# Hydroisomerization of *cis*-Stilbene into *trans*-Stilbene on Supported Heterogeneous Metal Catalysts (Rh, Pd, Pt, Ru, Ir/α-Al<sub>2</sub>O<sub>3</sub>)

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Abstract—The hydroisomerization of a *cis*-isomer to produce a *trans*-isomer on Rh, Pd, Pt, Ru, and  $Ir/\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts is studied. It is shown that Rh and Ru catalysts on which the hydroisomerization reaction mostly takes place exhibit the most favorable characteristics, whereas on the other metals, the main route is the hydrogenation reaction. Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is the optimum catalyst, since it has much higher activity than Ru/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. It is found that the increased selectivity of the *trans*-isomer formation is facilitated by a decrease in the hydrogen pressure and by an increase in the substrate concentration. The maximum selectivity is achieved when the reaction is carried out in nonpolar *n*-hexane and toluene, whereas in the case of the more polar tetrahydrofuran (THF), dimethylformamide (DMFA), and methanol both the reaction rate and the selectivity of the *trans*-isomer formation decline.

*Keywords:* hydroisomerization, *trans*-stilbene, *cis*-stilbene, Rh, hydrogenation **DOI:** 10.1134/S0023158417060064

# **INTRODUCTION**

In recent years, specialists in the field of organic chemistry and heterogeneous catalysis are being increasingly attracted by the selective hydrogenation of disubstituted alkyne compounds to produce *trans*-alkenes. This is caused by the fact that many compounds used in the pharmaceutical and food industries contain a double C=C bond in their structure and that the nature of their biological activity is largely determined by the geometry of substituent arrangement (*cis* or *trans*) with respect to the double bond. Typical examples of such structures are the beta-carotene molecules [1], the polyene molecules of antifungal agents [2, 3], polyunsaturated fatty acids, pheromones [4–6], and other biologically active compounds [7, 8].

One of the most efficient traditional methods for preparing *cis*-isomers is the selective hydrogenation of disubstituted alkyne compounds on heterogeneous metal catalysts. The use of modified Pd catalysts allows to carry out this process with a selectivity level higher than 95% and an acceptable rate [9, 10].

However, the synthesis of *trans*-isomers is much more complicated. Methods based on alkene metathesis reactions [11, 12], cross coupling [13] and other methods for the formation of a new double bond are used to produce them [14–19].

Nevertheless, the reaction of selective hydrogenation remains a very attractive alternative to the abovementioned methods due to the ease of performing it and the absence of by-products. In this respect, many research groups are trying to develop new catalytic systems that allow to obtain *trans*-isomers via the selective hydrogenation of disubstituted alkyne compounds. In recent years, a number of publications have appeared that show the fundamental possibility of making a highly selective hydrogenation catalyst in the *trans*-alkene isomers formation.

Thus the authors of [20] proposed a heterobimetallic complex (IMes)Ag–RuCp(CO)<sub>2</sub> capable of hydrogenating DPA to produce highly selective *trans*-stilbene (*trans*-ST). A number of works have shown the possibility of making selective hydrogenation catalysts based on Ru complexes. Lindhardt et al. [21] described the selective hydrogenation of DPA and other arylacetylenes on a commercial catalyst Ru(PPh<sub>3</sub>)<sub>3</sub>(CO)(H)Cl that highly selectively formed *trans*-ST at a hydrogen pressure of 3 bar. In a later paper [22], a comparative study was performed concerning the selectivity and activity of 17 metalcomplex Ru catalysts in the hydrogenation of DPA into *trans*-ST using formic acid as a hydrogen source.

