

HYDROGENATION AND ISOMERIZATION OF OLEFINS
IN THE PRESENCE OF A CATALYST SYSTEM THAT
CONTAINS THE RHODIUM - TRIPHENYLPHOSPHINE - DIMETHYL
SULFOXIDE COMPLEX

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Tris(triphenylphosphine)rhodium chloride (I) exhibits great activity in the hydrogenation of olefins, but accelerates their isomerization only slightly [1]. In contrast to (I), the reduced dimethyl sulfoxide rhodium complex (II) catalyzes both the hydrogenation and the isomerization of olefins [2]. It was shown by us that the $(\text{DMSO})(\text{PPh}_3)_2\text{RhCl}$ complex, which contains both types of ligands (Ph_3P and DMSO), exhibits catalytic activity in the hydrogenation of dienes in DMSO solution only when the system contains NaBH_4 [3]. In the present paper the behavior of this system was studied in the isomerization and hydrogenation of straight-chain and branched olefins. The ascertained properties of the $(\text{DMSO})(\text{PPh}_3)_2\text{RhCl}-\text{NaBH}_4$ (III) system in DMSO solution made it possible to study the rate and selectivity of the indicated processes as a function of the structure of the hydrocarbon.

EXPERIMENTAL METHOD

The complex $(\text{DMSO})(\text{PPh}_3)_2\text{RhCl}$ was obtained as described in [4]. All of the operations of preparing the complex and catalyst solution were run in an inert atmosphere. The gases were removed from the DMSO in vacuo. The catalyst solution was obtained by mixing a solution of the $(\text{DMSO})(\text{PPh}_3)_2\text{RhCl}$ or $(\text{PPh}_3)_3\text{RhCl}$ complex ($0.5 \cdot 10^{-4}$ mole of the complex in 10 ml of DMSO) with a solution of NaBH_4 ($5 \cdot 10^{-4}$ mole in 10 ml

*Deceased.

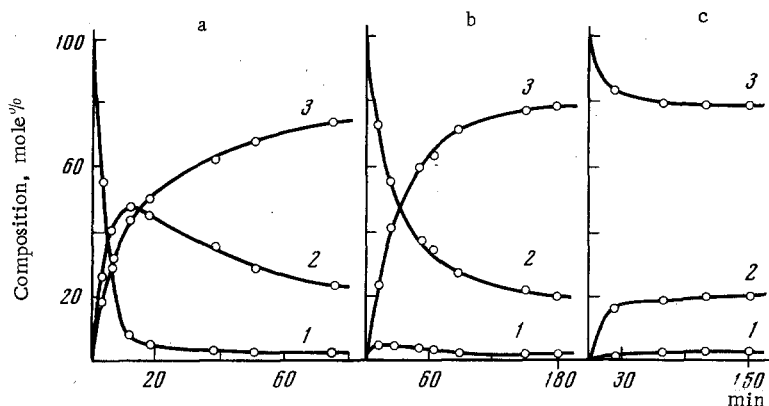


Fig. 1. Isomerization of 1-pentene (a), cis-2-pentene (b) and trans-2-pentene (c): 1) 1-pentene; 2) cis-2-pentene; 2) trans-2-pentene; 3) trans-2-pentene.

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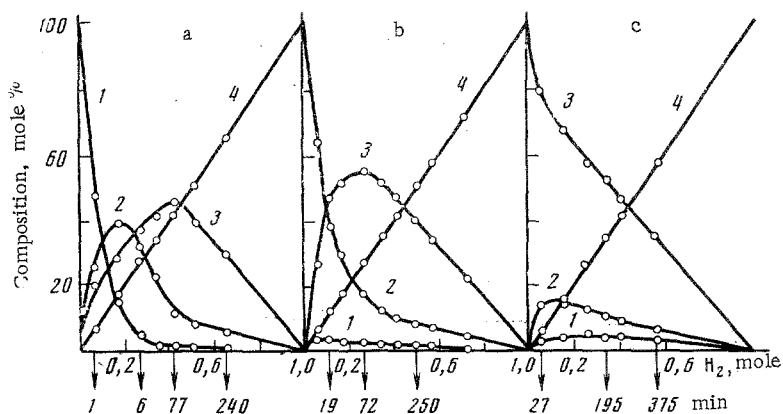


Fig. 2. Transformation of 1-pentene (a), cis-2-pentene (b) and trans-2-pentene (c) under hydrogenation conditions. The designations are the same as in Fig. 1; 4) n-pentane.

