JOURNAL OF CATALYSIS 29, 213-223 (1973)

Infrared Study of CO Adsorbed on Pt/Al_2O_3. A Method for Determining Metal–Adsorbate Interactions

M. PRIMET, J. M. BASSET, M. V. MATHIEU, AND M. PRETTRE

Institut de Recherches sur la Catalyse,
39, Bd. du 11 Novembre 1918,
69 - Villeurbanne, France

Received September 7, 1972; revised December 8, 1972

When CO is adsorbed on platinum, two types of bonding are involved: a σ bond and a π bond obtained by back-bonding of metal "*d*" electrons to an antibonding orbital of CO. This model takes into account most of the experimental results obtained when CO is adsorbed on platinum. In the present paper, various gases having electron donor or electron acceptor properties have been adsorbed on platinum previously covered ($\theta = 0.2$) by CO. When Lewis bases are adsorbed on platinum, the effect of the adsorbed base is to increase the electronic density of the platinum crystallite and the back donation to the carbonyl group. This results in a shift of the ν(CO) frequency towards low wave numbers. This kind of interaction involves the collective properties of the metal.

When atoms having electron acceptor properties, such as chlorine or oxygen, are fixed to platinum, the back donation is lowered resulting in a shift of the ν(CO) frequency towards high wave numbers. This kind of interaction is noticeable only when CO and the electron acceptor atom are fixed to the same platinum atom. In contrast with Lewis bases, the collective properties of the crystallites are not detected. The highest shift ($\Delta\nu = 75\ cm^{-1}$) is observed when two chlorine atoms are adsorbed on the same platinum atom as CO. When benzene is adsorbed on platinum, the shift observed indicates a net "flow of charge" towards the platinum crystallites; this is a proof of the existence of a π complex between benzene and platinum as an intermediate state in benzene hydrogenation. The ν(CO) frequency shift technique can be applied to the study of various catalytic reactions on metals.

INTRODUCTION

Numerous papers (*1*) have already been devoted to the infrared study of CO adsorption on supported metals. CO, which has electron donor properties, interacts easily with transition metals having incompletely filled orbitals, the very high extinction coefficient for the vibration ν(CO) making easy its detection by infrared spectroscopy.

Eischens and Pliskin (*2*) were the first to report an infrared study of CO adsorption on supported or unsupported platinum. The band corresponding to the stretching vibration ν(CO) of the species Pt–CO was observed at around 2060 cm^{-1} but the wavenumber increased with increasing coverage of the metallic surface. Using ^{12}CO and ^{13}CO molecules these authors concluded that this variation of frequency with platinum coverage was due to dipole–dipole coupling interactions. Heyne and Tompkins (*3*) also observed an increase of the frequency, and in addition an increase of the extinction coefficient when the coverage increases. Studying the interaction of Lewis bases with CO preadsorbed on platinum films, Queau and Poilblanc (*4*) observed a shift of the ν(CO) frequency towards low wave numbers. Eischens and Pliskin (*2*) mentioned a shift towards high wave numbers of the same

ν(CO) band when HCl was contacted with CO preadsorbed on platinum, but did not give further explanation.

It seems, therefore, that the vibration ν(CO) is modified when various gases interact with the metal. If the direction and the extent of the shift are determined by simple parameters such as the electron donor or acceptor properties of the adsorbate, it could be possible to predict by determining the frequency of the vibration, the nature of the bond between the adsorbed species and the metal, or the collective electronic properties of the metal.

It is for these reasons that we undertook a general investigation of the parameters able to modify the frequency of CO adsorbed on Pt/Al_2O_3 and tried to explain the results on the basis of electronic transfer.

EXPERIMENTAL METHODS

The catalyst used was a 10% platinum deposited on aluminum oxide P (Degussa). Its preparation has already been described in a previous paper (*5*). The pretreatment procedure was the following: after a reduction at 500°C under H_2 during 16 hr, the catalyst was evacuated under 10^{-6} Torr during 10 hr at the same temperature. We shall refer to the catalyst resulting from such a standard pretreatment as solid A.