At the 100% conversion level of the initial DPA, a selectivity higher than 98-99% was achieved using the [RuPPh<sub>3</sub>]Cl<sub>2</sub> and Ru(PPh<sub>3</sub>)<sub>3</sub>(CO)(H)Cl catalysts, as well as a Grubbs–Hoveda type metathesis catalyst representing a benzylidene complex of Ru. The latter catalyst also highly selectively formed *trans*-isomers upon the hydrogenation of a number of substituted alkyne compounds having different structures. By

studying the mechanism of hydrogenation, the authors concluded that the reaction process via a twostorage mechanism. At the first stage, a disubstituted alkyne molecule is hydrogenated to form *cis*-alkene that further isomerizes into a more thermodynamically stable *trans*-isomer (see Scheme 1):





Unfortunately, there is almost no data available in the literature concerning a selective liquid-phase hydrogenation of the substituted alkynes to yield the corresponding trans-isomers on heterogeneous catalysts. Only in recent years, Japanese scientists have shown the possibility of obtaining *trans*-isomers on heterogeneous catalysts using this method. Thus, Komatsu et al. [23] achieved a high yield of trans-ST (74%) via DPA hydrogenation on a composite system obtained by mechanically mixing the bimetallic  $(Pd_3Bi/SiO_2)$  and zeolite (H–USY) components. In a later work [24], a yield of about 58% of trans-ST was obtained on a bimetallic Rh<sub>2</sub>Sb/SiO<sub>2</sub> catalyst. The yield of the trans-isomer was increased to 88% when changing the monocomponent Rh<sub>2</sub>Sb/SiO<sub>2</sub> catalyst to the tandem  $[RhSb/SiO_2 + Pd_3Bi/SiO_2]$  catalytic system.

The investigation of the reaction in the presence of heterogeneous catalysts showed that the process proceeds according to a two-stage mechanism similar to the mechanism proposed for a Ru metal-complex catalyst: at the 1st stage, the DPA is hydrogenated to form *cis*-stilbene (*cis*-ST) that is then isomerized at the second stage to give *trans*-ST (see Scheme 1). The isomerization on the [Pd<sub>3</sub>Bi/SiO<sub>2</sub> + H–USY] catalyst proceeds according to the mechanism of acid catalysis on the zeolite component. On [RhSb/SiO<sub>2</sub> + Pd<sub>3</sub>Bi/SiO<sub>2</sub>], the hydroisomerization of *cis*-ST occurs on the RhSb surface, whereas the hydrogenation proceeds on Pd<sub>3</sub>Bi/SiO<sub>2</sub>.

It should be noted that it is possible to hydroisomerize *cis*-ST into *trans*-ST on the monocomponent  $Rh_2Sb/SiO_2$ , although in this case the yield of the trans product is somewhat lower (~58%) [24]. A key parameter determining the yield of the *trans*-isomer is the activity of the catalyst in the hydroisomerization. As a rule, hydroisomerization rate is slower than the rate of the competing hydrogenation of the resulting olefin. Unfortunately, in the current literature there is almost no data on the activity of heterogeneous catalysts based on different metals in the liquid-phase hydroisomerization of complex molecules.

The aim of this work consisted in comparing the hydroisomerization activity of the supported catalysts based on Pd, Ir, Pt, Rh, and Ru, as well as in determining the optimal process parameters such as hydrogen pressure, substrate concentration, and solvent nature. *Cis*-ST was used as the model substrate, since most of the works devoted to liquid-phase *cis*-*trans*isomerization were performed using this compound.

#### **EXPERIMENTAL**

## Preparation of Catalysts

To obtain a series of metal-supported catalysts,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Alfa Aesar,  $S_{sp} = 8 \text{ m}^2/\text{g}$ ), preliminarily calcined in air flow (550°C) was used as the carrier. Metals were applied using an incipient wetness impregnation.

Pd was supported from a solution of Pd(NO<sub>3</sub>)<sub>2</sub> in 10% nitric acid. After impregnation, the sample was dried in air at room temperature, then reduced at a 5 vol % H<sub>2</sub>/Ar flow for 1 hour at 600°C. The metal content in the catalyst was 1 mass %.

