trichloroacetonitrile, 1.765Å., is comparable to that in carbon tetrachloride,[12] 1.766Å., and in chloroform, 1.77Å.[13]

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY, CLEVELAND, OHIO]

The Chemisorption of Carbon Monoxide on Metals[1]

BY R. A. GARDNER[2] AND R. H. PETRUCCI

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The adsorbed species resulting from the chemisorption of carbon monoxide on copper oxide, nickel and cobalt were studied by infrared spectroscopy. An infrared technique developed by Eischens was used to obtain the spectra. The observations made in this investigation serve to support and extend the Wolkenstein hypothesis of the mechanism of chemisorption. Surface atoms can act as strong or weak electron donors and acceptors; the adsorbed species assume the opposite role. Adsorbed carbon monoxide species displayed vibration frequencies corresponding to the possession of non-integral numbers of electrons ranging from $(CO)^{+0.70}$ to $(CO)^{-1.30}$ with absorption bands from 2173 to 2000 cm.$^{-1}$.

Introduction

In the past, the basic problem of chemisorption has been one of explaining the bonding between a single adsorbed species and a surface. Among the many techniques that have been used in adsorption studies are: electron microscopy,[3] mass spectrometry,[4] magnetic susceptibility,[5] field emission studies,[6] conductivity[7] and spectroscopy.[8] The vast number of experiments reported in the literature on chemisorption, while generally showing qualitative agreement, still leave many questions unanswered. Recent improvements in the sensitivity of the various experimental techniques used in the study of chemisorption have further complicated the problem—in many investigations evidence has been found for the existence of several different species resulting from chemisorption of a single gas on a single solid. The presence of several chemisorbed species also has been observed in the experiments presented in this work.

Experimental

The method used in this investigation involved "*in situ*" preparation of the adsorbent, evacuation of the infrared cell to 1 × 10^{-6} mm. pressure, admission of purified carbon monoxide and determination of the spectrum of the sample. This method is similar to that successfully applied by Eischens, Pliskin and Francis[9] in their pioneer work in the determination of the infrared spectra of chemisorbed molecules.

The vacuum system contained a Welch Duo Seal mechanical vacuum pump, a mercury diffusion pump and a liquid nitrogen trap. The pressure gauges used were: a Phillips cold cathode gauge type PHG-09, a McLeod gauge graduated at 0.005 microns, for calibration of the Phillips gauge, and a closed end mercury manometer. All gauges could be isolated from the system by vacuum stopcocks. Vacuums as low as 10^{-7} mm. were obtainable.

The gases used were stored in bulbs with mercury seals to prevent contamination by Apiezon N stopcock grease. The gases from commercial tanks were purified before storage. Hydrogen (99%) from the Air Reduction Corporation was further purified by passage over activated cocoanut charcoal at −195°. The charcoal had been activated at 2 × 10^{-5} mm. pressure at 350° for 14 hr. Carbon monoxide (95%), from the Matheson Company, was purified by passage through concentrated sulfuric acid, activated charcoal at −78° and cobaltous oxide at 25°. Oxygen from Linde Air Products Corporation was stored directly from the commercial tank.

The adsorbents were prepared from the metal nitrates in an "*in situ*" cell by the method desdribed by Eischens, Pliskin and Francis.[10] The spectra were obtained with a Perkin–Elmer Model 112 spectrometer which was modified by the installation of a vertical source unit. The spectra were recorded from 2500 to 1200 cm.$^{-1}$ with fixed monochromator slits.

The path of the infrared beam was flushed with commercial nitrogen to suppress atmospheric carbon dioxide and water vapor bands in the spectra. Several blank spectra of the sample were recorded at room temperature and at the final pressure of approximately 1 × 10^{-7} mm. The introduction of carbon monoxide gas was accomplished in small increments. Duplicate computed spectra were determined between the introduction of each increment.

