INFRARED SPECTRA OF CARBON MONOXIDE ADSORBED ON RUTHENIUM, RHODIUM, AND PALLADIUM OVER A WIDE TEMPERATURE RANGE

1965

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

N. N. KAVTARADZE, N. P. SOKOLOVA

INFRARED SPECTRA OF CARBON MONOXIDE ADSORBED ON RUTHENIUM, RHODIUM, AND PALLADIUM OVER A WIDE TEMPERATURE RANGE

(Presented by Academician V. I. Spitsyn, November 20, 1964)

The study of the nature and structure of adsorption complexes of gases, in particular CO, on metals, as well as of the mechanism of their formation and transformation, previously led [1] to the supposition that, in addition to the sharply expressed periodic dependence of the chemisorption properties of metals with respect to hydrogen, carbon monoxide, nitrogen, and olefins [1,2], a dependence may also be observed of the structure and properties of the surface compounds themselves on the nature of the metal [1]. Using infrared spectroscopy methods [3], it proved possible to verify one of the conclusions and to establish that on copper, silver, and gold, strongly chemisorbed CO is present in the form of a single linear structure [4,5]. In the present work, using the example of CO adsorption on Ru, Rh, and Pd, results are presented from testing the supposition that on all metals of group 8 strongly chemisorbed CO forms surface compounds of bridge and linear structure.

The spectra of CO adsorbed on Ru, Rh, and Pd were studied in the temperature range from -150 to 120° and at pressures $\ll 10^{-5}$ and 1.3 mm Hg. The metal samples for obtaining infrared spectra were prepared by the method described earlier [3]. Their transmittance was 8-12% for Ru, 20% for Rh, and 20% for Pd. The spectra were recorded on an IKS-12 infrared spectrometer with a NaCl prism in the frequency interval 1700-2200 cm^{-1} by the method proposed by Z. A. Markova [6]. The spectral slit width for Ru, Rh, and Pd was, respectively, 26, 24, and 21 cm^{-1}. The results of studying the spectra of carbon monoxide adsorbed on these metals are presented in Figs. 1-3 and in Tables 1 and 2. They show that in the spectrum of CO adsorbed on Ru, at all temperatures from -150 to 120° and pressures of 1.3 and 10^{-5} mm Hg, one strong absorption band is observed in the region of 2020 cm^{-1} and three weak bands at 2160, 1850, and 1780 cm^{-1}.

Table 1

Positions of absorption bands in the spectra of CO adsorbed on Ru, Rh, and Pd.

Figure 1

Figure 1: Figure 1

P—pressure in mm Hg

T, °C	Ruthenium P	Ruthenium ν_L	Ruthenium ν_{M1}	Ruthenium ν_{M2}	Rhodium ν_L	Rhodium ν_M	Palladium ν_L	Palladium ν_M
−150	1.3	2020 s	1850 w	1780 w	2080 s	1880 m	2050 m	1910 s
−150	10^{-5}	2020 s	1850 w	1780 w	2080 s	1850 m	2080 m	1860 s
−60	1.3	2020 s	1850	1780 w	2060 s	1880 m	2080 m	1910 s
−60	10^{-5}	2020 s	1850 very w	1780 w	2040 s	1850 m	2080 m	1860 s
50	1.3	2020 s	1850 very w	1780 w	2060 s	1870 m	2080 m	1900 s
50	10^{-5}	2020 s	1850 very w	1780 w	2030 s	1860 m	2060 m	1860 s
120	1.3	2020 s	1850 very w	1780 w	2030 s	1870 m	2080 m	1900 s
120	10^{-5}	2020 s	1850 very w	1780 w	2030 s	1860 m	2050 m	1860 s

Note. T—temperature, L—linear form, M—bridge form, s—strong, m—medium, w—weak, very w—very weak.

The intensity of all bands during evacuation of the gas to 10^{-5} mm Hg over 30-50 min decreases somewhat; however, the positions of their maxima do not shift appreciably. In the spectra of CO adsorbed on Rh and Pd under the same conditions, two absorption bands are observed—respectively at 2080, 1880 and 2050, 1910 cm^{-1}—the positions of which, upon increasing the temperature and changing the pressure, shift only slightly: a small

Fig. 1. Spectrum of carbon monoxide adsorbed on one and the same ruthenium sample: *a*—at a temperature of −150°, —at a temperature of −50°, —at 50°, —at 120°; 1—at a pressure of 1.3 mm Hg, 2—at 10^{-5} mm Hg.

Fig. 2. Spectrum of carbon monoxide adsorbed on one and the same rhodium sample; designations as in Fig. 1.

Figure 2

Figure 2: Figure 2

shift is observed for rhodium for the band at 2080 cm^{-1}. With an increase in temperature from −150 to 120°, it shifts successively to 2030 cm^{-1}. The position of this absorption band for rhodium agrees well with the data of Pickering and Eckstrom (^{7}), who at room temperature observed a band at 2060 cm^{-1}, shifting upon evacuation to 10^{-4} mm Hg to 2035 cm^{-1}, and also with the data of Yang and Garland (^{8}), according to whose spectra the absorption band characteristic of the linear structure lies in the region 2040-2062 cm^{-1}. A small discrepancy is observed for the band usually assigned to the bridged structure. In the case of Pd, the position of the absorption band for the linear structure coincides with results previously obtained in the laboratory (^{9}).

The absorption bands assigned to the linear and bridged structures, as is evident from the data in Table 1, shift toward the short-wavelength region of the spectrum on going from Ru to Rh and Pd. This indicates an increase in the strength of the C=O bond and a decrease in the strength of the Me—C bond in the series Ru—Rh—Pd. The intensities of each of the bands (Figs. 1-3), with a decrease in pressure from 1.3 to $\leq 10^{-5}$ mm Hg at each temperature, as a rule decrease, which indicates a decrease in the coverage of the metal surface by adsorbed CO complexes having linear and bridged structures.

