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Abstract

Full Text

PHYSICAL CHEMISTRY

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SPECTROSCOPIC STUDY OF ADSORPTION AND CATALYTIC TRANSFORMATION OF CYCLOHEXADIENE ON TRANSPARENT PALLADIUM FILMS

(Presented by Academician A. A. Balandin, 24 IV 1958)

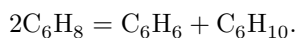
The study of the spectra of substances in adsorbed layers is of great interest for elucidating the state of molecules in the force field of the surface of an adsorbent or catalyst. Most investigations in this field have been carried out on sufficiently transparent adsorbents and aluminosilicate catalysts. In recent years, the experimental difficulties that hindered the obtaining of spectra of substances adsorbed on metals have been overcome. Eischens, Pliskin, and Francis⁽¹⁾ studied the spectra of carbon monoxide chemisorbed on copper, platinum, palladium, and nickel. Pliskin and Eischens⁽²⁾ obtained the infrared spectra of ethylene, propylene, and acetylene chemisorbed on nickel. In these works the metals were prepared by heating, in a stream of hydrogen, a paste made from porous silica spheres and a solution of a metal salt. A thin layer of the paste was applied by hand to a fluorite plate. The authors note⁽³⁾ the difficulty of preparing a specimen that transmits about 6% of infrared radiation with a wavelength of 5μ and at the same time has a sufficiently large surface to permit measurement of the absorption bands of chemisorbed substances. Certain complications are also connected with the presence of hydrogen on the surface of the reduced metal.

It seemed desirable to develop a procedure for the spectroscopic study of adsorption and catalytic transformations on metal layers of specified optical density and, as far as possible, free from extraneous gases and vapors. We used distillation of the metal in vacuum onto the windows of an optical cell. In the ultraviolet region of the spectrum, an all-fused quartz cell 16 mm long was used. The conditions for preparing mirror palladium films about 1000 Å thick and the results of a study of the hydrogen redistribution reaction in cyclohexadiene-1,3 occurring on them have been published previously⁽⁴⁾. In the present work, palladium films of the order of 100 Å thick were deposited on the cell windows at a residual pressure of $1 \cdot 10^{-6}$ mm Hg; these films transmitted 30% of radiation with a wavelength of 2600 Å that had passed through the cell before

Figure 1

Figure 1: Figure 1

metal distillation. Even at room temperature these films possessed considerable catalytic activity. The absorption spectrum of cyclohexadiene-1,3 vapors*, admitted into the cell, changed within only a few minutes to the characteristic absorption bands of benzene vapors, which indicated practically complete completion of the reaction



Palladium films of thickness had lower catalytic activity

* Cyclohexadiene-1,3, 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. Hydrocarbon constants: b.p. 78.5°/740 mm; $n_D^{20} = 1.4740$.

of the order of 100 Å on the fluorite windows of the cell, which was used for work in the infrared region. The fluorite windows were glued with a special picein to flat polished flanges of a cylindrical glass cell 25 mm long. Before palladium films were deposited on the cell windows, absorption spectra of cyclohexadiene vapor at various pressures were obtained in it. The spectra were recorded on an IKS-2 double-beam spectrometer with a lithium fluoride prism. The spectral width of the slits is indicated on the frequency scale along the abscissa in Fig. 1a. Curve 1 in Fig. 1a

Fig. 1. Absorption spectra of cyclohexadiene obtained in a cell with fluorite windows. **a** –before palladium films were deposited on the windows; **b** and **c** –with palladium films transmitting, respectively, 25 and 70% of radiation with frequency 2000 cm⁻¹.

corresponds to the transmittance of the cell at a residual pressure of $1 \cdot 10^{-4}$ mm Hg; curves 2 and 3 are spectra of cyclohexadiene vapor at pressures of, respectively, 15 and 75 mm Hg. The cyclohexadiene absorption bands at 2945 and 3050 cm⁻¹ do not change their character when the pressure is decreased, while the bands at 2830 and 2880 cm⁻¹, at 15 mm Hg and for the given layer thickness, are no longer resolved. After the cell was evacuated at room temperature to $1 \cdot 10^{-3}$ mm Hg, the transmittance curve coincided with the initial curve 1.

Palladium films were then deposited on both windows of the cell; these reduced the transmittance at 2000 cm⁻¹ to 25% of the initial value, and, after diaphragming the comparison beam, the spectra shown in Fig. 1b were recorded. Curve 1 shows that the palladium films have no absorption bands in this spectral region. The spectrum of cyclohexadiene vapor at 75 mm Hg, which had been in