Aqueous solutions of Rh(NO<sub>3</sub>)<sub>3</sub>, [Pt(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>, IrCl<sub>3</sub>, and RuCl<sub>3</sub> were used to prepare the Rh-, Pt-, Ir-, and Ru-based catalysts, respectively. After impregnation, the samples were dried at room temperature, then calcined in air flow: Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> for 4 h at 450°C, Ir, Ru/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> for 3 h at 450°C, and Pt/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> for 4 h at 500°C. The catalysts were activated in a flow of 5 vol % H<sub>2</sub>/Ar for 1 h: Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at 550°C, Pt/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at 500°C, and Ir, Ru/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at 450°C. Since the activity of Rh, Pt, Ir, and Ru in the studied reaction is significantly lower than that of Pd, catalysts were prepared with a 3 wt % metal content.

#### Electron Microscopy

The catalysts were examined by transmission electron microscopy (TEM) using an HT7700 electron microscope (Hitachi, Japan). The analytical measurements were optimized as described elsewhere [25]. Before the imaging, the powder samples were deposited from an isopropanol suspension onto copper grids (d = 3 mm) covered with a layer of carbon. Images were acquired in bright-field TEM mode at 100 kV accelerating voltage. The average size and the particle size distribution were calculated based on the measurement of 300–1000 particles on the TEM images of different parts of the samples.

#### Hydroisomerization of cis-Stilbene

The hydroisomerization of *cis*-ST (97%, Alfa Aesar) was carried out in an autoclave-type reactor mounted on a magnetic stirrer and equipped with a gas supply and a pressure control system. The substrate, catalyst, and solvent (6 mL) were mixed in a glass vial (12 mL) and placed into the autoclave. The setup was purged with He to remove air and was filled with hydrogen to the required pressure. The reaction occurred at a temperature of  $25^{\circ}$ C. The kinetic mode of the process was confirmed according to a technique described in details earlier [26].

The process was monitored by periodically sampling and analyzing the reaction mixture using a Crystal 5000 chromatograph (Chromatec, Russia) with a flame ionization detector. The components of the mixture were separated using a HP5–MS column (5% phenyl dimethylsiloxane, 30 m, 0.25 mm internal diameter, 0.25  $\mu$ m thick fixed film, and helium as the carrier gas).

Only hydroisomerization products such as *trans*-ST and hydrogenation products such as diphenylethane (DPE) have been found in the reaction mixture. The substrate conversion level was calculated using the following formula:

$$K = \frac{X_{\text{DPE}} + X_{trans-\text{ST}}}{X_{cis-\text{ST}} + X_{\text{DPE}} + X_{trans-\text{ST}}},$$

where  $X_{\text{DPE}}$ ,  $X_{trans-ST}$ , and  $X_{cis-ST}$  are the mole fractions of DPE, *trans-ST* and *cis-ST*, respectively, in the reaction mixture.

The specific rates of hydroisomerization ( $r_{h-isom}$ ) and hydrogenation ( $r_{hydr}$ ) (mmol min<sup>-1</sup> g<sup>-1</sup><sub>cat</sub>) were determined at the conversion level of *cis*-ST amounting to less than 15% using the following formula:

$$r = \frac{n}{\tau m_{\rm cat}}$$

where *n* is the amount of product (mmol) formed in time  $\tau$  (min) and  $m_{cat}$  is the mass of the catalyst (g). The conversion rate of the substrate was calculated using the following formula:

$$r_{\rm conv} = r_{\rm h-isom} + r_{\rm hydr}$$

The catalytic activity of metals in the hydrogenation and hydroisomerization reactions was evaluated basing on the turnover number (TOF, min<sup>-1</sup>), i.e., the ratio between the number of DPE or *trans*-ST molecules formed per minute and the total number of active metal atoms in the catalyst. The calculation was carried out according to the following formula:

$$TOF = \frac{rM_{Me}}{[Me] \times 1000}$$

where [Me] and  $M_{\rm Me}$  are the active metal content in the catalyst (wt %) and its molar weight (g/mol), respectively.

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The following solvents were used: *n*-hexane (98%, LiChrosolv), methanol (99.8%, LiChrosolv), toluene (99.9%, LiChrosolv, tetrahydrofuran ((THF), 99.9%, LiChrosolv), and dimethylformamide ((DMFA), 99%, Acros).