It also follows from the data of Table 2 that at all $T°$ and P values in the series Ru—Rh—Pd the ratio D_l/D_m decreases, i.e., the concentration of adsorption-

Table 2

Optical densities of various forms of surface compounds of carbon monoxide

Metal	Metal	Ru	Ru	Ru	Ru	Ru	Rh	Rh	Rh	Pd	Pd	Pd
$T°$, C	P, mm Hg	D_l	D_{m2}	D_{m2}	$\frac{D_l}{D_{m2}}$	$\frac{D_l}{D_{m2}}$	D_l	D_m	$\frac{D_l}{D_m}$	D_l	D_m	$\frac{D_l}{D_m}$
−150	1.3	1.61	0.20	0.22	8.05	7.32	1.12	0.60	1.87	0.67	1.20	0.56
−150	10^{-5}	0.71	0.16	0.20	4.38	3.55	0.80	0.40	2.00	0.05	0.60	0.10
−60	1.3	1.17	0.22	0.25	5.32	4.68	1.43	0.84	1.70	0.51	1.11	0.46
−60	10^{-5}	0.83	0.19	0.25	4.37	3.32	1.05	0.58	1.81	0.07	0.78	0.10
50	1.3	1.05	0.21	0.27	5.00	3.89	1.52	0.96	1.59	0.36	1.17	0.31
50	10^{-5}	0.78	0.20	0.26	3.90	3.00	1.24	0.74	1.68	0.15	0.78	0.19
120	1.3	1.17	0.25	0.27	4.68	4.33	1.43	0.90	1.59	0.24	1.02	0.23
120	10^{-5}	1.14	0.26	0.33	4.38	3.45	1.27	0.80	1.59	0.12	0.90	0.13

Note. D_l is the optical density of the linear structure, D_m of the bridged

Fig. 3

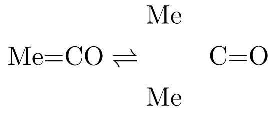
Figure 3: Fig. 3

structure, D_l/D_m is the ratio of the linear to the bridged structure.

···of CO complexes of linear structure, predominating on Ru, steadily decreases, while that of the bridged structure increases and becomes predominant on Pd.

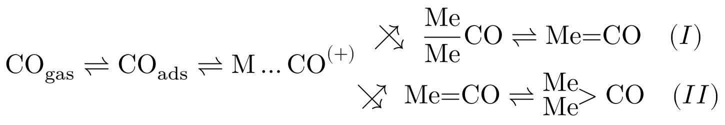
Fig. 3. Spectrum of carbon monoxide adsorbed on one and the same palladium sample; designations as in Fig. 1

From the fact that, with increasing temperature at $P = 1.3$ mm Hg, D_l/D_m decreases, i.e., the concentration of the linear structure decreases in comparison with the bridged one, it may be assumed that the equilibrium



$$\mathrm{Me{=}CO} \rightleftharpoons \begin{array}{c}\mathrm{Me}\\ \qquad\quad \mathrm{C{=}O}\\ \mathrm{Me}\end{array}$$

is shifted toward the bridged structure. Let us note that this is analogous to the behavior of bulk carbonyls; upon heating they split off CO and are converted into di- and trinuclear carbonyl compounds, which have a bridged structure. If these considerations are correct, then in the chain of possible successive stages of the mechanism of chemisorption of CO on metals



$$\mathrm{CO_{gas}} \rightleftharpoons \mathrm{CO_{ads}} \rightleftharpoons \mathrm{M\ldots CO^{(+)}} \begin{array}{l} \nearrow\!\!\!\swarrow\ \frac{\mathrm{Me}}{\mathrm{Me}}\mathrm{CO} \rightleftharpoons \mathrm{Me{=}CO} \quad (I) \\ \searrow\!\!\!\nwarrow\ \mathrm{Me{=}CO} \rightleftharpoons {}^{\mathrm{Me}}_{\mathrm{Me}}\!>\mathrm{CO} \quad (II) \end{array}$$

the first path appears the most probable.

Thus, the results of the study using the example of Ru—Rh—Pd, confirming the assumption of the existence of surface CO compounds of linear and bridged structures on metals of Group 8 of the periodic system, reveal new regularities: the influence of temperature and

pressure on the concentration of adsorption complexes of different structures, the regular change in their ratio, and also the strengths of the Me—C and C=O bonds in the series Ru—Rh—Pd, i.e., the dependence on the nature of the metals, on the electronic structure of their valence orbitals.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
16 XI 1964

CITED LITERATURE

1. N. N. Kavtaradze, ZhFKh, **36**, 628 (1962).
2. N. N. Kavtaradze, ZhFKh, **32**, 1214 (1958).
3. N. N. Kavtaradze, V. M. Luk' yanovich et al., *Kinetics and Catalysis*, **5**, 1095 (1964).
4. N. N. Kavtaradze, N. P. Sokolova, DAN, **146**, 1367 (1962).
5. N. N. Kavtaradze, N. P. Sokolova, ZhFKh, **36**, 2804 (1962).
6. Z. A. Markova, Dissertation, Moscow, 1962.
7. H. L. Pickering, H. Eckstrom, *J. Phys. Chem.*, **63**, 512 (1959).
8. A. C. Jang, C. W. Garland, *J. Phys. Chem.*, **61**, 1504 (1957).
9. N. N. Kavtaradze, V. I. Lygin, DAN, **138**, No. 3, 616 (1961).

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