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Interactions of Chlorine and Bromine with Chemisorbed Carbon Monoxide on Evaporated Platinum, Rhodium, and Iridium Films

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The action of bromine and chlorine on surface carbonyl complexes of platinum, rhodium, and iridium has been studied by ir spectroscopy. At room temperature chlorine and bromine cause partial removal of chemisorbed CO molecules, and produce two other main effects. The stretching frequency of the remaining CO molecules progressively shifts to higher values, corresponding to an increase of the CO bond strength, due to a lowering of the electron back donation $d\pi \rightarrow 2\pi^*$ from the metal to the $2\pi^*$ antibonding orbitals of the chemisorbed CO molecules. This electron-withdrawing ligand effect of halogen is a long-range effect which uses the collective properties of the metal surface. In the case of Rh and Pt, new carbonyl species which exhibit ir bands at higher frequencies (range 2135–2100 cm^{-1}) have also been detected; the corresponding metal atoms are oxidized. The observation that these metal atoms are insensitive to the ligand electron-donor effect of $P(CH_3)_3$ is justified in terms of "demetallization."

INTRODUCTION

The stretching frequency of chemisorbed CO is a function of the surface coverage. This frequency shift is generally discussed in terms of three important mechanisms (*1*), dipole–dipole coupling, direct intermolecular repulsion, and indirect chemical interaction via the metal atom, by modification of the CO force constant. The relative importance of each effect is currently under study and subject to controversy. The dipole–dipole coupling effect may be responsible for only a small part (*2, 3*) or for the whole of the frequency shift (*4*). When electron-donor molecules such as amines, phosphines, and isocyanides react with chemisorbed CO, its stretching frequency is lowered and some is removed from the surface (*5*). However, the observed shift is greater than that expected from the surface coverage decrease, and must be attributed (at least partly) to the lowering of the C–O bond strength (*6*). Using the model first proposed by Blyholder (*7*) for the M–CO chemisorption bond, it was proposed that electron-donor molecules release an electron to the metal and then to the $2\pi^*$ antibonding CO orbitals, producing the effect of a C–O bond strength lowering. This progressive frequency shift suggests that this property of the metal atoms to permit an electron transfer between coadsorbed species is a "collective property" of the metal surface atoms as a whole, and is therefore a "long-range effect" (*6*).

Halogens react with some molecular carbonyl complexes via a so-called "oxidative addition reaction" (see for example, (*8*)); in the resulting complexes, the metal atoms are oxidized and the back bonding $d\pi \rightarrow 2\pi^*$ from the metal to the $2\pi^*$ antibonding orbitals of CO is significantly lowered. The stretching frequency of the carbonyl group then rises to higher values close to the gaseous CO frequency. For example, in the platinum complexes $(PtX_2(CO))_2$, where the formal oxidation state of Pt is 2, the antisymmetric CO stretching frequencies are 2146 cm^{-1} for X = Cl, 2135 cm^{-1} for Br, and 2122 cm^{-1} for I (*9*). The purpose of this work was to ascertain whether such a phenomenon occurs on transition metal sur-

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faces, namely, whether there is a shift to higher values of the vibrational frequency of chemisorbed CO by the action of such electrophilic substances, and thus to explore further the validity of the model proposed by Blyholder (*7*) for the M–CO chemisorption bond. We have studied by ir spectroscopy the action of chlorine and bromine on chemisorbed carbon monoxide on evaporated metal films of platinum, rhodium, and iridium.

EXPERIMENTAL

Technique. Films were prepared directly in the infrared cell, according to the following procedure (*5*). Metals were evaporated from a tungsten filament on NaCl windows maintained at room temperature, in the presence of 100 mTorr of CO. Evaporation rates of 15 Å s^{-1} produced porous and rough films of about 100-Å thickness. For platinum films, the mean particle size was about 60 Å, calculated after volumetric adsorption measurement; the roughness ratio (ratio of the metal surface area accessible to the gas phase, to the geometric area) was near 30.