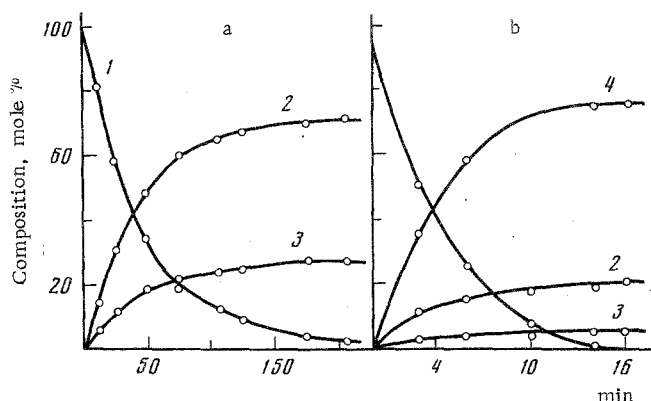


Fig. 3. Isomerization of 3-methyl-1-butene (a) and its hydrogenation (b): 1) 3-methyl-1-butene; 2) 2-methyl-2-butene; 3) 2-methyl-1-butene; 4) 2-methylbutane.

of DMSO). Here the dark orange solution became bright yellow. Then the olefin ($8 \cdot 10^{-3}$ mole) was added and samples of the catalyzate were removed at definite time intervals for analysis.

The reaction was run with vigorous stirring at 20° in either an Ar or H_2 atmosphere (0.4 at) [gauge atmosphere]. The composition of the catalyzate was determined chromatographically at $\sim 20^\circ$ on an 800×0.2 cm column packed with the stationary phase β, β' -thiodipropionitrile (17.5%) deposited on Celite C-22; a flame-ionization detector was used.

DISCUSSION OF RESULTS

In the absence of H_2 the studied system (III) catalyzes the isomerization of α -olefins. 1-Pentene is isomerized with the predominant formation of cis-2-pentene, which is then converted more slowly to the trans-isomer (Fig. 1a). It was established by separate experiments that the rate of the mutual transformations of the cis- and trans-2-pentenes is nearly one order of magnitude lower than the rate of shift of the C-C bond in 1-pentene (Fig. 1b and c). In the presence of H_2 the main direction of the process is also isomerization, which accompanies the hydrogenation (Fig. 2). The ratio of the yields of the isomerization and hydrogenation products at the start of reaction is equal to 6.5 for 1-pentene, and 4.5 for cis-2-pentene.

3-Methyl-1-butene is isomerized in an inert atmosphere to give a nonequilibrium mixture of 2-methylbutenes (Fig. 3a). Under hydrogenation conditions the main reaction product is isopentene. At the start of reaction the hydrogenation rate of 3-methyl-1-butene exceeds its isomerization rate by 2.8 times. It was established by separate experiments that 2-methyl-1-butene and 2-methyl-2-butene fail to hydrogenate and do not undergo mutual transformations.

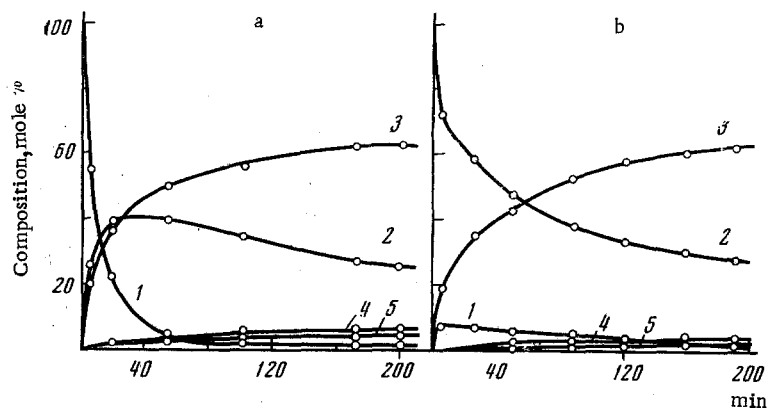
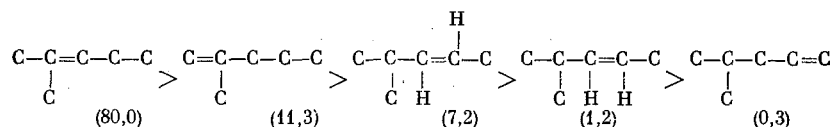


Fig. 4. Isomerization of 4-methyl-1-pentene (a) and cis-4-methyl-2-pentene (b): 1) 4-methyl-1-pentene; 2) cis-4-methyl-2-pentene; 3) trans-4-methyl-2-pentene; 4) 2-methyl-2-pentene; 5) 2-methyl-1-pentene.