Several experiments were performed to examine the chemisorption of CO on reflecting metal films for comparison with the results obtained for CO on supported metals. A cell was designed for the vacuum evaporation of the metal from an electrically heated tungsten wire onto the inner surface of a Pyrex tube. The tungsten wire was positioned along the longitudinal axis of the glass tube which was 1.6 cm. in diameter and 23.0 cm. in length. When the cell was placed on the diverging portion of the infrared beam (below the focus point), the beam was collimated by multiple reflections from the evaporated film. The collimated beam was directed onto the 45° angle mirror in the lower source unit and then into the monochromator. In this manner the spectra of surface chemisorbed species were obtained.

Experimental Results

To facilitate the discussion of the several systems and the numerous infrared absorption bands found for the adsorption of carbon monoxide, the experimental data are compiled in Table I; explanatory notes follow the table.

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[1] Based on the doctoral dissertation of R. A. Gardner, Western Reserve University, June, 1959. Presented at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September 14–18 1959.

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TABLE I

SUMMARY OF SPECTRAL DATA

System	Assignments, cm.$^{-1}$	Characteristics			
		Strong	Weak	Sym.	Skewed
Blank[a]	2174	X			X
	2115	X			X
Cu oxide[b]	2173		X	X	
	2127	X		X	
	2000		X	X	
Ni films[c]	2174	X			X
	2115	X			X
	2060	X		X	
Cobalt[d]	2179	X			X
	2160		X		
	2091		X		

[a] Blank or control experiments were conducted using the standardized technique for sample preparation, however without a metal salt and with and without Cab-O-Sil. At CO pressures of 11 mm. or more, absorption bands were obtained at 2174 and 2115 cm.$^{-1}$. [b] Samples of copper oxide supported on Cab-O-Sil were prepared by two methods. Copper nitrate was decomposed and evacuated to 1 × 10^{-6} mm. at 400° then cooled to room temperature without hydrogen reduction, or a reduced copper sample was oxidized either before or after admission of carbon monoxide. The absorption bands for carbon monoxide on copper oxide were at 2173, 2127 and 2000 cm.$^{-1}$. [c] Six nickel films were prepared in the reflectance cell. Bands at 2174, 2115 and 2060 cm.$^{-1}$ were observed in each experiment. The intensity of these bands was proportional to the pressure of gaseous carbon monoxide in the cell. At low pressures of carbon monoxide only the 2060 cm.$^{-1}$ band was observed. All three absorption bands vanished upon evacuation. [d] A sample of cobalt nitrate supported on Cab-O-Sil was decomposed to form the oxide at 400°. The sample was reduced with hydrogen at 450° and then cooled to room temperature in a vacuum of 1 × 10^{-7} mm. The admission of carbon monoxide produced infrared absorption bands at 2179, 2160 and 2091 cm.$^{-1}$.

Discussion

In the present study infrared absorption spectra were observed from 2500 to 1200 cm.$^{-1}$. The spectra of gaseous carbon monoxide and carbon monoxide with and without Cab-O-Sil showed absorption bands at 2174 and 2115 cm.$^{-1}$. These two bands, which occur in the same region of the spectrum as the known carbon monoxide doublet, were assigned to gaseous carbon monoxide. Upon admission of carbon monoxide to the three adsorbent systems used, the following nine bands were observed: Cab-O-Sil supported copper oxide, 2173, 2127 and 2000 cm.$^{-1}$; Cab-O-Sil supported reduced cobalt oxide, 2179, 2160 and 2091 cm.$^{-1}$; and a vacuum evaporated nickel film, 2174, 2115 and 2060 cm.$^{-1}$. These nine absorption bands were the only ones that appeared as a result of the contact of carbon monoxide with these adsorbents. The data for carbon monoxide on nickel films agree well with the results of Pickering and Eckstrom,[11] who observed infrared absorption bands at 2166, 2121 and 2062 cm.$^{-1}$ in their study of carbon monoxide on evaporated nickel films.