After evacuation of CO to a pressure below 1 mTorr, infrared transmission spectra were recorded on a 225 Perkin–Elmer spectrometer. The mean transmission coefficient of the ir cell was 20% in the CO stretching region.

Materials. Platinum, rhodium, and iridium were obtained from Johnson and Matthey or Alfa Inorganics as 0.1-mm high-purity wires (99.9%). Carbon monoxide from Air Liquide (99.995%) and chlorine from Matheson were used without further purification. Bromine from R. P. Prolabo was carefully degassed and distilled under vacuum before use.

RESULTS AND DISCUSSION

Infrared spectra of chemisorbed CO on platinum, rhodium, and iridium were in agreement with our previous results (Table 1) (*4*, *5*).

TABLE 1

Infrared Frequencies (cm^{-1}) for Chemisorbed CO on Metal Films

Pt	Rh	Ir
2045	2025 1885	2035

For the CO stretching mode, one main band was detected in the case of platinum and iridium, attributed to linearly chemisorbed CO. In the case of rhodium, two bands of similar intensity were detected; the higher frequency band can be attributed to linearly chemisorbed CO and the lower one to bridging chemisorbed CO species.

Platinum

The introduction of chlorine or bromine in the infrared cell, under a pressure of 1 to 10 Torr, caused partial removal of chemisorbed CO from the platinum surface, as shown by the decrease of the intensity of the ir band. Simultaneously the frequency was progressively shifted to higher values. Assuming that the extinction coefficient of CO remains constant in this spectral range, the surface coverage of the remaining CO molecules could be estimated as proportional to the ir band intensities. Figure 1 shows the ir frequency plotted against the

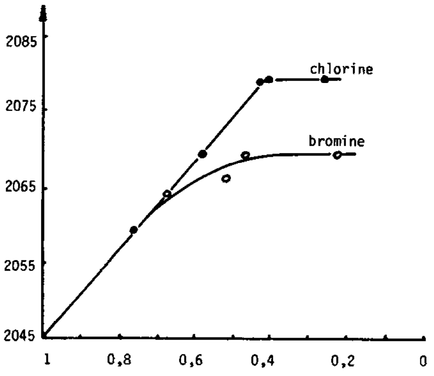

FIG. 1. Stretching frequency of chemisorbed CO as a function of surface coverage. Data refer to Pt films on which CO has been presorbed and halogen gas (●, Cl_2; ○, Br_2) subsequently dosed.

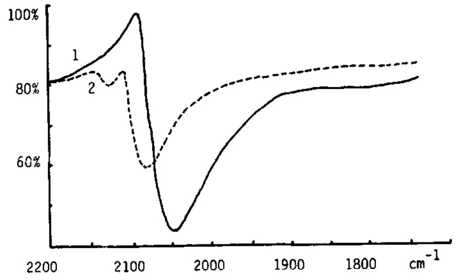

FIG. 2. Infrared spectra of chemisorbed CO on Pt; 1, initial spectrum; 2, after addition of chlorine.

coverage (the initial coverage was assumed to be unity).

The maximum shift (35 cm^{-1} for chlorine and 25 cm^{-1} for bromine) was obtained at a surface coverage ratio near 0.5. Then a new weak band appeared at 2130 cm^{-1} for chlorine (Fig. 2) or 2120 cm^{-1} for bromine. By further introduction of trimethylphosphine, the main band was shifted to lower frequencies; the 2130-cm^{-1} band (2120 cm^{-1} in the case of bromine) disappeared in an hour, without a frequency change (Fig. 3).

In coordination chemistry the shift of the ν-CO stretching mode to higher frequencies can be interpreted in terms of an increase in the CO force constant as a result of a decrease of the back donation $d\pi \rightarrow 2\pi^*$ from the metal to the CO $2\pi^*$ antibonding orbitals; so by analogy, the chemisorbed halogens produce an "Electron-withdrawing" ligand effect. The ability of the metal to permit this electron transfer is a "collective property" of the surface metal atoms. This idea is strongly supported by the observation of the progressive shift to higher frequencies produced by the chemisorption of halogens, which is followed by a progressive shift to lower frequencies due to a further addition of $P(CH_3)_3$.

