JOURNAL OF CATALYSIS 27, 200–206 (1972)

Interactions Between Lewis Bases Chemisorbed on Transition Metal Surfaces. Infrared Spectroscopic Studies

R. QUEAU AND R. POILBLANC

U.E.R. Chimie Inorganique 31-Toulouse, France

Received December 9, 1971

Carbon monoxide chemisorbed alone, and simultaneously with the Lewis bases $(CH_3)_3N$ and C_2H_5NC, has been studied by ir spectroscopy over Fe, Co, Ni, Rh, Pd and Pt evaporated films. CO is chemisorbed on transition metals forming a σ bond by donation of the lone pair of the carbon atom, and a π bond by back donation of metallic d electrons to the antibonding π^* orbital of CO. This produces a decrease of the carbon–oxygen bond strength and consequently a decrease of the vibrational frequency of CO. $(CH_3)_3N$ is chemisorbed by donation of the nitrogen lone pair to form a σ bond; C_2H_5NC is chemisorbed by donation of the carbon lone pair to form a σ bond, and the possibility also exists to form a π bond by back donation from the metal d orbitals. However the π acceptor ability of C_2H_5NC is weaker than for CO.

When $(CH_3)_3N$ and C_2H_5NC react with chemisorbed CO, a number of CO molecules are replaced. In either case, the net effect is to provide more electrons for back donation from the metal to CO π^* orbitals. A lowering of the CO surface coverage and the shift of the CO stretching frequencies to lower frequencies has been observed. From this point of view, the metal surface exhibits a similar behavior to that of the central metal atom of transition metal complexes.

INTRODUCTION

Since the early studies of Eischens, Pliskin and Francis (*11*) in 1954, numerous articles have been published concerning the infrared spectra of carbon monoxide chemisorbed on highly dispersed transition metal particles. However, relatively few studies have been made of the interactions between chemisorbed carbon monoxide and other species simultaneously adsorbed on metal surfaces. The cases of simple molecules such as oxygen, nitrogen, hydrogen, water vapor, ammonia (*1–3*) and hydrogen sulfide (*3*) have been reported.

The vibrational behavior of carbon monoxide during such interactions would suggest that an atom of the metal surface must have an analogous behavior to that of the metallic atom of the complexes of coordination chemistry. The recent paper of Goodsel and Blyholder (*4*) shows a striking example of this analogy. One of the fundamental properties of transition metal complexes in their low valent states is the electronic transfer which takes place between different ligands through the metal atom. We have sought manifestations of the analogy by exploring whether such a phenomenon occurs through metal surface atoms between different species simultaneously chemisorbed.

In our work we have studied by ir spectroscopy the interactions of Lewis bases with carbon monoxide chemisorbed on metal films. The behavior of the Lewis bases like trimethylamine and ethylisocyanide are described below.

EXPERIMENTAL SECTION

Technique. Metal films were prepared by evaporation (*5*) from a filament, on NaCl windows, in the presence of a small amount of carbon monoxide (10^{-3}, 10^{-1} Torr). The design of the infrared cell used in this study is illustrated in Fig. 1. The body of the cell, built in Pyrex glass, was blown out to

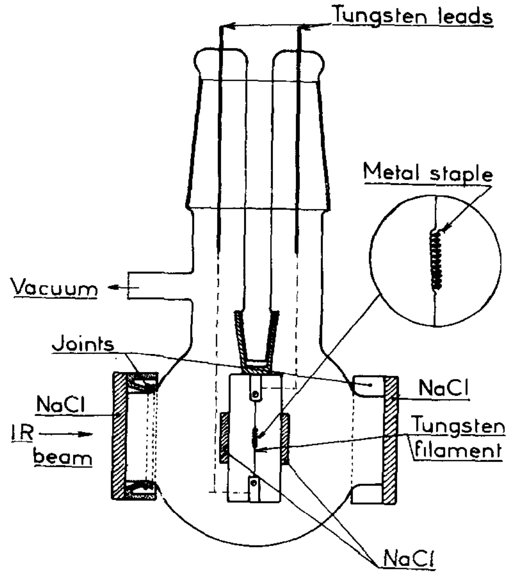

FIG. 1. Infrared cell.

produce two 35 mm diameter openings, closed with two NaCl windows. These windows were sealed, with "Scotch weld"* epoxy resin on Paulstra** joints. The upper part of the cell consisted of a 45/55 standard taper joint.