In order to avoid pollution of the catalyst, we used sample holders made of quartz. For the same purpose, the tightness of CaF_2 discs was obtained with "Viton" O-rings (*6*). The various gases used were dried, before each experiment, on molecular sieves (Zeolite 5A, Union Carbide).

RESULTS AND DISCUSSION

A. CO Adsorption on Pt/Al_2O_3

CO adsorption on solid A at room temperature gave two bands at 2050 and 1870 cm^{-1} for low metallic surface coverage. When a coverage of unity was reached the first band, very intense and broad, was then centered between 2090 and 2060 cm^{-1}, whereas the second one was shifted to 1850 cm^{-1}. For higher pressures of CO, a third band at 2190 cm^{-1} appeared; this band which was eliminated under vacuum at room temperature corresponds to CO adsorbed on Lewis centers of the alumina (*7*).

The evacuation of the solid at increasing temperatures shifted the broad band towards low frequencies although the intensity was unchanged up to 300°C. Beyond this temperature, the intensity decreased whereas the frequency was fixed at a value of 2050 cm^{-1}. The 1870 cm^{-1} band of much lower intensity had the same thermal stability as the 2050 cm^{-1} one; both bands persisted until ca. 400°C.

These two bands at 2050 and 1870 cm^{-1} have already been mentioned in the literature by many authors. They were attributed either to linear (2050 cm^{-1}) and bridged forms (1870 cm^{-1}) of adsorbed CO (*8*) or to CO adsorbed on various sites of the surface (*9*) (linear form).

In order to explain the shift of the ν(CO) band observed for increasing coverage of the platinum surface, it is necessary to consider the type of bonding between CO and metals in carbonyl complexes (*10*). Such a model has already been extended to the case of CO chemisorption on metals and we shall see later in the paper that it can take into account most of our experimental data concerning the shifts of frequencies observed. We have represented in Fig. 1a the energy-level diagram of carbon monoxide according to Jaffe (*11*). The σ_C doublet on the carbon atom has the highest energy level and therefore the lowest ionization potential (14 eV). The formation of a σ bond results from the overlap of this σ_C orbital with an empty metal "*d*" orbital. This results in a rather weak bond: CO has low electron donor properties and gives stable complexes only with typical electron acceptors such as BH_3 (*12*). The thermal stability of the carbonyl complexes has been explained by the formation of a π bond between partially filled "*d*" orbitals of the metal and π^* orbitals of CO (Fig. 1b). This back bonding increases the force constant of the metal–carbon bond. Con-

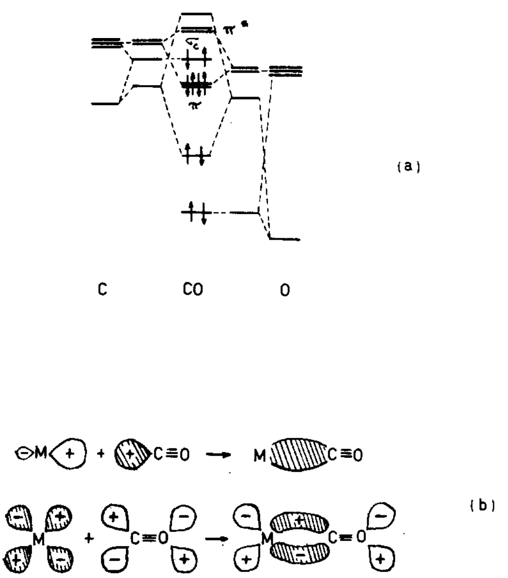


FIG. 1. (a) Energy-level diagram for CO molecule (*10*), (b) metal carbonyl bonding (*9*): formation of metal ← carbon σ bond, formation of metal → carbon π bond.

sequently when CO is adsorbed on the metal, it is assumed that electrons are transferred from the σ_C orbital of CO to the π^* level. Therefore, the chemisorption leads to a decrease of the force constant of the CO bond and a lowering of the CO frequency in comparison with gaseous CO.