#### **RESULTS AND DISCUSSION**

# Electron Microscopy

The TEM images of the studied catalysts and the histograms of the size distribution for the metal particles are shown in Figs. 1 and 2. All the catalysts are characterized by a rather broad monomodal particle size distribution. In the 1% Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> sample, metal particles with the average size ( $D_{av}$ ) ~ 14 nm are formed. The particles of Pt in the 3% Pt/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst are much larger; their average size is ~ 26 nm. The size of metal nanoparticles in the catalysts based on Ru, Rh, and Ir is ~10, 5, and 4 nm, respectively. The significantly larger size of the supported metal particles in the 3% Pt/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> sample compared to the other catalysts could be caused by the fact that a complex salt containing NH<sub>3</sub> ligands was used for its preparation.

## Activity and Selectivity of Various Metals in the Hydroisomerization of cis-Stilbene

The experimental results presented in Table 1 allow us to compare the hydrogenating and hydroisomerizing activity of various metals based on the formation rates for DPE (hydrogenation) and *trans*-ST (hydroisomerization).

It is clearly seen from the comparison of the data that 1%Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> has the highest hydrogenation activity, whereas the hydrogenation rate for 3% Rh/ $\alpha$ -

Al<sub>2</sub>O<sub>3</sub> is slightly lower: 0.26 and 0.23 mmol min<sup>-1</sup>  $g_{cat}^{-1}$ , respectively. It should be taken into account that the Rh content in the sample is triple that of Pd; therefore, the TOF value for the Rh catalyst is lower by a factor of 3.5 than for Pd. A slightly lower hydrogenation activity is observed for the platinum catalyst with DPE formation rate ~0.18 mmol min<sup>-1</sup>.

The systems based on Ru and Ir are much less active than the Pd, Rh, and Pt ones. The rate of DPE formation on Ru and Ir is lower by 7–8 factors: 0.034

and 0.048 mmol min $^{-1}$   $g_{cat}^{-1}$  , respectively.

The obtained results make it possible to arrange the investigated metals in the following series according to their activity in the hydrogenation of *cis*-ST, which is in good agreement with the published data [27]:

From the standpoint of using the studied catalysts in the synthesis of *trans*-isomers, the most important parameters are their hydroisomerizing activity, as well as the ratio between the rates of hydroisomerization and



Fig. 1. TEM images of catalysts: (a) 1%Pd/α-Al<sub>2</sub>O<sub>3</sub>, (b) 3%Pt/α-Al<sub>2</sub>O<sub>3</sub>, (c) 3%Rh/α-Al<sub>2</sub>O<sub>3</sub>, (d) 3%Ru/α-Al<sub>2</sub>O<sub>3</sub>, (e) 3%Ir/α-Al<sub>2</sub>O<sub>3</sub>.



**Fig. 2.** Histograms of size distribution for metal particles in catalysts: (a) 1% Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, (b) 3% Pt/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, (c) 3% Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, (d) 3% Ru/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, (e) 3% Ir/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

hydrogenation. Since these two processes are competing, particular interest is provided to catalysts with the following characteristics: (1) the cis-stilbene conversion proceeds predominantly via the hydroisomerization route and (2) the ratio of the  $r_{h-isom}/r_{hydr}$  rates is maximal. The analysis of the data on the hydroisomerization rates presented in Table 1 shows that  $3\% \text{Ru}/\alpha$ -Al<sub>2</sub>O<sub>3</sub> is the most active catalyst with the rate of *trans*-isomer formation about 0.69 mmol min<sup>-1</sup> g<sup>-1</sup><sub>cat</sub>, which is triple the hydrogenation rate ( $r_{h-isom}/r_{hydr} = 3.0$ ). As a result,

