



Soviet-era science, translated into English

Chemistry

L. Kh. Freidlin, E. F. Litvin, and Yu. Yu. Kaup

1961

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196101.16105>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

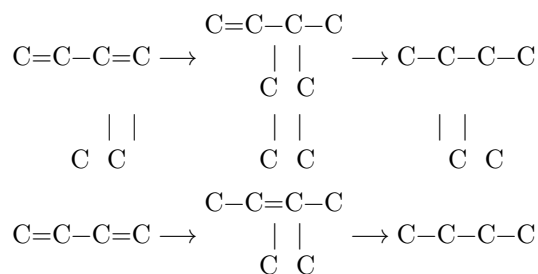
Chemistry

L. Kh. Freidlin, E. F. Litvin, and Yu. Yu. Kaup

On the Sequence of Reactions in the Hydrogenation of 2,3-Dimethylbutadiene-1,3 on a Skeletal Nickel Catalyst

(Presented by Academician M. I. Kabachnik, February 24, 1961)

The hydrogenation reaction of 2,3-dimethylbutadiene-1,3 has repeatedly been used as an example in studying the mechanism of hydrogen addition to conjugated diene systems. In the course of hydrogenation of 2,3-dimethylbutadiene-1,3, two monoolefins may be formed (2,3-dimethylbutene-1 and 2,3-dimethylbutene-2) and a paraffin (2,3-dimethylbutane).



According to Lebedev's data (¹), in the presence of Pt black the reaction proceeds nonselectively: after the addition of one mole of hydrogen, the hydrogenation products contain, along with monoolefins, 2,3-dimethylbutane (28%) and the initial diene (28%). Dupon (³) found that on a skeletal nickel catalyst the process proceeds selectively: after absorption of one mole of hydrogen, only monoolefins were detected in the catalyzate: 63% 2,3-dimethylbutene-1 and 37% 2,3-dimethylbutene-2. Gostunskaya, Loza, and Kazanskii (²) investigated the hydrogenation of this diene on Pt, Pd, and Ni catalysts. In the presence of skeletal nickel, after the addition of one mole of hydrogen, the reaction products isolated were, in addition to 66.6% 2,3-dimethylbutene-1 and 25.5% 2,3-dimethylbutene-2, also 8.3% of the initial diene.

Thus, in the cited investigations the direction of the hydrogen-addition reactions was established. At the same time, the degree of selectivity was determined from the composition of the catalyzate at a single point—at the moment of absorption of one mole of hydrogen. The absence of a convenient and accurate method for

analyzing the hydrocarbon mixture formed made it difficult to study the kinetics of the individual stages.

In the present work, the hydrogenation of 2,3-dimethylbutadiene on a skeletal nickel catalyst was studied. The use of gas-liquid partition chromatography enabled us to carry out a complete analysis of the catalyzate in the course of the reaction and thus to study the kinetics of the process and the sequence of its individual stages. The hydrogenation was carried out in a duck-shaped vessel at 25° and with intensive shaking (800 oscillations per min.). The initial diene had b.p. 69–70°, n_D^{20} 1.4310. Chromatographic analysis showed the absence of impurities of other hydrocarbons. The catalyst was prepared by leaching a Ni–Al alloy (1:1) with a 25% aqueous solution of sodium hydroxide. For each experiment, 0.2 g of catalyst and 0.01 mole of diene in 20 ml of solvent (methanol or 96% ethyl alcohol) were taken. During the reaction, samples were withdrawn from the duck-shaped vessel for analysis. β, β' -Oxydipropionitrile was used as the stationary phase for chromatography. The fractions emerging from the chromatographic column were burned and converted to hydrogen by the method described (⁴). Calibration with individual hydrocarbons had first been carried out.

Figure 1 presents the kinetic curves for the hydrogenation of 2,3-dimethylbutadiene in methyl and ethyl alcohols. From Fig. 1 it is seen that in both solvents the first mole of hydrogen is absorbed at a constant rate: 20 ml/min in methyl alcohol and 15.3 ml/min in ethyl alcohol. Further hydrogenation proceeds at a continuously decreasing rate and practically ceases after absorption of 1.6 moles of hydrogen. In calculating the hydrogen consumption, a correction for the volatility of the hydrocarbon was introduced, determined by analysis of the composition of the gas phase.