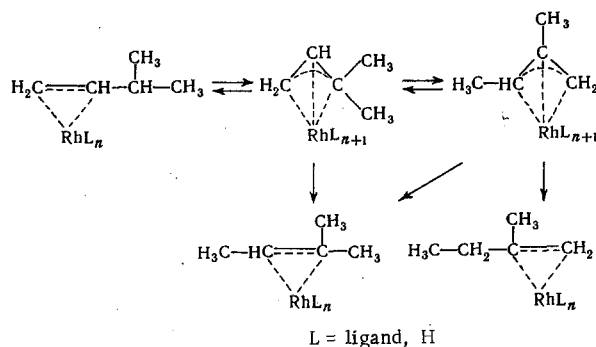
4-Methyl-1-pentene is isomerized to give all of the possible isomers, the amount of which in the equilibrium mixture at 55° decreases in the order [5]:



From Fig. 4a it follows that the terminal C=C bond of 4-methyl-1-pentene undergoes rapid shift to the β -position, in which connection the thermodynamically unstable cis- and trans-4-methyl-2-pentenenes are obtained. The shift of the C=C bond to the γ - and δ -position proceeds very slowly: the total amount of 2-methyl-2-pentene and 2-methyl-1-pentene at the start of reaction does not exceed 1-2%. 4-Methyl-1-pentene is isomerized to a greater degree than it is hydrogenated in the presence of H_2 . The amount of isomeric hexenes formed in 1.5 min from the start of reaction is three times greater than the amount of isohexane; they are obtained in approximately the same yield at the point of complete 4-methyl-1-pentene conversion (Table 1). cis-4-Methyl-2-pentene is slowly isomerized to the trans form (Fig. 4b) and it is also hydrogenated (Table 2).

It was established by separate experiments that the most stable isomers are very inert: 2-methyl-1-pentene fails to either hydrogenate or isomerize, while 2-methyl-2-pentene is not reduced, but is slowly isomerized to 4-methyl-2-pentene (to the extent of 5% in 2 h).

The obtained data show that the system, containing the rhodium complex, exhibits a high catalytic activity in the reactions for the shift of the C=C bond of α -olefins and the cis-trans transformation of β -olefins in an argon atmosphere. The isomerization rate increases in the presence of H_2 (Table 3). Apparently the process proceeds via the intermediate formation of the hydride complex. Under the conditions of an inert atmosphere the Rh complex probably cleaves hydrogen from the allylic C atom of the transformed olefin, i.e., the isomerization proceeds by the π -allylic mechanism.



This is in agreement with the fact that 2-methyl-1-butene is formed directly from 3-methyl-1-butene in the isomerization process, since 2-methyl-2-butene does not isomerize under the selected conditions. The hydride

TABLE 1. Change in Catalyzate Composition with Time during Hydrogenation of 4-Methyl-1-pentene

| Composition, mole % | Time, min | | | | |
|--------------------------|-----------|------|------|------|------|
| | 1,5 | 21 | 51 | 175 | 255 |
| 4-Methyl-1-pentene | 69,6 | 0,6 | 0,4 | 0,2 | 0,2 |
| 2-Methylpentane | 10,5 | 51,7 | 55,1 | 70,1 | 72,1 |
| trans-4-Methyl-2-pentene | 19,2 | 22,6 | 22,3 | 18,6 | 17,4 |
| cis-4-Methyl-2-pentene | 10,7 | 23,4 | 20,2 | 9,0 | 7,5 |
| 2-Methyl-1-pentene | Traces | 1,0 | 1,2 | 1,2 | 1,6 |
| 2-Methyl-1-pentene | Traces | 0,7 | 0,8 | 0,9 | 1,2 |

TABLE 2. Change in Catalyzate Composition with Time during Hydrogenation of cis-4-Methyl-2-pentene

| Composition, mole % | Time, min | | | | |
|--------------------------|-----------|------|------|------|------|
| | 25 | 55 | 80 | 110 | 130 |
| cis-4-Methyl-2-pentene | 53,5 | 35,1 | 31,4 | 25,0 | 22,8 |
| trans-4-Methyl-2-pentene | 21,4 | 26,6 | 26,7 | 25,5 | 25,3 |
| 2-Methylpentane | 20,9 | 34,7 | 38,5 | 45,8 | 48,1 |
| 2-Methyl-2-pentene | Traces | 1,1 | 1,2 | 1,1 | 1,2 |
| 2-Methyl-1-pentene | Traces | 0,7 | 0,8 | 1,4 | 1,5 |