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Catalyst	<i>r</i> <sub>conv</sub>	<i>r</i> <sub>hydr</sub>	<i>r</i> <sub>h-isom</sub>	r /r	TOF <sub>conv</sub>	TOF <sub>hydr</sub>	TOF <sub>h-isom</sub>
	m	$mol min^{-1} g_c^{-1}$	-1 at	h-isom/hydr	min <sup>-1</sup>		
$3\%$ Rh/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	0.92	0.23	0.69	3.0	3.14	0.78	2.36
$1\%$ Pd/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	0.27	0.26	0.011	0.04	2.83	2.71	0.12
$3\%$ Pt/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	0.22	0.18	0.035	0.19	1.42	1.19	0.23
$3\%$ Ru/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	0.11	0.034	0.072	2.1	0.36	0.11	0.24
$3\%$ Ir/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	0.051	0.048	0.003	0.06	0.33	0.31	0.02

 Table 1. Kinetic characteristics of cis-ST hydroisomerization on different metals\*

\* Substrate concentration, 0.33 mol/L; 2.5 bar H<sub>2</sub>; catalyst loading: 3%Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 2.5 mg; 3%Pt/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, 1%Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 15.0 mg; 3%Ru/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, 3%Ir/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, 30.0 mg, solvent *n*-hexane.

the overall conversion rate of *cis*-ST on this catalyst is significantly higher than for all the tested samples—0.92 mmol min<sup>-1</sup>  $g_{cat}^{-1}$ , including the Pd catalyst exhibiting the maximal hydrogenation activity (see below).

In addition to the Rh catalyst, a high ratio of  $r_{h-isom}/r_{hydr} = 2.1$  is observed for the reaction occurring on  $3\% \text{Ru}/\alpha$ -Al<sub>2</sub>O<sub>3</sub>; however, its activity in both hydrogenation and hydroisomerization processes is low and the overall conversion rate of *cis*-ST on this catalyst is almost an order of magnitude lower than that for

 $3\% Rh/\alpha\text{-}Al_2O_3\text{:}$  0.11 and 0.92 mmol min^{-1}  $g_{cat}^{-1},$  respectively.

The 1%Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst exhibits a low activity in hydroisomerization; the rate of *trans*-ST formation on the catalyst is ~0.011 mmol min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. Since this sample is most active in hydrogenation, the lowest ratio  $r_{h-isom}/r_{hydr}$  among the studied catalysts (0.04) is observed, which agrees with the published data concerning the high selectivity of Pd in the formation of *cis*-isomers in the course of the hydrogenation of alkyne compounds [9]. Somewhat higher ratios between the rates of hydroisomerization and hydrogenation are exhibited by the Pt and Ir catalysts (0.19 and 0.06, respectively); however, the values of  $r_{h-isom}/r_{hydr}$ inherent in them are substantially smaller than the values for the Rh and Ru samples.

Thus, the analysis of the activities of catalysts based on various metals in hydrogenation and hydroisomerization reactions shows that Rh and Ru exhibit the best characteristics for *trans*-isomers formation. Figure 3 shows a comparison of product compositions for the *cis*-ST's interaction with hydrogen on the studied samples when the initial substrate reaches a 35% conversion level. The maximum selectivity in the formation of *trans*-ST is exhibited by 3%Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and 3%Ru/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, for which the fraction of the *trans*isomer in the reaction products is ~75 and 68%, respectively. In the case of a catalyst containing Pt as the active component, the product of complete hydrogenation of DPE is predominant, and the amount of *trans*-isomer does not exceed 15%. The fraction of *trans*-ST in the reaction products obtained on 3%Ir/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is much lower, whereas the selectivity of *trans*-product formation on 1%Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is less than 5%.

The obtained data allow us to conclude that the most promising system is  $Rh/\alpha$ -Al<sub>2</sub>O<sub>3</sub>, since it has the best  $r_{h-isom}/r_{hydr}$  ratio and a high activity in hydroisomerization. Therefore, for this catalytic system a detailed study was made of the hydroisomerization efficiency as a function of the solvent nature, the hydrogen pressure, and the substrate concentration.