Filaments were prepared from tungsten wire of 0.25 mm diameter in the form of a coil (10 turns) of 1.5 mm diameter and 8 mm length. The filament was charged with the appropriate metal for evaporation by placing a sample as shown in Fig. 1.

Materials. Evaporated films of iron, cobalt, nickel, rhodium, palladium and platinum were prepared. These metals, stated to be 99.99% pure, were obtained from Johnson Matthey or Comptoir Lyon Alemand. Tungsten wire (Purity 99.98%) was obtained from Alfa Inorganics. The carbon monoxide used in this study was obtained from Air Liquide (Purity 99.995%).

Infrared spectra. The spectra of chemisorbed molecules were recorded on an unmodified Perkin-Elmer model 225 double beam grating spectrometer, in the region 2200–1600 cm^{-1}; the frequencies were measured with an accuracy greater than ± 5 cm^{-1}.

Structure of metal films. Many of the evaporated metal films used in this work were examined by means of electron microscopy with a Philips EM 300 instrument. The films were easily floated onto water from the sodium chloride window. Films appeared to be made up of a cluster of particles. As in previous observations, the size of the particles was a function of the melting point of the metal and the carbon monoxide pressure. For a given metal, the particle size increased with CO pressure, in agreement with Garland, Lord and Troiano (*6*).

Preparation of surface carbonyl complexes. The iron, cobalt, nickel, rhodium, palladium and platinum films were evaporated on the sodium chloride windows in the presence of carbon monoxide at 0.1 Torr. After evaporation, the cell was filled with carbon monoxide at a pressure of 700 Torr, and after a few minutes the cell was placed in the infrared spectrometer and pumped down to a pressure of 0.1 Torr. The spectrum was then recorded. Each experiment was reproduced several times; the discrepancies between observed frequencies in each experiment on the same metal were smaller than 5 cm^{-1}.

The infrared spectra of chemisorbed CO are presented in Fig. 2, and the frequencies of the absorption bands are summarized in Table 1.

Platinum films were also evaporated in helium at pressure of 10^{-1} Torr. It is noticeable that after introduction of CO in the cell, the infrared spectrum was identical to that obtained on the surface evaporated in carbon monoxide. The frequencies of chemisorbed carbon monoxide agree largely with previously published results, in the case of iron (*7, 8*), cobalt (*9*), nickel (*8*), rhodium (*10*) and platinum (*1, 10–15*). Only in the case of palladium are the observed frequencies lower than those previously reported (*1, 13*).

Structures of surface carbonyl complexes. In most cases, two absorption bands were obtained. The highest frequency band was designated by A and the lowest by B. Following Eischens the assignment of structure for the adsorbed carbon monoxide was made by using information derived from spectroscopic studies of metal carbonyls (*2*). Thus it

---

* Trade mark of the 3M Company.