Table 1

Composition of the products of the hydrogenation reaction of 2,3-dimethylbutadiene-1,3 in methyl alcohol

Catalyst composition, %	H ₂ ab-	H ₂ ab-	H ₂ ab-	H ₂ ab-	H ₂ ab-	H ₂ ab-	H ₂ ab-	H ₂ ab-	H ₂ ab-	H ₂ ab-
	sorbed, mol. equiv.	sorbed, mol. equiv.	sorbed, mol. equiv.	sorbed, mol. equiv.	sorbed, mol. equiv.	sorbed, mol. equiv.	sorbed, mol. equiv.	sorbed, mol. equiv.	sorbed, mol. equiv.	sorbed, mol. equiv.
2,3-Dimethylbutadiene-1,3	0.17	0.28	0.48	0.69	0.93	1.03	1.11	1.21	1.39	1.69
	82.5	72.3	50.5	29.7	4.9	—	—	—	—	—

Catalyst	H ₂	H ₂	H ₂	H ₂	H ₂	H ₂	H ₂	H ₂	H ₂	H ₂
com-										
po-	ab-	ab-	ab-	ab-	ab-	ab-	ab-	ab-	ab-	ab-
si-										
tion,	sorbed,	sorbed,	sorbed,	sorbed,	sorbed,	sorbed,	sorbed,	sorbed,	sorbed,	sorbed,
mol.	mol.	mol.	mol.	mol.	mol.	mol.	mol.	mol.	mol.	mol.
%	equiv.	equiv.	equiv.	equiv.	equiv.	equiv.	equiv.	equiv.	equiv.	equiv.
2,3-Dimethylbutene-1	9.8	16.2	31.4	43.0	58.2	60.4	51.1	42.0	21.4	—
2,3-Dimethylbutene-2	7.7	11.5	18.1	27.3	36.9	38.2	38.5	38.7	39.8	41.6
2,3-Dimethylbutane	—	—	—	—	—	1.4	10.4	19.8	38.4	58.4

Table 1 and Fig. 2 show the change in the composition of the catalyst with increasing amount of hydrogen absorbed. From the data presented it is seen that this dependence is exactly the same in both solvents. In the process of absorption of the first mole of hydrogen, both olefins are formed simultaneously. Their concentration in the catalyst increases linearly with increasing amount of hydrogen absorbed. The dependence of the rate of formation of both monoolefins on the amount of hydrogen absorbed, calculated from chromatographic analysis data for the catalysts, is shown in Fig. 1. As can be seen from Fig. 1, the rates of formation of 2,3-dimethylbutene-1 (curve *III*) and 2,3-dimethylbutene-2 (curve *IV*) in both alcohols are constant; although they are different, the ratio of the rates also remains constant (3 : 2).

Fig. 1. Hydrogenation of 2,3-dimethylbutadiene-1,3 in ethyl alcohol (*a*) and in methyl alcohol (*b*): *I* —total rate of formation of monoolefins, *II* —rate of formation of 2,3-dimethylbutane, *III* —2,3-dimethylbutene-1, *IV* —2,3-dimethylbutene-2 (on the abscissa axis —amount of hydrogen in moles)

Under the selected conditions, hydrogenation of the diene proceeds strictly selectively. At the moment of absorption of one mole of hydrogen, a mixture consisting of 62% 2,3-dimethylbutene-1 and 38% 2,3-dimethylbutene-2 is formed; diene and paraffin are absent from the catalyst. During absorption of the second mole of hydrogen, the concentration of 2,3-dimethylbutene-1 in the catalyst decreases linearly and, correspondingly, the concentration of 2,3-dimethylbutane increases. The content of 2,3-dimethylbutene-2 in the catalyst, however, not only does not decrease but even increases somewhat (by 3-4%). By the time 1.6 moles of hydrogen have been absorbed, 2,3-dimethylbutene-1 completely disappears from the solution and the reaction practically ceases. The remaining 2,3-dimethylbutene-2 is hydrogenated extremely slowly: hydrogen is absorbed at a rate of 1 ml/hour.