## Effect of the Solvent

Since the hydroisomerization reaction of complex organic molecules such as *cis*-ST needs to be carried out in the liquid phase, the nature of solvent is an important factor that can significantly affect the overall process rate and the ratio between the hydroisom-



**Fig. 3.** Composition of products of *cis*-ST hydroisomerization on different metals. Substrate concentration 0.33 mol/L, 2.5 bar H<sub>2</sub>, catalyst loading: 3%Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 2.5 mg; 3%Pt/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, 1%Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 15.0 mg; 3%Ru/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, 3%Ir/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 30.0 mg, solvent *n*-hexane. Substrate conversion level 35%.

Solvent	<i>r</i> <sub>conv</sub>	<i>r</i> <sub>hydr</sub>	r <sub>h-isom</sub>	10 / 10	TOF <sub>conv</sub>	TOF <sub>hydr</sub>	TOF <sub>h-isom</sub>
	mmol min <sup>-1</sup> $g_{cat}^{-1}$			h-isom/hydr	min <sup>-1</sup>		
<i>n</i> -Hexane	0.92	0.23	0.69	3.0	3.14	0.78	2.36
Toluene	0.55	0.14	0.42	3.0	1.89	0.47	1.43
THF	0.44	0.12	0.31	2.5	1.50	0.43	1.08
DMFA	0.31	0.15	0.16	1.1	1.05	0.51	0.54
MeOH	0.66	0.26	0.40	1.6	2.27	0.88	1.38

Table 2. Effect of solvent on kinetic characteristics of cis-ST hydroisomerization\*

\* Substrate concentration—0.33 mol/L, 2.5 mg %Rh/α-Al<sub>2</sub>O<sub>3</sub>, 2.5 bar H<sub>2</sub>.

erization and hydrogenation rates. In connection with this, we studied the effect of the solvent on the *cis*-ST hydroisomerization. Both polar and nonpolar solvents such as *n*-hexane, toluene, THF, DMFA, and methyl alcohol were used.

From the data presented in Table 2 we can see that the maximum rate of *cis*-ST conversion is achieved when the reaction is carried out in *n*-hexane— 0.92 mmol min<sup>-1</sup>  $g_{cat}^{-1}$ . In the case of toluene and methanol, the rate is somewhat lower amounting to 0.55 and 0.66 mmol min<sup>-1</sup>  $g_{cat}^{-1}$ , respectively. The lowest rate is observed for DMFA 0.31 mmol min<sup>-1</sup>  $g_{cat}^{-1}$ . The most probable cause consists in the different solubility of hydrogen in these solvents [28].

It should also be noted that the nature of the solvent has a significant effect on the ratio of  $r_{h-isom}/r_{hydr}$  and on the overall selectivity of the process. The analysis of the data presented in Table 2 shows that when the reaction proceeds in nonpolar solvents such as *n*-hexane and toluene, the  $r_{h-isom}/r_{hydr}$  ratio is maximal



Composition of products, %

Fig. 4. Effect of solvent on composition of *cis*-ST hydroisomerization products. Substrate concentration 0.33 mol/L, 2.5 mg of 3%Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, 2.5 bar H<sub>2</sub>, substrate conversion level 35%.

and the selectivity of *trans*-isomer formation reaches 75% (Fig. 4). As the polarity of the solvent increases, the selectivity decreases, and DMFA is the most unfavorable from this standpoint. In the case of DMFA, the  $r_{h-isom}/r_{hydr}$  ratio is 1.1, which leads to low selectivity in the formation of *trans*-isomer (Fig. 4). A somewhat higher selectivity is observed when the reaction is carried out in the less polar THF and methanol (71 and 62%, respectively).

The observed relationship between the selectivity of the process and the polarity of the solvent can be explain in the following way. A significant role can be played by the competitive adsorption of the solvent and substrate on the catalyst surface, which leads to a reduction in the surface concentration of the latter, and thus negatively affects the selectivity of *trans*-isomer formation (Fig. 4). This allows us to suggest that the displacement of the substrate's molecules from the catalyst surface by the solvent's molecules results in a decrease in the selectivity of the entire process due to the substantial decrease in the rate of the hydroisomerization reaction.