** Paulstra, 92-Levallois, France.

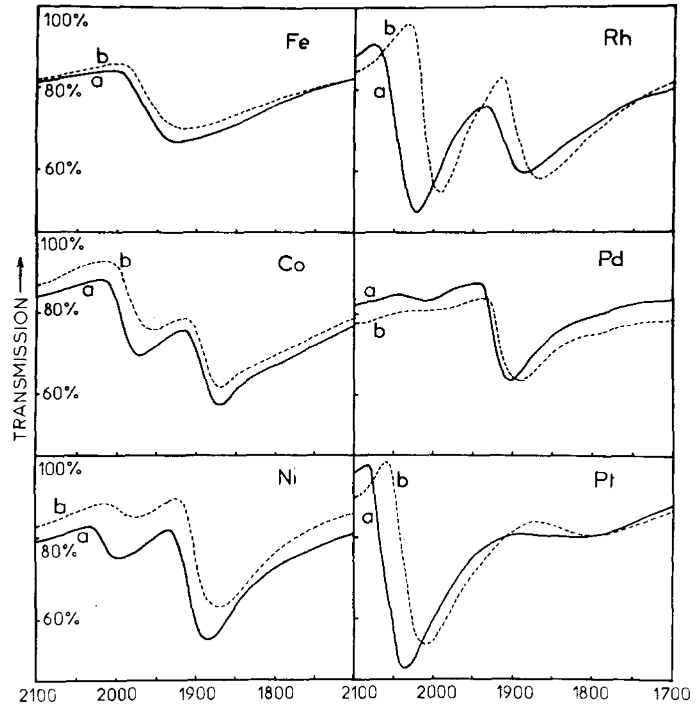

FIG. 2. Infrared spectra of chemisorbed carbon monoxide on various metals and interaction with $(CH_3)_3N$. All frequencies (cm^{-1}); (a) initial spectra; (b) after interaction with $(CH_3)_3N$.

can be assumed in agreement with the conclusions of earlier studies (*1*, *16*, *17*), that frequencies ranging from 2050 to 1950 cm^{-1} are due to "linear" carbon monoxide, where a molecule is linked to only one metal atom. Frequencies below 1950 cm^{-1} are considered to be due to bridging carbon monoxide, where a molecule is linked to two metal atoms. However, Blyholder (*18*) and Blyholder and Allen (*9*) thought that it is not necessary to hypothesize the existence of a bridging structure to explain infrared bands below 1950 cm^{-1}. They believe that these bands may be due to a linear M–C–O structure, where carbon monoxide is chemisorbed on special sites such as edges, corners, and dislocations.

RESULTS AND DISCUSSION

Action of trimethylamine on surface carbonyl complexes. According to Yung-Fang (*19*) amines are chemisorbed on metal surfaces by means of the nitrogen lone pair and this chemisorption at 25°C is essentially nondissociative. Trimethylamine was distilled into the cell containing 10^{-1} Torr of carbon monoxide. The maximum shifts to lower frequencies of the carbon monoxide stretching frequency were obtained with a pressure of 200 Torr of trimethylamine. The cell was then evacuated by pumping to a residual pressure of 0.1 Torr, and the infrared spectrum was then recorded. The shift to lower frequencies of the CO stretch-

TABLE 1

CO STRETCHING FREQUENCIES OF SURFACE CARBONYL COMPLEXES[a]

Iron	Cobalt	Nickel	Rhodium	Palladium	Platinum
A 1915	A 1980	A 2010	A 2020	A 2010	A 2040
	B 1880	B 1890	B 1885	B 1902	B 1850

[a] All frequencies (cm^{-1}).

TABLE 2

Shifts to Lower Frequencies of the CO Stretching Frequencies Obtained by Interaction of $(CH_3)_3N$[a]

Iron	Cobalt	Nickel	Rhodium	Palladium	Platinum
A 10	A 18 B 0	A 20 B 20	A 28 B 23	A disappears B 10	A 30

[a] All shifts (cm^{-1}).

ing frequencies are reported in Table 2 for each metal.

With the shift to lower frequencies, there is a small decrease of the intensity of band A. On the other hand, the intensity of band B does not change. This seems to prove that the decrease of CO surface coverage is small (*20*) and that the substitution of carbon monoxide by trimethylamine occurs preferentially on sites A. This observation has already been made in the case of water vapor and hydrogen (*1*, *10*).

From a structural point of view, it can be assumed that when CO forms coordination compounds with transition metals, the molecule of CO is linked to the metal via its carbon atom, whose lone pair forms a dative σ bond. A back donation of electrons takes place from a filled metal *d* orbital into a vacant carbon monoxide π^* antibonding orbital, so the carbon–oxygen bond strength decreases, and its stretching frequency also decreases.

When a more basic Lewis base reacts with chemisorbed carbon monoxide, its chemisorption on free sites and the replacement of chemisorbed carbon monoxide tends to augment the electronic charge on the metal. This increases the π bond from the metal to CO, producing a new shift to lower frequencies of the CO stretching frequency.