The 2174 and 2115 cm.$^{-1}$ bands for carbon monoxide on the nickel film were assigned to gaseous carbon monoxide. The remaining seven bands, which resulted from the chemisorption of carbon monoxide on these adsorbents, were assigned by making the assumptions:

(1) There exists a relationship between the vibration frequency of the carbon monoxide unit and the number of valence electrons associated with that unit. For example, Herzberg[12] presents these data: CO (10 valence electrons), ν = 2143 cm.$^{-1}$, $(CO)^+$ (9 valence electrons), ν = 2184 cm.$^{-1}$.

(2) A single relationship between the vibration frequencies of carbon monoxide units and the number of valence electrons exists for all of the carbon monoxide species observed in this investigation.

(3) The various carbon monoxide species resulting from the chemisorption of carbon monoxide on a single adsorbent differ from each other by *integral* numbers of valence electrons. This assumption follows the Wolkenstein[13] hypothesis of the mechanism of chemisorption. (For example, Wolkenstein postulates that three forms of hydrogen atoms exist on a sodium chloride surface, having 0, 1 and 2 electrons, respectively, associated with the hydrogen nucleus.)

(4) In addition to the data obtained in this investigation the data given by Herzberg for CO and $(CO)^+$ are assumed to fit the relationship noted above (assumption 2).

There are eight frequencies to be correlated by a single curve relating the carbon to oxygen vibration frequency and the number of valence electrons associated with a carbon monoxide unit. These are the three frequencies for carbon monoxide on Cab-O-Sil supported copper oxide, the three frequencies for carbon monoxide on Cab-O-Sil supported cobalt and the frequencies assigned to the neutral carbon monoxide molecule and to the positive ion. The eight frequencies are 2173, 2127, 2000; 2179, 2160, 2091; 2143, and 2184 cm.$^{-1}$, respectively. The numbers of valence electrons are known for only two of the frequencies, which are 2143 cm.$^{-1}$ (10 valence electrons) and 2184 cm.$^{-1}$ (9 valence electrons). A very extensive literature search failed to provide independent data for the vibration frequency and number of electrons for any other carbon monoxide ion or species. Therefore it was necessary to use the Wolkenstein hypothesis that the number of electrons associated with adsorbed species on a single adsorbent would differ by one electron. The hypothesis presented by Wolkenstein considers only integral numbers of electrons but the presence of an absorption band at 2173 cm.$^{-1}$ for carbon monoxide on the copper oxide sample leads immediately to the concept of non-integral numbers of valence electrons. Since the 2173 cm.$^{-1}$ frequency is between the 2184 cm.$^{-1}$ frequency of the positive ion (9 valence electrons) and the 2143 cm.$^{-1}$ frequency of the neutral molecule (10 valence electrons) a vibration frequency of 2173 cm.$^{-1}$ must correspond to a non-integral number of valence electrons between 9 and 10. A graph of the vibration frequency of carbon monoxide units as a function of the number of electrons associated with these units was constructed in the following manner. The 2184 cm.$^{-1}$ and the 2143 cm.$^{-1}$ frequencies were assigned to 9 valence electrons and 10

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(13) Th. Wolkenstein, "Advances in Catalysis," Vol. IX, Academic Press, Inc., New York, N. Y., 1957, pp. 807–817.

valence electrons, respectively. The carbon monoxide species on copper oxide (2173, 2127 and 2000 cm.$^{-1}$) were placed at intervals separated by one electron, as were the carbon monoxide species on cobalt (2179, 2160 and 2091 cm.$^{-1}$). The excellent fit of the data to the smooth curve shown in Fig. 1 supports the hypothesis that the vibration frequency of a carbon monoxide unit is a function of the number of valence electrons associated with the unit. Thus it has been possible to assign a specific adsorbed species to each of the infrared absorption bands observed in this investigation.

The experimental results of Eischens and Pliskin[8] on the chemisorption of carbon monoxide on iron and iron oxide may be examined with respect to Fig. 1. These investigators found infrared absorption peaks at 4.95 (2020 cm.$^{-1}$) and 4.70 microns (2128 cm.$^{-1}$). According to the curve of Fig. 1 the numbers of electrons corresponding to these two species of CO on iron are 11.23 ± 0.05 and 10.23 ± 0.05, respectively. The agreement shown here gives added support to the graph of Fig. 1 as representing a fundamental property of the CO unit.