The increase of the frequency ν(CO) with increasing coverage can be explained with the same model: for a given particle, the number of electrons available for the back donation decreases when the coverage increases, hence the ν(CO) frequency increases. This model is also able to explain why the absorption intensity increases when the coverage decreases, as found experimentally. Brown and Darensbourg (*13*) found that in metal carbonyls, the variations of the CO dipole moment increases with the extent of the π bond.

B. Interaction Between Adsorbed CO and Lewis Bases

In substituted carbonyl complexes $M(CO)_X L_Y$, the ν(CO) frequency depends upon the extent of the back bonding which is determined by the σ donor and π acceptor properties of the ligand L (*14*). Following the work of Queau and Poilblanc (*4*) on platinum films, we have studied the interaction of some Lewis bases with carbon monoxide preadsorbed on supported platinum. For this study, a known amount of CO was adsorbed on solid A so that the final platinum coverage was equal to 0.2 (solid B). Solid B which presented both bands at 2065 and 1850 cm^{-1}, was contacted with various Lewis bases of known ionization potential.

a. Water (ionization potential 12.6 eV). The introduction of an excess of water vapor on solid B resulted in a shift of the ν(CO) band from 2065 to 2050 cm^{-1}. Assuming that water is coordinately bonded to the metal by means of the oxygen doublet, the low shift observed must be connected with a small increase of the back donation; this result agrees with the low electron donor properties of the water molecule.

b. NH_3 (I.P. = 10.5 eV). NH_3 adsorption on solid B shifts the ν(CO) band from 2065 to 2040 cm^{-1} ($\Delta\nu \simeq 25$ cm^{-1}). Other bands situated at 3360, 3320, 3220, 3140, 1625, and 1265 cm^{-1} attributed to ammoniated complexes, were also obtained on the alumina support (*15*). As in the case of NH_3 adsorption on Pt/SiO_2 (*16*), no peak corresponding to $Pt\text{–}NH_2$ species was observed. Therefore, NH_3 adsorption on platinum does not seem to be dissociative; NH_3 is more likely coordinately bonded to the platinum by means of the nitrogen doublet, and the high shift observed corresponds to a high electron donor property of the molecule.

In order to determine the thermal stability of the $Pt\text{–}NH_3$ species, solid A was treated with ammonia at room temperature and then evacuated at 300°C. This treatment resulted in the disappearance of the bands corresponding to NH_3 adsorbed on the acidic sites of the solid. A known amount of CO was then adsorbed on the solid in order to reach a platinum coverage of 0.2. The resulting ν(CO) band had the same frequency as solid B, which means that NH_3 was no longer adsorbed on the platinum surface.