TABLE 3. Dependence of Catalyzate Composition and Half-Conversion Time on Olefin Structure

| Olefins | $\tau/2$, min | | Catalyzate composition during hydrogenation of olefin at time $\tau/2$, mole % | |
|------------------------|---------------------|---------------|---|---------------|
| | isomerization in Ar | hydrogenation | products | |
| | | | isomerization | hydrogenation |
| 1-Pentene | 3 | 1 | 43 | 7 |
| 4-Methyl-1-pentene | 8 | 2 | 35 | 15 |
| 3-Methyl-1-pentene | 33 | 3 | 15 | 35 |
| cis-2-Pentene | 30 | 15 | 40 | 10 |
| trans-2-Pentene | — | 200 | 13 | 37 |
| cis-4-Methyl-2-pentene | 46 | 25 | 30 | 20 |

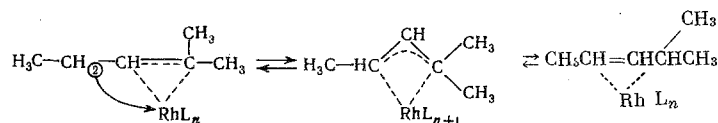
mechanism does not explain this route of the reaction.

Branching of the hydrocarbon chain leads to a decrease in the isomerization rate of the olefin, which becomes greater the closer the point of branching is located to the C=C bond: 1-pentene > 4-methyl-1-pentene > 3-methyl-1-butene. The transformation rate of cis-2-pentene is higher than that of cis-4-methyl-2-pentene. Apparently the reactivity of the olefins is associated with the relative ease of hydrogen cleavage from the allylic C atom of the olefin, which depends on the structure of the substituent at the double bond.

Hydrogen is drawn out of the gas phase under the hydrogenation conditions needed to form the hydride. Here the isomerization rate increases markedly and also depends on the structure of the olefin. The ratio of the yield

of isomerization products to the yield of hydrogenation product at the point of half conversion of the olefin is 6.2 for 1-pentene, 2.3 for 4-methyl-1-pentene, 0.4 for 3-methyl-1-pentene, 4.0 for cis-2-pentene, and 1.5 for cis-4-methyl-2-pentene. The effect of the steric factor is also manifested in the fact that 2-methyl-2-butene does not isomerize (and does not hydrogenate), probably due to the weak coordination on the investigated Rh complex and because of the difficulty of cleaving hydrogen from the methyl groups that surround its C=C bond.

2-Methyl-1-butene and 2-methyl-1-pentene also do not isomerize (and do not hydrogenate). Here the methyl radical at the C=C bond apparently interferes with the cleavage of hydrogen from the methylene group. In contrast to this, although 2-methyl-2-pentene also does not hydrogenate it is capable of isomerizing to 4-methyl-2-pentene. In this case the methyl substituents at the C=C group probably do not interfere with the cleavage of hydrogen from the methylene group



The results of the study make it possible to compare the catalytic properties of Rh complexes (I), (II) and system (III). System (III) inherits some of the traits of the corresponding Rh complexes (I) and

(II) and acquires some new catalytic properties. Similar to (I) and (II), system (III) exhibits a high activity in the reactions for the hydrogenation of α - and β -olefins, in which connection the reaction rate correlates with the structure characteristics of the olefin.

In contrast to (I) and similar to (II), system (III) exhibits a strong isomerizing action. Its catalytic activity in the reactions of migration of the C=C bond of an α -olefin and the cis-trans transformation of a β -olefin in several orders of magnitude greater than the activity of the (I) complex, it is substantial in an inert atmosphere, and increases in the presence of H_2 .

Similar to (I) and in contrast to (II), the rhodium complex in system (III) apparently forms an unstable bond with dienes and catalyzes their selective reduction to olefins. System (III) catalyzes the isomerization of 3-methyl-1-butene to give a nonequilibrium mixture of 2-methyl-2-butene and 2-methyl-1-butene. Only the β -olefin is obtained in the presence of (II), while the separately taken 2-methyl-1-butene forms a stable bond with it, and in this way deactivates the complex with respect to isomerization and hydrogenation reactions.

CONCLUSIONS

1. The insertion of the dimethyl sulfoxide ligand into tris(triphenylphosphine)rhodium chloride and subsequent treatment with sodium borohydride in dimethyl sulfoxide solution increases the catalytic activity of the complex by several orders of magnitude in the reactions for shift of the terminal C=C bond and the cis-trans transformation of β -olefins.

2. Branching of the hydrocarbon chain of the olefin leads to a decrease in its isomerization rate.

3. The isomerization rate increases sharply in the presence of hydrogen, which can serve as an indication of the intermediate formation of the hydride.

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