SPECTROSCOPIC STUDY OF THE REDISTRIBUTION OF HYDROGEN IN 1,3-CYCLOHEXADIENE ON PALLADIUM FILMS

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Abstract

Full Text

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V. M. GRYAZNOV and V. D. YAGODOVSKII

SPECTROSCOPIC STUDY OF THE REDISTRIBUTION OF HYDROGEN IN 1,3-CYCLOHEXADIENE ON PALLADIUM FILMS

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The transformation of 1,3-cyclohexadiene in the presence of palladium and platinum catalysts was discovered and investigated by N. D. Zelinskii and G. S. Pavlov ([1,2]). They established that the process proceeds in two stages: $2C_6H_8 = C_6H_6 + C_6H_{10}$; $3C_6H_{10} = C_6H_6 + 2C_6H_{12}$, the rate of the first reaction being much greater than that of the second. An analogous transformation is undergone by 1,4-cyclohexadiene.

J. Bell and S. Thomson ([3]) studied the deuteration of cyclohexadienes and cyclohexene on platinum black, as well as the accompanying redistribution of hydrogen. The authors note that the results of their experiments do not agree with the above-indicated mechanism of the transformation of 1,3-cyclohexadiene.

Fig. 1. Diagram of the vacuum apparatus for studying catalytic transformations on palladium films

In this connection it seemed of interest to study the redistribution of hydrogen in 1,3-cyclohexadiene under such conditions that this process would not be complicated by anything else.

In the present work the catalysts were palladium films obtained on glass by sublimation of the metal in vacuum. The method of obtaining the films differed from that used by D. P. Dobychin and A. V. Frost ([4]) only in that the sublimation was carried out directly from a palladium wire heated by an electric current, without a tungsten heater. This made it possible to avoid possible contamination of the film with tungsten and not to introduce an extraneous metal into the reactor.

The first series of experiments was carried out in the apparatus shown in Fig.

1. A wire (1) of spectroscopically pure palladium, 0.33 mm in diameter,

was fastened on molybdenum leads, and the reactor (2), together with the ampoules (5—7), was connected to the apparatus through a ground joint. The reactor was evacuated for one and a half hours while being heated to 350°, in order to remove gases and moisture adsorbed on the walls. The palladium wire was heated several times by an electric current to a temperature of about 700°, until a subsequent heating no longer led to an increase in the residual pressure, which was $6 \cdot 10^{-6}$ mm Hg. At the beginning of palladium sublimation the pressure rose to $1 \cdot 10^{-5}$ mm. After several minutes the pressure of $6 \cdot 10^{-6}$ mm Hg was restored, at which the film condensation took place, lasting on average 40 min. The reactor was cooled with liquid nitrogen. A light gray deposit appeared on the walls of the reactor; it became increasingly dark, and then the layer acquired a metallic luster. The thickness of the film, calculated on the assumption that the density of the film is equal to the density of massive palladium, was close to 1000 Å for a mirror layer. The geometrical surface of the film was 80 cm^2. The reactor was heated in a water thermostat to the experimental temperature, and, with stopcock (4) closed, a thin-walled bulb in ampoule (5) was broken by means of a magnetic striker.

Table 1

Mixture No.	Mixture composition (mol. %)	Mixture composition (mol. %)	Mixture composition (mol. %)	$\lg(I/I_0)$	$\lg(I/I_0)$	$\lg(I/I_0)$
	C_6H_8	C_6H_6	C_6H_{10}	for 745 cm^{-1} (C_6H_8)	for 1484 cm^{-1} (C_6H_6)	for 715 cm^{-1} (C_6H_{10})
1	81.0	9.3	9.7	0.364	0.210	0.060
2	61.3	19.3	19.4	0.324	0.331	0.068
3	39.9	29.8	30.3	0.242	0.422	0.088
4	18.2	40.5	41.3	0.124	0.488	0.094

Previously, into ampoules (5—7), on another vacuum apparatus, 1,3-cyclohexadiene had been distilled.*

The trap (3) and ampoule (5) were cooled alternately with liquid nitrogen so that the cyclohexadiene vapors passed through the reactor with the palladium film. At the end of the experiment the ampoule was unsoldered, and the catalyzate was transferred into a potassium chloride cell for recording the infrared absorption spectrum.

