases, while that of methylheptenone changes little (Table 1).

Thus, on skeletal nickel and in the presence of nickel catalysts on supports, the dienone is hydrogenated predominantly at the 5,6 double bond, with formation of the isomeric ketone.

The low yield of methylheptenone is due to the mechanism of hydrogen addition to the dienone on the catalysts indicated. In order to direct the process toward methylheptenone, it is necessary to change the mechanism of hydrogenation of the 3,4 double bond. The 3,4 double bond is strongly influenced by the neighboring $C = O$ group. In particular, this is confirmed by the fact that, for example, on a $Pd–CaCO_3$ catalyst, 6-methylheptadien-3,5-ol-2 is hydrogenated predominantly at the 3,4 bond, whereas the dienone is hydrogenated at the 5,6 bond (3).

[[structural scheme: 6-methylheptadien-3,5-ol-2]] + H_2 ⟶ [[structural scheme: unsaturated alcohol]] (70%) +

We assumed that the influence of the carbonyl group is manifested in the fact that the dienone molecule is selectively adsorbed on the catalyst by the enone group ($C = C—C = O$), and its $C = C$ and $C = O$ bonds participate in conjugate hydrogenation. In this process, for example, 1,4-addition of hydrogen may occur, followed by rapid isomerization of the intermediate vinyl alcohol formed into methylheptenone:



$$C = C—C = C—\overset{C}{|}C = O \xrightarrow[\text{cat.}]{+H_2} [\underset{\overset{|}{H}}{C} = C—C—C = \underset{\overset{|}{H}}{C}—O] \longrightarrow C = C—\underset{\overset{|}{H}}{C}—\underset{\overset{|}{H}}{C}—\overset{C}{|}C = O$$

Cases of 1,4-addition of hydrogen to the conjugated system $C = C—C = O$, with formation of an unstable vinyl alcohol, are known (4).

The concept advanced here concerning the mechanism of selective hydrogenation of the 3,4 double bond makes it possible to choose the modifying component deliberately. The conjugated system $C = C—C = O$ is unsymmetrical, and its ends must differ in their chemical affinity for the catalyst. Taking into account the probable participation of the $C = O$ group in conjugate hydrogenation leading to saturation of the 3,4 double bond, it seemed advisable to modify the catalyst in such a way that, in the composition of its active centers, along with nickel, there would also be another component capable–

to enhance activation of the adsorption of the dienone molecule by the carbonyl group. Zinc oxide was chosen as such a modifying component. It is known that zinc oxide and catalysts based on it ($ZnO—Cr_2O_3$) selectively catalyze the reduction of the C=O- and COOR-groups of unsaturated aldehydes, ketones, acids, and esters (^{5}). Metallic zinc selectively catalyzes reduction of the carbonyl group of α, β-unsaturated aldehydes and ketones (^{6}).

Our investigation showed that, in the hydrogenation of the dienone over a Ni—ZnO catalyst, in contrast to nickel catalysts on all other supports, the isomeric ketone is indeed absent from the reaction products. Apparently, this confirms the proposed directing action of zinc oxide.

Even better results were obtained with the catalyst Ni—ZnO—Cd (20 : 80 : 0.4). Under optimal conditions in the presence of pyridine, the content of saturated ketone in the catalyzate decreased to 8-10%, and the yield of methylheptenone reached 80-90% of theory (^{1}). Consequently, under ordinary conditions, in the absence of pyridine, the saturated ketone is formed from methylheptenone.

Preliminary experiments showed that on the Ni—ZnO—Cd catalyst it is also possible to carry out selective hydrogenation of the 3,4 double bond of the dienone group in the more complex molecule pseudoionone.

[[structural formula: substituted cyclohexadienone, positions 3,4,5,6 indicated]] $+ H_2 \longrightarrow$ [[structural form

There is a similarity in the catalytic properties of zinc and cadmium. Cadmium is capable of catalyzing reduction of the C=O-group of butyraldehyde (^{7}), and cadmium chromite, the selective reduction of the C=O-group of α, β-unsaturated aldehydes and ketones (^{8}). Cd-ion and metallic Cd deactivate metallic catalysts with respect to the hydrogenation reaction of the C=C bond (^{9}). The indicated similarity made it possible to expect that nickel modified with cadmium would also catalyze the selective addition of hydrogen at the ends of the unsymmetrical conjugated system C=C—C=O of the dienone. Since the modifying action of cadmium is due to its interaction with nickel, it should appear independently of the nature of the support.