Figure 2

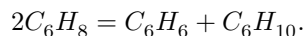
Figure 2: Figure 2

the cell with palladium films for 10 hours at 20° (curve 4), differs from the analogous spectrum obtained before the palladium films were deposited on the cell windows (cf. curve 3 in Fig. 1a). Instead of the narrow 3050 cm^{-1} band, which was well resolved even with a fivefold decrease in the pressure of cyclohexadiene vapor, a $3050\text{--}3090\text{ cm}^{-1}$ band appeared. This is precisely the result that should be expected in the case of partial conversion of cyclohexadiene into benzene and cyclohexene on the palladium films. Of these hydrocarbons, only benzene has intense absorption bands with frequencies above 3050 cm^{-1} . Brodersen and Langseth⁽⁶⁾ showed that the most intense absorption bands of benzene vapor have frequencies of 3047, 3083, and 3100 cm^{-1} . Consistent with these data is the spectrum of benzene vapor shown by dashed curve 3 in Fig. 1b, which was obtained in the same cell at a pressure of 75 mm Hg after evacuation of cyclohexadiene vapor. The 3083 and 3100 cm^{-1} bands when used

the layer lengths and spectral slit widths used by us are not resolved, as was also the case in the work of Bailey, Hale, Ingold, and Thompson⁽⁷⁾, but form a “shoulder” on the more intense band at 3047 cm^{-1} . Therefore, broadening of the cyclohexadiene spectral band at 3050 cm^{-1} to 3090 cm^{-1} , or the appearance of a “shoulder” on it on the high-frequency side, indicates the presence of benzene vapors. As can be seen from curve 2 in Fig. 1b, this is also observed when the initial vapor pressure of cyclohexadiene is reduced to 15 mm Hg. At lower pressures, absorption bands of cyclohexadiene vapors are not detected, which indicates the absence of strong adsorption of cyclohexadiene on palladium films about 100 \AA thick, as well as on fluorite windows.

Fig. 2. Absorption spectra of cyclohexadiene obtained in a cell with rock-salt windows coated with palladium films. Explanations are given in the text.

A qualitatively different result was obtained on still less dense palladium films deposited on the same fluorite windows after they had been polished. The new films transmitted 70% of infrared radiation with a frequency of 2000 cm^{-1} passing through the fluorite windows. In Fig. 1b, curve 3 represents the spectrum of cyclohexadiene vapors, whose initial pressure was 75 mm Hg, after remaining for 2 h 40 min at room temperature in a cell with very thin palladium films on the windows. After another half hour a spectrum was obtained which exactly coincided with curve 3, except for the regions shown by dotted lines. In this case the 3050 cm^{-1} band has a “shoulder” on the high-frequency side. Absorption in precisely this region increases with increasing time of contact of cyclohexadiene vapors with the palladium films, while the intensities of the cyclohexadiene absorption bands decrease somewhat. Consequently, extremely thin palladium films on fluorite also possess catalytic activity with respect to the reaction



In contrast to experiments with denser palladium films and in the absence of palladium films on the fluorite windows, evacuation of the same cell with thin films to a residual cyclohexadiene vapor pressure of 10^{-3} mm Hg did not lead to the disappearance of all absorption bands. Increasing the duration of evacuation at room temperature to 30 min did not change the character of the spectrum shown by curve 2 in Fig. 1b. This spectrum cannot belong to cyclohexadiene vapors, since at the given layer length they do not give absorption bands even at a pressure a thousand times greater. The coincidence of the frequency of the 2945 cm^{-1} band with the frequency in the spectrum of cyclohexadiene vapors permits one to assume that the spectrum obtained is that of cyclohexadiene strongly adsorbed on a very thin palladium film.

palladium. The indicated band disappears only when the spectrum is recorded during evacuation, when the pressure in the cell does not exceed $1 \cdot 10^{-4}$ mm Hg (curve 3 in Fig. 1b).

It is noteworthy that in the spectrum of strongly adsorbed cyclohexadiene there is no band at 3050 cm^{-1} . As is known (see, for example, ⁸), in the region $3000\text{--}3150\text{ cm}^{-1}$ lie the stretching bands of C—H bonds when the given carbon atom has unsaturated or aromatic bonds. Consequently, in the spectrum of cyclohexadiene strongly adsorbed on palladium, vibrations of the bonds of



do not appear.

An analogous result was obtained with very thin palladium films on rock-salt windows, which transmitted about 80% of the radiation with frequency 2000 cm^{-1} passing through windows without films. In this case the 3050 cm^{-1} band was likewise not detected, and at a cyclohexadiene vapor pressure of $1 \cdot 10^{-4}$ mm Hg the spectrum represented by curve 1 in Fig. 2 was obtained. The character of this spectrum did not change after evacuation for 8 hours while heating the cell to 50° , nor after admission and evacuation of benzene vapor. These experiments were carried out with a glass cell 145 mm long, to the flat flanges of which rock-salt windows were attached with vacuum grease. At a residual pressure of 10^{-4} mm, 10 recordings of the spectrum were made, which showed its reproducibility. Since a similar spectrum could not be obtained on windows without a palladium film, it may be assumed that the spectrum belongs to cyclohexadiene strongly adsorbed on the palladium film.

Comparison of the spectrum of strongly adsorbed cyclohexadiene with the vapor spectra at pressures of 12, 30, and 50 mm, which are represented in Fig. 2 by curves 2, 3, and 4, shows that a number of bands in both spectra are close in

frequency. At the same time, the spectrum of adsorbed cyclohexadiene has no bands at 750 and 925 cm^{-1} , which are intense in the vapor spectrum and probably belong to out-of-plane deformation vibrations of C–H bonds. The band at 1608 cm^{-1} , characteristic of stretching vibrations of C=C bonds, is expressed more weakly than in the vapor at comparable absorption at other frequencies. It may be supposed that the indicated differences between the spectra of cyclohexadiene adsorbed on palladium and the vapor spectrum are due to the formation of carbon–palladium bonds as a result of rupture or weakening of both π -bonds of the cyclohexadiene molecule upon strong adsorption on palladium.

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