Using a two-beam IKS-2 infrared spectrometer, the absorption spectra of 1,3-cyclohexadiene, benzene, and cyclohexene were obtained. The frequencies of the absorption bands of benzene and cyclohexene agree with literature data ([6,7]). No information on the infrared absorption spectrum of 1,3-cyclohexadiene was found in the literature. The absorption spectrum obtained by us for liquid 1,3-cyclohexadiene at room temperature and a layer thickness of 0.02 mm is shown in Fig. 2. The spectral slit width of the spectrometer is indicated on the frequency scale along the abscissa axis.

For the quantitative analysis of the transformation products of 1,3-cyclohexadiene, absorption spectra were recorded for ternary mixtures of 1,3-cyclohexadiene, benzene, and cyclohexene, the compositions of which are given in Table 1.

In the absorption spectra of the mixtures, bands were selected for 1,3-cyclohexadiene (745 cm^{-1}), benzene (1484 cm^{-1}), and cyclohexene (715 cm^{-1}), which overlap to the least extent with other bands. For these bands the values of the optical density $\lg(I_0/I)$ were calculated, where I and I_0 are the intensities of the radiation passed through the cell with the mixture and through the empty cell, respectively. As can be seen from Table 1, for each of the three hydrocarbons the values of $\lg(I_0/I)$ increase linearly with increasing concentration from 9 to 60%. This facilitated the analysis of the catalyzates.

On a freshly prepared palladium film with a visible surface of 80 cm^2 and a thickness of about 800 Å, three experiments were carried out consecutively with equal amounts of 1,3-cyclohexadiene (0.4 ml) at 50.4; 73.5 and again at 50.4°. The duration of each experiment was 4 hours. The composition of the catalysts is presented in Table 2. When the temperature was raised from 50.4 to 73.5°, the degree of conversion of cyclohexadiene increased from 39 to 91%. The third experiment, carried out under the same conditions as the first, revealed a decrease in the catalytic activity of the palladium film. However, the molar ratio of benzene to cyclohexene in the catalysts remained equal to 1, which is in complete agreement with the mechanism established by N. D. Zelinsky and G. S. Pavlov (2) for the first, rapidly occurring stage of the conversion of 1,3-cyclohexadiene.

The following series of experiments were carried out in an all-glass apparatus, in order to eliminate the possible influence of stopcock grease on the catalytic activity of the palladium film.

Fig. 2. Infrared absorption spectrum of liquid 1,3-cyclohexadiene (layer thickness 0.02 mm)

of the palladium film. The reactor of the all-glass apparatus had an internal surface three times larger (250 cm^2) than that shown in Fig. 1. The residual pressure in the system before sublimation of the film was $2 \cdot 10^{-7}$ mm. During

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* The preparation of 1,3-cyclohexadiene, synthesized by the method of Hofmann and Damm (5), was kindly provided by Prof. R. Ya. Levina, to whom the authors express their deep gratitude. Constants of 1,3-cyclohexadiene: b.p. 78.5°/740 mm; $n_D^{20} = 1.4740$.

Fig. 2. Infrared absorption spectrum of liquid 1,3-cyclohexadiene (layer thickness 0.02 mm)