In order to confirm the supposition that cadmium alone, independently of ZnO, is capable of exerting a directing action, experiments were carried out on the hydrogenation of the dienone in the presence of nickel catalysts deposited on various supports, with and without addition of cadmium. Al_2O_3, activated carbon, and TiO_2 were used as supports. From the data of Table 2 it is seen that, in the absence of cadmium, hydrogen was added on these catalysts both at the 3,4 double bond and at the 5,6 bond.

A different picture was observed in the presence of cadmium. Thus, for example, in the products of hydrogenation of the dienone over the catalyst $Ni—Al_2O_3—Cd$, the isomeric ketone was absent. However, the yield of saturated ketone was 48.4%. To clarify the pathway of formation of the latter, experiments were carried out in the presence of pyridine. As expected, in the presence of pyridine the yield of saturated ketone sharply decreased, methylheptenone increased, and the isomeric ketone was not formed. Consequently, on the cadmium-modified catalyst the saturated ketone is obtained from methylheptenone, i.e., the dienone is selectively hydrogenated at the 3,4 double bond conjugated with the C=O-group.

The addition of cadmium also changes the selectivity of the action of the catalysts Ni—TiO_2 and Ni—C. The amount of cadmium required to impart

Table 2

Catalyst	Specific surface area of support, m^2/g	Cd, wt. %	Dienone	Methylheptenone	Isomeric ketone	Methylheptanone
Ni–Al_2O_3	142	0,0	27,4	10,0	10,2	52,4
Ni–Al_2O_3	142	5,0	7,0	36,0	0,0	57,0
Ni–Al_2O_3	142	20,0*	21,0	68,0	0,0	11,0
Ni–Al_2O_3	218	0,0	16,3	6,3	5,0	72,4
Ni–Al_2O_3	218	5,0	41,5	14,1	6,5	37,9
Ni–Al_2O_3	218	20,0	0,0	51,6	0,0	48,4
Ni–Al_2O_3	218	20,0*	11,9	78,5	0,0	9,6
Ni–C	510	0,0	0,0	6,3	11,2	82,5
Ni–C	510	5,0	0,0	47,7	0,0	52,3
Ni–C	510	5,0*	0,0	74,0	0,0	26,0
Ni–TiO_2	10	0,0	42,5	9,1	9,0	39,4
Ni–TiO_2	10	5,0	17,9	21,2	19,2	41,7
Ni–TiO_2	10	20,0	5,6	68,3	0,0	26,1
Ni–ZnO	40	0,0	24,0	12,5	0,0	63,5
Ni–ZnO	40	2,0	29,0	63,0	0,0	8,0
Ni–ZnO	40	2,0*	0,0	90,0	0,0	10,0

Catalyst	Specific surface area of support, m^2/g	Cd, wt. %	Dienone	Methylheptenone	Isomeric ketone	Methylheptanone
Co–Al_2O_3	218	0,0	11,9	34,6	35,0	18,5
Co–Al_2O_3	218	10,0	10,0	35,7	28,2	36,1
Co–Al_2O_3	218	20,0	15,4	52,2	0,0	32,4

* Experiments were carried out in the presence of pyridine (7% by weight).

to the catalyst selectivity of action depends on the nature and macrostructure of the support.

The modifying action of Cd confirms our supposition that the selective hydrogenation of the 3,4 double bond proceeds by the mechanism of conjugated hydrogenation. Otherwise it is difficult to understand why the addition of Cd suppresses the activity of the catalyst with respect to the hydrogenation reaction of only one C=C bond, namely the 5,6 double bond, and not the 3,4 bond. Similarly, this explains why the addition of cadmium sharply changes the relative rates of hydrogenation of the C=C and C=O bonds of crotonaldehyde[10] in the presence of the Ni–Al_2O_3 catalyst.

Under the influence of cadmium the selectivity of the action of the cobalt catalyst also changes in the process of hydrogenation of the dienone.

Thus, the work has shown the modifying action of Cd and ZnO in the process of hydrogenation of the dienone group on Ni and Co catalysts. The selective hydrogenation of the double bond of the dienone adjacent to the C=O group on the modified catalyst is explained by the mechanism of conjugated 1,4 addition of hydrogen.

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Received
8 I 1965

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