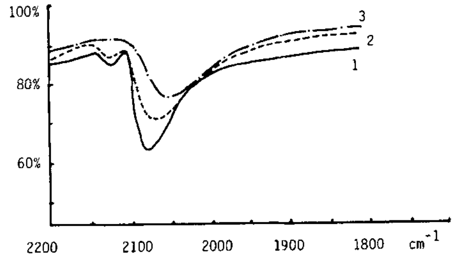

FIG. 3. Infrared spectra of chemisorbed CO on Pt; 1, spectrum of chlorinated surface; 2, after addition of $P(CH_3)_3$ for a few minutes; 3, after addition of $P(CH_3)_3$ for 1 h.

By analogy to platinum (II) complexes (*9*) and in agreement with previous results (*10, 11*) it is suggested that the species which exhibits an infrared band near 2130 cm^{-1} in the case of chlorine, and 2120 cm^{-1} in the case of bromine, are formed by a CO molecule and two halogen atoms bonded to the same metal atom, which is oxidized Pt^{II}.

In these species which are insensitive to the ligand donor effect of chemisorbed $P(CH_3)_3$, the corresponding metal atoms can be considered as "demetallized," i.e., they have lost the collective properties of the metal surface; this effect is a short-range effect. Moreover, these species might be a step in the formation of a true molecular carbonyl halide complex, a "premolecular step." These species are easily destroyed by a long exposure to $P(CH_3)_3$ or CO. The formation of such a species was proposed by Primet *et al.* during the chlorination of a Pt/Al_2O_3 catalyst by CCl_4 (*12*).

Rhodium

In the case of rhodium, chlorine and bromine again produce similar effects. CO is removed from the surface and the stretching frequency of the remaining chemisorbed CO, both linear and bridging, is progressively shifted to higher values. Two new species are formed producing two ir bands at 2130 and 2090 cm^{-1} in the case of chlorine and 2110 and 2090 cm^{-1} in the case of bromine. By further introduction of $P(CH_3)_3$, the main bands due to linear and bridging CO molecules are shifted to lower frequencies; the 2130- (or 2110-) cm^{-1} band disappears in a few minutes without frequency change, whilst the 2090-cm^{-1} band remains unchanged (Fig. 4).

As for platinum, the CO stretching frequency change can be interpreted in terms of a CO force constant change, due to

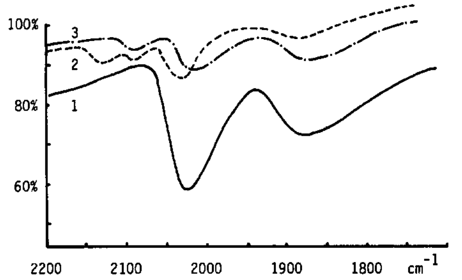

FIG. 4. Infrared spectra of chemisorbed CO on Rh; 1, initial spectrum; 2, after addition of Cl_2; 3, after addition of $P(CH_3)_3$ for 1 h.

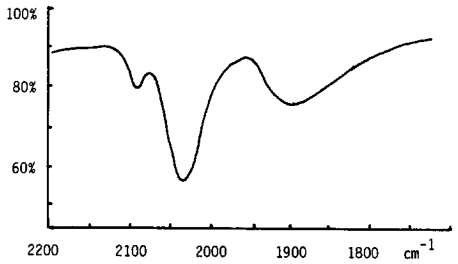

FIG. 5. Infrared spectra of chemisorbed CO on a Rh film obtained by thermal decomposition of $Rh_2Cl_2(CO)_4$.

modification of the back donation $d\pi \rightarrow 2\pi^*$.