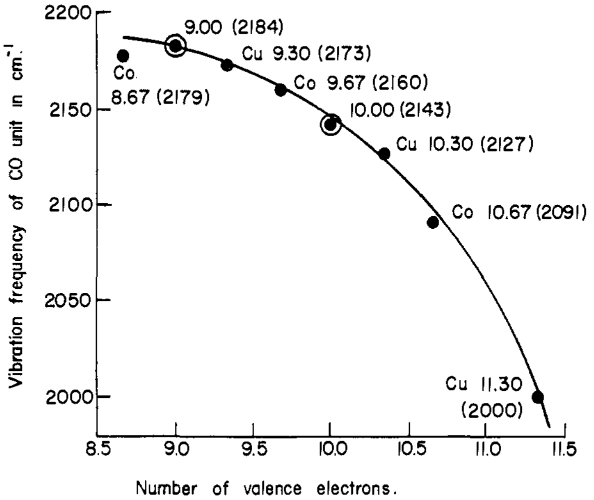

Fig. 1.—Vibration frequency of CO units *vs.* number of electrons associated with the CO unit: ◉, data from Herzberg; ●, data from this study.

Conclusions

This investigation was concerned with the chemisorption of carbon monoxide on metals and metal compounds. The adsorbents used were copper oxide, nickel and cobalt. An infrared technique was used to obtain the spectra of chemisorbed carbon monoxide on these solids. The interpretation of the data became possible through the use of the basic concepts of the Wolkenstein hypothesis on the mechanism of chemisorption.

1. The observations made in this investigation serve to support and extend the Wolkenstein hypothesis by conclusively demonstrating the existence of multiple forms of a single adsorbate on a single adsorbent. As proposed by Wolkenstein, the numbers of electrons associated with each adsorbed species have been shown to differ by one electron between successive forms of the adsorbate. But whereas Wolkenstein considered only integral numbers of valence electrons for the chemisorbed species, the vibration frequencies for chemisorbed CO observed in this investigation correspond to non-integral numbers of valence electrons.

2. A fundamental characteristic of the carbon monoxide unit has been discovered: namely, that the vibration frequency of the carbon monoxide unit, as electrons are added or removed from it, changes by a predictable amount. This relationship has been represented graphically. The existence of chemisorbed carbon monoxide units ranging from $(CO)^{+0.70}$ to $(CO)^{-1.30}$ has been experimentally observed; the stretching vibration frequencies of these forms range from 2173 to 2000 cm.$^{-1}$.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RENSSELAER POLYTECHNIC INSTITUTE, TROY, NEW YORK]

Charge-transfer Spectra of Iodine Atom–Aromatic Hydrocarbon Complexes[1]

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Iodine atoms, produced by the flash photolysis of molecular iodine in various aromatic solvents, form charge-transfer complexes that absorb light in the visible region. The charge-transfer absorption spectra have been measured at room temperature for complexes between iodine atoms and benzene, toluene, *o*-xylene, *p*-xylene and mesitylene. Absorption maxima are at 495, 515, 570 520 and 590 mμ, respectively. Decreases in charge-transfer transition frequencies with decreasing ionization potentials of the donor molecules are the same as those for complexes involving I_2, Br_2, and ICl as acceptor species. The I atom–*p*-xylene band is at a lower wave length than expected and is quite broad and may be the resultant of charge-transfer transitions from two slightly different donor orbitals of the *p*-xylene molecule.

In a previous paper,[3] the formation of a transient intermediate in the flash photolysis of iodine in benzene was reported. This intermediate, which was proposed to be a complex between an iodine atom and a benzene molecule comparable to similar

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(1) From the thesis by S. J. Rand, submitted in partial fulfillment of the requirements for the Ph.D. degree to the Graduate School, Rensselaer Polytechnic Institute (1960). Available from University Microfilms, Ann Arbor, Michigan.

(2) Participant in the National Science Foundation Research Participation for Teacher Training Program conducted at Rensselaer Polytechnic Institute during the summer of 1959.

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