Eischens Francis and Pliskin (*20*) have studied the value of the stretching frequency of chemisorbed carbon monoxide on platinum as a function of the surface coverage. In comparison with their results, the shifts we have observed which were greater than the shifts which would have been produced by a simple decrease of the carbon monoxide surface coverage, must be attributed to an electronic effect of the ligand.

Action of ethylisocyanide on surface carbonyl complexes. This ligand is most interesting, because if offers additional information through the C–N stretching frequency simultaneously with the shift of the CO stretching frequency. Indeed, the carbon–nitrogen bond of the ethylisocyanide has a similar structure to carbon–oxygen bond. In transition metal complexes, Bigorgne (*21*) has shown that ethylisocyanide is linked to the metal atom by the carbon atom, and if the σ donor ability is the same as carbon monoxide, the π acceptor ability is weaker.

Reaction of this ligand with platinum, cobalt and rhodium surface carbonyl complexes has been carried out using the same method as for trimethylamine.

To increase the ratio CO/L on the surface the cell was filled with carbon monoxide at a pressure of 700 Torr for 24 hr and a new spectrum was then recorded.

Platinum. Results are presented in Fig. 3(3). After the evacuation of gaseous isocyanide, the infrared spectrum exhibits a shift to lower frequencies of the CO stretching frequency of 65 cm^{-1} and the band intensity decreases. The C–N stretching frequency is then 2150 cm^{-1}. This state is due to a given but unknown ratio CO/L on the surface. After 24 hr in 700 Torr of CO, CO/L increases and both the stretching frequencies of CO and C–N shift to higher frequencies, respectively 10 and 17 cm^{-1}. The CO band intensity also increases.

Rhodium. As shown in Fig. 3(2), both bands A and B shift to lower frequencies, by 65 and 60 cm^{-1}, respectively, and the intensity of band A decreases significantly; the C–N stretching frequency is 2137 cm^{-1}. After 24 hr in carbon monoxide, as in the case of platinum, a 20 cm^{-1} shift to higher frequencies of the stretching CO and the