Fig. 2. Dependence of the composition of the catalyzate on the amount of hydrogen absorbed. I –2,3-dimethylbutadiene-1,3, II –2,3-dimethylbutene-1, III –2,3-dimethylbutene-2, IV –2,3-dimethylbutane. a –in methyl alcohol, b – in ethyl alcohol (on the abscissa axis –amount of hydrogen in moles)

Figure 1: Fig. 2. Dependence of the composition of the catalyzate on the amount of hydrogen absorbed. I –2,3-dimethylbutadiene-1,3, II –2,3-dimethylbutene-1, III –2,3-dimethylbutene-2, IV –2,3-dimethylbutane. a –in methyl alcohol, b –in ethyl alcohol (on the abscissa axis –amount of hydrogen in moles)

The slight increase in the concentration of 2,3-dimethylbutene-2 in the catalyst during addition of the second mole of hydrogen can be explained by slow isomerization of 2,3-dimethylbutene-1. To confirm this assumption, hydrogenation was studied under analogous conditions for 2,3-dimethylbutene-1 (b.p. 55.2–56.6°, n_D^{20} 1.3902), obtained by hydrogenation

2,3-dimethylbutadiene-1,3 on skeletal nickel and isolated by fractionation on a column. By the chromatographic method, an impurity of 2,3-dimethylbutane (1%) was found in the prepared olefin. Figure 3 presents the dependence of the composition of the catalyzate on the depth of hydrogenation. It is seen from Fig. 3 that, during hydrogenation, 2,3-dimethylbutene-1 is indeed partially isomerized into 2,3-dimethylbutene-2. Toward the end of the reaction, up to 4% of this olefin accumulates in the solution. When 2,3-dimethylbutene-1 was shaken in a nitrogen atmosphere with a skeletal nickel catalyst saturated with hydrogen, no isomerization was observed, but part of the olefin (3%) was hydrogenated at the expense of hydrogen sorbed by the catalyst.

The results of our work show that on a skeletal nickel catalyst in an alcoholic medium, 2,3-dimethylbutadiene is hydrogenated strictly selectively: during absorption of the first mole of hydrogen, the monoolefins formed are not hydrogenated. In this process, 2,3-dimethylbutene-1 and 2,3-dimethylbutene-2 are formed at a constant rate in the ratio 3 : 2.

Fig. 2. Dependence of the composition of the catalyzate on the amount of hydrogen absorbed. I –2,3-dimethylbutadiene-1,3, II –2,3-dimethylbutene-1, III –2,3-dimethylbutene-2, IV –2,3-dimethylbutane. a –in methyl alcohol, b – in ethyl alcohol (on the abscissa axis –amount of hydrogen in moles)

Fig. 3. Dependence of the composition of the catalyzate on the amount of hydrogen absorbed. I –2,3-dimethylbutene-1, II –2,3-dimethylbutane, III – 2,3-dimethylbutene-2. a –in methyl alcohol, b –in ethyl alcohol (on the abscissa axis –amount of hydrogen in moles)

In the second stage, 2,3-dimethylbutene-1 is hydrogenated first and selectively; during hydrogenation, slight isomerization of the α -olefin into the β -olefin is observed. 2,3-Dimethylbutene-2 is apparently weakly adsorbed and hydrogenates very slowly. The sequence of the observed reactions is thus governed by adsorp-

Fig. 3. Dependence of the composition of the catalyzate on the amount of hydrogen absorbed. I –2,3-dimethylbutene-1, II –2,3-dimethylbutane, III –2,3-dimethylbutene-2. a –in methyl alcohol, b –in ethyl alcohol (on the abscissa axis –amount of hydrogen in moles)

Figure 2: Fig. 3. Dependence of the composition of the catalyzate on the amount of hydrogen absorbed. I –2,3-dimethylbutene-1, II –2,3-dimethylbutane, III –2,3-dimethylbutene-2. a –in methyl alcohol, b –in ethyl alcohol (on the abscissa axis –amount of hydrogen in moles)

tion displacement: in the first stage, monoolefins are displaced by the diene, and in the second, the β -olefin by the α -olefin.

Since 2,3-dimethylbutene-1 isomerizes extremely slowly and is displaced by the diene, the formation of 2,3-dimethylbutene-2 may be regarded as the result of addition of hydrogen to the diene in the 1,4-position, if one does not take into account the possibility of isomerization of the α -olefin at the moment of its formation before its desorption.

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

Received
19 II 1961

CITED LITERATURE

1. S. V. Lebedev, A. I. Yakubchik, ZhRKhO, **61**, 551 (1929).
2. I. V. Gostunskaya, G. V. Loza, B. A. Kazanskii, Izv. AN SSSR, OKhN, **1955**, p. 863.
3. G. Dupont, C. Paquot, C. R., **205**, 805 (1937).
4. G. E. Green, *Nature*, **180**, No. 4580, 295 (1957).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.