c. Pyridine (I.P.: 9.2 eV). The ad-

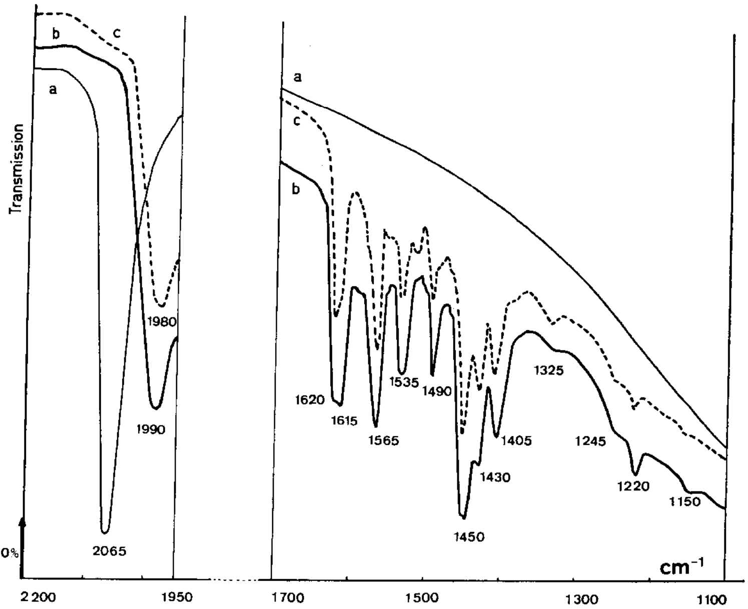


FIG. 2. Infrared spectra of pyridine adsorbed on Pt/Al_2O_3: (a) solid B, (b) introduction of pyridine at room temperature, (c) evacuation of sample at 150°C.

sorption of pyridine at room temperature shifted the ν(CO) band from 2065 to 1990 cm^{-1} (Fig. 2). Besides, the spectrum presented many peaks at 1620, 1565, 1535, 1490, 1450, 1430, 1325, 1245, 1220 and 1150 cm^{-1}.

If we compare this spectrum with that of pyridine adsorbed on γ-alumina (*17*) (see Table 1), we can conclude that the bands situated at 1620, 1490, 1450, 1245–1220, and 1150 cm^{-1} are due to pyridine adsorbed on the alumina carrier. However, the presence of pyridine alone cannot account for the peaks at 1535, 1430, and 1325 cm^{-1}. In fact the formation of dipyridyl, which would occur on platinum by cleavage of two CH bonds, can explain the new bands. By comparing these peaks with those of 2-2′-dipyridyl we can easily ascribe them to the vibration modes ν_{19a} (1535 cm^{-1}), ν_{14} (1430 cm^{-1}), and ν_3 (1325 cm^{-1}) of this compound. Most of the peaks of 2-2′-dipyridyl overlap the bands of adsorbed pyridine so that their identification is difficult. The attribution of the bands observed is given in Table 1.

The shift towards low frequencies for the ν(CO) band is a proof of an electron pair donation from the Lewis base (pyridine or dipyridyl) to the platinum crystallite.

d. Trimethylamine (I.P. = 7.9 eV). The shift observed when this compound interacted with CO at room temperature was equal to 75 cm^{-1}. This must be related with the low ionization potential of the trisubstituted amine.

e. Collective properties of the metal. As we have shown in the preceding paragraph, the adsorption of Lewis bases on platinum is able to increase the back-donation of the metal "*d*" electrons to the antibonding orbital of CO. This is a rather common phenomenon encountered in coordination chemistry, although it is not proved so far that "*d*" electrons are localized at the surface of a metallic particle. At this point, the question rises to know whether or not the collective properties of the metallic phase are able to play a role: is there any "long distance" interaction between the Lewis base and the Pt–CO bond? In order to elucidate this problem we introduced very small amounts of pyridine on solid B for which the platinum coverage by CO was equal to 0.2 (Fig. 3). The initial band was progressively shifted from 2065 to 1990 cm^{-1},

TABLE 1

INFRARED BANDS OBSERVED BY INTERACTION OF PYRIDINE AND 2,2′-DIPYRIDYL WITH LEWIS ACID CENTERS[a]

	Pyridine
Vibration	Pyridine adsorbed on aluminum oxide P (cm^{-1}) (17)
ν15	1145 (w)
ν 9a	1220–1235 (m)
ν19b	1444 → 1449 (v.s.)
ν19a	1487 → 1492 (m)
ν 8b	1576 (s)
ν 8a	1606 → 1620 (s)

	2,2′-dipyridyl	
Vibration	Liquid (19)	Ligand in the complexes of metallic ions (18)
ν15	1136 (s)	between 1170 and 1183
ν 3	1205 (s)	between 1112 and 1227
	1250 (s)	ca. 1258
	1266 (w)	between 1274 and 1324
ν14	1408 (v.s.)	between 1429 and 1449
ν19b	1449 (v.s.)	between 1449 and 1481
ν19a	1504 (m)	between 1512 and 1527
ν 8b	1550 (v.s.)	between 1582 and 1600
ν 8a	1575 (v.s.)	between 1600 and 1639