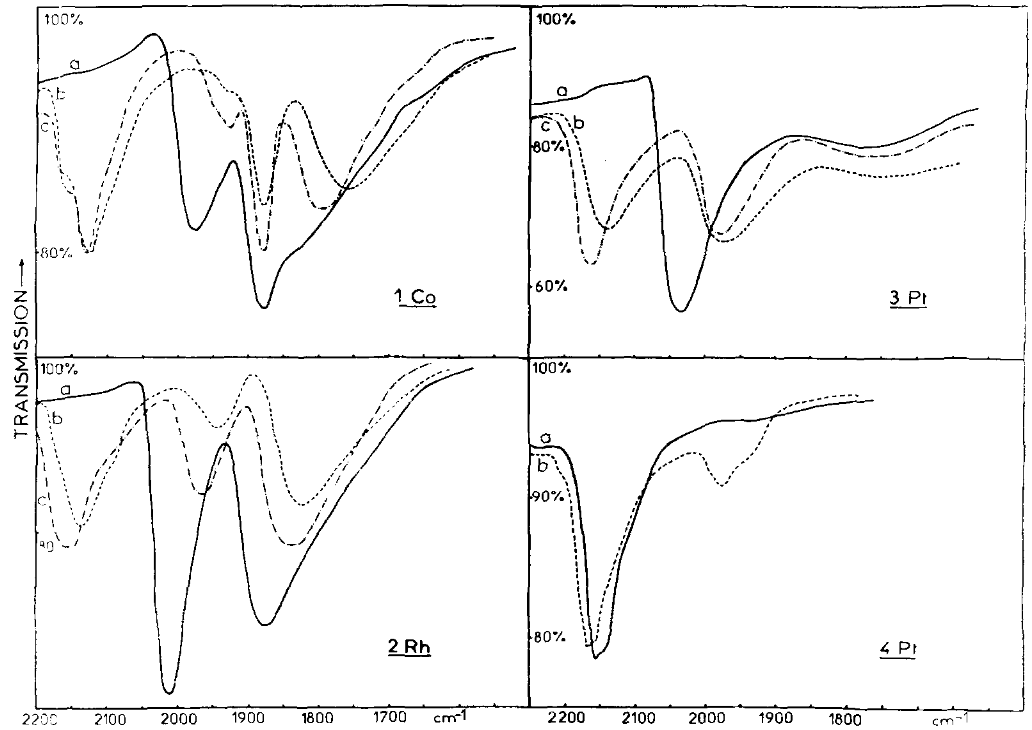

FIG. 3. Infrared spectra of chemisorbed CO, and interaction with C_2H_5NC. (1 Co, 2 Pt, 3 Pt) (a) initial spectra, (b) after interaction with C_2H_5NC, (c) after further introduction of CO. (4 Pt) (a) spectrum of C_2H_5NC chemisorbed on Pt film evaporated in 10^{-1} Torr He, (b) after interaction with CO.

stretching C–N can be observed. The intensity of band A increases.

Cobalt. When ethylisocyanide reacts with chemisorbed carbon monoxide on cobalt [Fig. 3(1)], the infrared spectrum shows a very important decrease of the band A intensity, and its shift to lower frequency is 50 cm^{-1}. It was discovered that band B was composed in fact of two bands. The lower frequency band shifted towards lower frequencies as in the case of rhodium. This band is still designated by the letter B. The higher frequency band which displays practically no shift is designated by C. The observed frequency of band B is 1757 cm^{-1}. The initial frequency of this band, masked by the tail of the band C, may be estimated at 1830 cm^{-1}; the shift is then 73 cm^{-1}. Two stretching C–N bands were observed at 2155 and 2125 cm^{-1}, respectively. After 24 hr under CO, the infrared spectra showed a shift to higher frequencies of the stretching frequency of B type molecules. Again, no change in band C occurs. The intensity of band A increases slowly but the frequency remained 1925 cm^{-1}. The two CN bands shift weakly to higher frequencies 12 and 2 cm^{-1}, respectively.

After the description of these three examples we can see that, as in the case of trimethylamine, the A molecules disappear first, and the electronic effect appears on all types of molecules if the C type on cobalt is excepted.

The shift to higher frequencies of the C–N stretching frequency when the ratio CO/L increases at the surface agrees with the results obtained by Bigorgne on metal carbonyl complexes (*21*). To explain this shift it can be proposed that the ethylisocyanide accepts some π donation from the metal; for a given ratio CO/L on the surface, the stretching frequency of the C–N bond is then determined. If C–N is substituted by CO, as the σ donor ability of the two types of molecules is almost identical, the metal receives the same negative charge, but CO which is a better π acceptor effects the discharge of the metal more easily. Then the π bond from the metal to isocyanide decreases and the C–N stretching frequency increases. This explanation is well confirmed by the chemisorption of ethyl isocyanide alone, on a platinum film, prepared in 10^{-1} Torr of helium [Fig. 3(4)]. The CN stretching is then 2150 cm^{-1}; after introduction of carbon monoxide this C–N stretch shifts to 2170 cm^{-1} and the CO stretching band appears at 1980 cm^{-1}.

In the case of cobalt, the stability of band C cannot be explained at this time.* However, we can explain why the CN stretching band is as low as 2125 cm^{-1} and that the shift of CO stretching band is as high as 70 cm^{-1} for B type molecules. In fact the metal donation goes only to the unfilled orbitals of chemisorbed isocyanide, and chemisorbed CO of B type (A type disappears and C does not change). Gardner and Petrucci (*23*) have studied the CO stretching frequency as a function of the number of valency electrons in the CO bond. The conclusion was that for the same electron donation from the metal to the CO bond, the shift to lower frequencies is greatest for the CO molecules which have the lowest stretching frequency. For these different reasons, in the case of cobalt a large shift of the CO stretching frequency and a low CN stretching frequency can be expected.

When, in the same condition, $(CH_3)_3N$ and C_2H_5NC react with carbonyl surface complexes, C_2H_5NC produces a larger decrease of the CO surface coverage than $(CH_3)_3N$. This observation can be rationalized in that C_2H_5NC, which is a "softer" base than $(CH_3)_3N$, gives more stable complexes than $(CH_3)_3N$ with the metallic surface, which is a "soft" acid.