The effect of hydrogen pressure and substrate concentration on the kinetics and selectivity of hydroisomerization was investigated using *n*-hexane as the solvent in which a high selectivity and a high reaction rate were achieved.

# Effect of Hydrogen Pressure

The data concerning the effect of the hydrogen pressure in the range from 1 to 10 bar on the *cis*-ST hydro-conversion are presented in Table 3. It can be seen that as  $P_{\rm H_2}$  decreases the rate of the total conversion decreases from 1.28 to 0.75 mmol min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, which corresponds to the kinetic order of ~0.21 with respect to hydrogen. It should be noted that the effect of the hydrogen pressure on the rate of hydrogenation and hydroisomerization is significantly different: the rate of the hydrogenation decreases by a factor of ~3.5 from 0.44 to 0.13 mmol min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, while the rate of hydroisomerization decreases to a much lesser extent, by a factor of 1.3 (from 0.84 to 0.62 mmol min<sup>-1</sup>

$P_{\rm H_2}$ , bar	<i>r</i> <sub>conv</sub>	<i>r</i> <sub>hydr</sub>	r <sub>h-isom</sub>	$r_{\rm h-isom}/r_{\rm hydr}$	TOF <sub>conv</sub>	TOF <sub>hydr</sub>	TOF <sub>h-isom</sub>
	r	nmol min <sup>-1</sup> $g_{ca}^{-1}$	l it		min <sup>-1</sup>		
10.0	1.28	0.44	0.84	1.9	4.39	1.51	2.88
5.0	0.93	0.28	0.66	2.4	3.20	0.95	2.25
2.5	0.92	0.23	0.69	3.0	3.14	0.78	2.36
1.0	0.75	0.13	0.62	5.0	2.57	0.43	2.14

Table 3. Effect of hydrogen pressure on kinetic characteristics of *cis*-ST hydroisomerization\*

\* Substrate concentration—0.33 mol/L, 2.5 mg 3% Rh/α-Al<sub>2</sub>O<sub>3</sub>, solvent—*n*-hexane.

 $g_{cat}^{-1}$ ). The calculation of the orders of the hydrogenation and isomerization reactions (Fig. 5) has shown that the kinetic order of the hydrogenation with respect to H<sub>2</sub> is 0.52 and corresponds to the order observed for hydrogenation on palladium catalysts [26]. The dependence of the hydroisomerization rate on the hydrogen pressure is much less pronounced, and the order with respect to hydrogen pressure from 10 to 1 bar, leads to a significant increase in the selectivity of *trans*-isomer formation from 66 to 78% (Fig. 6).

The observed dependences are in good agreement with the existing concepts of the differences in the reactions of hydrogenation and hydroisomerization. The hydrogenation involves one C–C bond breaking with the simultaneous or sequential addition of two hydrogen atoms and the subsequent desorption of the formed alkane molecule. In contrast, the hydroisomerization proceeds through a double-bond semihydrogenation stage followed by a rotation around the C–C bond, after which 1–H–dehydrogenation and the desorption of the thermodynamically more stable *trans*-isomer take place. At the same time, the H atom remains on the surface of the catalyst, which makes the reaction significantly less sensitive to a change in the hydrogen pressure [24, 29, 30].

#### Effect of cis-Stilbene Concentration

The data concerning the effect exerted by the substrate concentration on the hydro-conversion of *cis*-ST are given in Table 4. A 10-fold increase in the concentration from 0.083 to 0.83 mol/L leads to a significant decrease in the total conversion rate of the substrate from 1.28 to 0.23 mmol min<sup>-1</sup>  $g_{cat}^{-1}$ . The character of the curves for the rates of the hydrogenation and hydroisomerization depending on the concentration of *cis*-ST is fundamentally different. Thus, the hydrogenation rate significantly decreases as the substrate concentration increases, and the order of the hydrogenation reaction with respect to the concentration of *cis*-ST in the range of 0.083–0.333 mol/L (Fig. 7) is -0.91. The negative order of alkene hydrogenation on Rh could most likely be related to the competitive





Fig. 5. Effect of hydrogen pressure on hydrogenation and hydroisomerization rates, and on rate of *cis*-ST conversion. Substrate concentration 0.33 mol/L, 2.5 mg 3% Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, solvent *n*-hexane.