Figure 2: Fig. 2. Infrared absorption spectrum of liquid 1,3-cyclohexadiene (layer thickness 0.02 mm)

the first 3 min of sublimation the pressure increased to $8 \cdot 10^{-6}$ mm, but the main quantity of palladium evaporated at $1 \cdot 10^{-6}$ mm Hg. The walls of the reactor were cooled not with liquid nitrogen, but only to 0°, in order to reduce sorption by the film of residual gases. Sublimation was carried out until an opaque mirror layer of palladium formed on the reactor walls. Upon completion of sublimation the pressure was $4 \cdot 10^{-7}$ mm. At this pressure the reactor with the ampoules was sealed off from the apparatus and placed in a water thermostat. In order to stabilize the film, it was kept for 1 hour at 80°, and the experiments were then conducted at temperatures from 30 to 70°. The ampoule with cyclohexadiene was thermostated at a higher temperature, and after the bulb of the ampoule was broken the hydrocarbon vapors entered the reactor. The catalyst was frozen out with liquid nitrogen in an ampoule and analyzed as described above.

It was found that, if the contact time was 2.5 hours, then at 30° the conversion of cyclohexadiene was insignificant, at 50° it was close to 40 mol. %, and at 70° it proceeded completely. Already at 50° the cyclohexene formed was partially converted into cyclohexane and benzene. Repetition of the experiment at 50° showed that a palladium film obtained in the all-glass apparatus at a vacuum of 10^{-6} mm Hg likewise gradually loses catalytic activity, as does one obtained in the apparatus with a stopcock.

In other experiments the palladium film was heated to 80° during evacuation, the rate of sublimation and the temperature of the reactor walls were varied, but in all cases the activity of the film gradually decreased. This agrees with the data of D. P. Dobychin and A. V. Frost (4, 8), obtained in studying the hydrogenation of ethylene, butylene, and acetylene on palladium films, and also

with other data available in the literature (see, for example, the review by J. Allen [9]) on the gradual recrystallization of sublimed metal films, which is accompanied by a decrease in their surface area and an increase in electrical conductivity.

As indicated above, the use of palladium films with a geometrical surface area of 250 cm^2 makes it possible also to follow the redistribution of hydrogen in cyclohexene formed from 1,3-cyclohexadiene. Consequently, the nature of the course of this process on a palladium film and on catalysts of the palladium-black type is qualitatively the same. N. D. Zelinskii [10] investigated whether saturation of palladium with oxygen or hydrogen is necessary for the conversion of cyclohexadiene. Palladized asbestos was heated in a stream of hydrogen at 150° to remove oxygen and, after the hydrogen had been displaced from the reactor by carbon dioxide, was heated to 300°. Removal of hydrogen in this way did not deactivate the catalyst.

Table 2

Annealing temperature, °C	Catalyst composition (mol. %)	Catalyst composition (mol. %)	Catalyst composition (mol. %)
	C_6H_8	C_6H_6	C_6H_{10}
50.4	61	20	19
73.5	9	45	46
50.4	81	10	9

In our experiments, carried out in the apparatus shown in Fig. 1, palladium was sublimed from a wire weighing 0.07-0.08 g. The weight of the film obtained was an order of magnitude smaller. The palladium wire was freed from the gases contained in it at a temperature of about 700° and a pressure in the system of $6 \cdot 10^{-6}$ mm. Even if it is assumed that all the residual gas was hydrogen, no more than $3 \cdot 10^{-10}$ mole of hydrogen could have been dissolved in the palladium wire. This result is readily obtained from J. Lecher's formula [11] for the solubility of hydrogen in palladium at temperatures above 600°:

$$\lg s = 0.241 + 0.5 \lg P_{\text{mm}} + \frac{251.4}{T},$$

where s is the volume of absorbed hydrogen (under normal conditions) per 100 g of palladium, and P_{mm} is the hydrogen pressure. From the same formula we find that during sublimation, when the film was heated to approximately 1000°, $4 \cdot 10^{-11}$ mole of hydrogen could have been liberated from it. If we assume that this entire amount of hydrogen is absorbed by the palladium film being formed, we obtain the limiting hydrogen content in the film. In each experiment about $4 \cdot 10^{-3}$ mole of cyclohexadiene was passed over the film, which exceeds by 8 orders of magnitude the possible hydrogen content in the film before the introduction of cyclohexadiene; nevertheless, the palladium films possessed catalytic activity.

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