Our results do not resolve the different interpretations of Eischens and Blyholder. From Blyholder's point of view, other species simultaneously chemisorbed with CO, according to the electronic balance (*18*), are expected to shift the vibrational frequencies of linear CO chemisorbed on either type of site. On the other hand, by analogy with substituted metal carbonyls, having linear and bridging CO, the effect of the Lewis bases are again expected on both types of CO (*24*, *25*).

These different experiments would suggest that as for metal complexes, there is an electronic balance between the different species simultaneously chemisorbed on a metallic surface. We consider it as one of the best justifications of the concept of "surface complexes."

---

* As obligingly pointed out by one of the referees, a band near 1840 cm^{-1} seems to appear or persist during oxidation of CO on an evaporated nickel surface (*6*). Moreover, some connections may be expected between the particular behavior of the band C and the existence of special sites (*22*).

REFERENCES

1. Eischens, R. P., and Pliskin, W. A., *in* "Advances in Catalysis" (W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal, eds.), Vol. 10. Academic Press, New York, 1958.

2. Little, L. H., "Infrared spectra of adsorbed molecules," Academic Press, New York, 1966.

3. Guerra, C. R., *J. Colloid Interface Sci.* **29**, 229 (1969).

4. Goodsel, A. J., and Blyholder, G., *Chem. Commun.* **17**, 1132 (1970).

5. Queau, R., thesis, Toulouse, 1971.

6. Garland, C. W., Lord, R. C., and Troiano, P. F., *J. Phys. Chem.* **69**, 1195 (1965).

7. Blyholder, G., *J. Chem. Phys.* **36**, 2036 (1962).

8. Baker, F. S., Bradshaw, A. M., Pritchard, J., and Sykes, K. W., *Surface Sci.* **12**, 425 (1968).

9. Blyholder, G., and Allen, M. C., *J. Amer. Chem. Soc.* **91**, 3158 (1969).

10. Harrod, J. F., Roberts, R. W., and Rissmann, E. F., *J. Phys. Chem.* **71**, 343 (1967).

11. Eischens, R. P., Pliskin, W. A., and Francis, S. A., *J. Chem. Phys.* **22**, 786 (1954).

12. Kavtaradze, N. N., and Sokolova, N. P., *Zh. Fiz. Khim.* **41**, 453 (1967).

13. Garland, C. W., Lord, R. C., and Troiano, P. F., *J. Phys. Chem.* **69**, 1188 (1965).

14. Zecchina, A., Versino, C., Coluccia, S., and Borello, E., *J. Chim. Phys. Physicochim. Biol.* **67**, 1237 (1970).

15. Blyholder, G., and Sheets, R., *J. Phys. Chem.* **74**, 4335 (1970).

16. Yang, C., and Garland, C. W., *J. Phys. Chem.* **61**, 1504 (1957).

17. Ferreira, L. C., and Leisegand, E. C., *J. S. Afr. Chem. Inst.* **23**, 136 (1970).

18. Blyholder, G., *J. Phys. Chem.* **68**, 2772 (1964).

19. Yung-Fang, Y. Y., *J. Phys. Chem.* **68**, 101 (1964).

20. Eischens. R. P., Francis, S. A., and Pliskin, W. A., *J. Phys. Chem.* **60**, 194 (1956).

21. Bigorgne, M., *J. Organometall. Chem.* **1**, 101 (1963).

22. Van Hardeveld, R., and Hartog, F., Proceedings of the Fourth International Congress on Catalysis" Vol. 2, p. 275. (Pap. 70). Nauka, Moscow, 1970.

23. Gardner, R. A., and Petrucci, R. H., *J. Phys. Chem.* **67**, 1376 (1963).

24. Pegot, C., and Poilblanc, R., *C. R. Acad. Sci., Ser. C* **268**, 955 (1969).

25. Labroue, D., and Poilblanc, R., *C. R. Acad. Sci., Ser. C* **271**, 1585 (1970).