**Fig. 6.** Effect of hydrogen pressure on composition of *cis*-ST hydroisomerization products. Substrate concentration 0.33 mol/L, 2.5 mg 3% Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, solvent *n*-hexane. Substrate conversion level 35%.

Concentration of <i>cis</i> -ST, mol/L	<i>r</i> <sub>conv</sub>	<i>r</i> <sub>hydr</sub>	r <sub>h-isom</sub>	10 / 10	TOF <sub>conv</sub>	TOF <sub>hydr</sub>	TOF <sub>h-isom</sub>
	n	1 mol min <sup>-1</sup> g <sub>c</sub> <sup>-1</sup>	1 at	/h-isom//hydr	min <sup>-1</sup>		
0.083	1.28	0.80	0.48	0.6	4.38	2.74	1.64
0.17	1.08	0.51	0.57	1.1	3.70	1.75	1.95
0.33	0.92	0.23	0.69	3.0	3.14	0.78	2.36
0.83	0.23	0.013	0.22	17.3	0.80	0.04	0.75

Table 4. Effect of substrate concentration on kinetic characteristics of cis-ST hydroisomerization\*

\* 2.5 mg 3% Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, 2.5 bar H<sub>2</sub>, solvent—*n*-hexane.



**Fig. 7.** Effect of substrate concentration on rates of hydrogenation and hydroisomerization, as well as on conversion rate of *cis*-ST. 2.5 mg 3%Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, 2.5 bar H<sub>2</sub>, solvent—*n*-hexane.



Fig. 8. Effect of substrate concentration on composition of *cis*-ST hydroisomerization products: 2.5 mg of 3% Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, solvent—*n*-hexane. Substrate conversion level 35%.

adsorption of olefin and hydrogen on the metal surface. As the olefin concentration increases, the amount of adsorbed hydrogen decreases, and the rate of the hydrogenation reaction slows to a significant extent [27] (Fig. 8).

At the same time, the hydroisomerization rate increases slightly with an increase in the substrate concentration from 0.083 to 0.333 mol/L, which corresponds to the observed order of the hydroisomerization rate with respect to the substrate of about ~0.21. It can be assumed that the hydroisomerization is less sensitive to the amount of adsorbed hydrogen, since, in contrast to the hydrogenation, this process requires only one H atom, which, in addition, is not consumed in the reaction and remains on the metal surface after the desorption of the *trans*-ST molecule.

When the concentration of *cis*-ST is increased from 0.33 to 0.83 mol/L, the rates of both reactions decrease to a considerable extent, and the linear dependence of the rate on the substrate concentration in logarithmic coordinates is violated for both the hydrogenation and the hydroisomerization (Fig. 7). This is associated with exceeding the solubility limit of the formed *trans*-ST in *n*-hexane used as a solvent.

#### **CONCLUSIONS**

Thus, the results of the study allow us to conclude that catalysts based on Rh and Ru are most promising for the formation of *trans*-isomers of complex organic molecules through the hydroisomerization of the corresponding *cis*-isomers or the selective hydrogenation of the disubstituted alkynes. The selectivity of their action can be significantly increased by carrying out the process in nonpolar solvents. A higher selectivity in the formation of *trans*-isomers is also facilitated by an increase in the concentration of the initial substrate, as well as by carrying out the process under a reduced hydrogen pressure.

## ACKNOWLEDGMENTS

The work was financially supported by the Russian Science Foundation (grant 16-13-10530). The authors are grateful to the Department of Structural Research of the Zelinsky Institute of Organic Chemis-

try, Russian Academy of Sciences for studying the samples using electron microscopy.

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Translated by O. Polyakov