By analogy with complexes such as $Rh_2X_2(CO)_4$, where Rh atoms are Rh^I (Table 2), the 2090-cm^{-1} band can be attributed to a CO molecule and a halogen atom on the same metal Rh^I atom. It is not impossible that this band also agrees with the formation of a small quantity of the complex $Rh_2X_2(CO)_4$. The second band which would be expected near 2035–2030 cm^{-1} would be shadowed by the band corresponding to linearly chemisorbed CO on Rh, near 2035 cm^{-1}. By thermal decomposition in the vapor phase of $Rh_2(CO)_4Cl_2$ we have obtained a metal film which exhibits three ir bands at 2090, 2033, and 1895 cm^{-1} (Fig. 5), frequencies which are very similar to those obtained by the reaction of Cl_2 on chemisorbed CO. In this case, the 2090-cm^{-1} band may be attributed to undecomposed complex; the 2104-cm^{-1} band, too weak, remains invisible.

As in the case of platinum, the 2120-cm^{-1} band (2110 cm^{-1} for bromine) can be attributed to Rh^{II} surface complexes, where a CO and two halogen atoms are bonded to the same metal atom.

TABLE 2

Infrared Frequencies (cm^{-1}) of $Rh_2X_2(CO)_4$ Complexes

$Rh_2Cl_2(CO)_4$	2104 (w)	2089 (s)	2034 (s)
$Rh_2Br_2(CO)_4$	2104 (w)	2085 (s)	2031 (s)

These two surface species deriving from Rh^{II} and Rh^I are also insensitive to the electron-donor effect of chemisorbed $P(CH_3)_3$. It is therefore also proposed that these Rh atoms are "demetallized." An interesting difference between the two species must be noted; the Rh^{II} species is easily decomposed by a short exposure to $P(CH_3)_3$ but the Rh^I is not, even after a long exposure. This concept of demetallized metal atoms is ascribed to the existence of "isolated" Rh atoms as proposed by Yates *et al.* (*13*) for a Rh/Al_2O_3 catalyst obtained by $RhCl_3$ reduction; the stretching frequency of chemisorbed CO on these special "isolated sites" is not coverage dependent.

Iridium

Chlorine at 300 Torr produces a slow displacement of chemisorbed CO, and the stretching frequency of the CO remaining chemisorbed is shifted to higher values (Fig. 6); however, "demetallized" species have never been detected. This chlorinated surface carbonyl complex of iridium is "air stable" for several hours, in contrast to the platinum and rhodium surface complexes which are destroyed in a few seconds.

CONCLUSION

Chlorine and bromine displace chemisorbed carbon monoxide on platinum and rhodium producing two main effects:

(1) a long-range electron-withdrawing li-

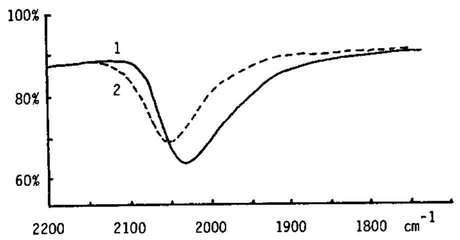

FIG. 6. Infrared spectra of chemisorbed CO on Ir 1, initial spectrum; 2, after addition of Cl_2.

gand effect which uses a collective property of the surface metal atoms,

(2) a short-range effect of a localized oxidative "demetallization" of some metal atoms, whereby they have lost the collective properties of the surface.

These observations support the model proposed by Blyholder (*7*) for the M–CO chemisorption bond and the fact that foreign substances can modify the CO force constant. In the case of iridium only the electron-withdrawing ligand effect has been observed.

These "demetallized" species may be obtained by extraction of the metal atom from the bulk, after the cleavage of the M–M bond. Such a phenomenon has been observed as a consequence of the chemisorption of sulfur or oxygen atoms on various transition metals (*14*).

To sum up, carbon monoxide which has been considered as a spectroscopic probe for the electronic state of the metal surface as a whole can also be considered as a probe for the discrete oxidation states of some surface metal atoms.

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