Bands observed (cm^{-1}) (present work)	Attribution
1615–1620	Pyridine (8a), 2,2′-dipyridyl (8a)
1565	2,2′-dipyridyl (8b), pyridine (8b)
1535	2,2′-dipyridyl (19a)
1490	Pyridine (19a)
1450	Pyridine (19b), 2,2′-dipyridyl (19b)
1430	2,2′-dipyridyl (14)
1405	—
1325	2,2′-dipyridyl (3)
1245–1220	Pyridine (9a)
1150	Pyridine (15)

[a] Intensity of the ir bands = very strong (v.s.), strong (s), medium (m), weak (w).

whereas a shoulder at 2065 cm^{-1} could still be detected during the first two increments. We have observed that the extent of the shift was proportional to the amount of pyridine introduced in the cell.

This experiment can be interpreted in the following way: pyridine is progressively adsorbed on the bare platinum so that the electronic density of the whole platinum particle increases and the back donation is progressively enhanced; the extent of the shift is maximum when all the platinum surface is covered with pyridine: we are therefore dealing here with a long-distance effect which implies collective properties of the metal. In our opinion the persistence of the 2065 cm^{-1} shoulder during the two first increments must be explained by a mass transfer due to the compressed disc: for very small doses of pyridine introduced some platinum particles, especially those in the bulk of the disc, are not touched due to slow diffusion. It is only when higher amounts of pyridine are introduced that all the platinum particles interact with pyridine.

It must be pointed out that the ν(CO) shift depends on the adsorbed Lewis base (L.B.). This shift increases when the first

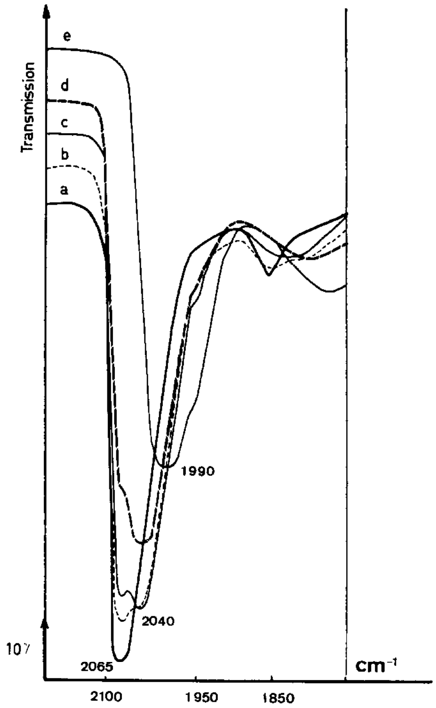


FIG. 3. Infrared spectra of pyridine adsorbed on Pt/Al_2O_3: (a) solid B, then introduction of increasing doses of pyridine in the order (b), (c), (d) up to the surface saturation (e).

ionization potential (I.P.) decreases. Two explanations can be advanced: (a) the coverage of the platinum by the L.B. increases when I.P. decreases so that the ratio L.B./CO is the highest for the lowest I.P. and (b) (for a given coverage by L.B.) the electron transfer from the L.B. to the metal is expected to vary inversely with I.P.

Since we do not know the ratio L.B./CO, it is not possible to distinguish between the two possibilities. Nevertheless, whether the two phenomena occur simultaneously or separately, both explanations account for the ν(CO) shift.

C. Interactions of Adsorbed CO with Electron Acceptor Compounds (or Atoms)

a. Hydrogen chloride. HCl adsorption on solid B shifted the 2065 cm^{-1} band to 2075 cm^{-1} (Fig. 4); the same shift was also observed when CO was adsorbed on solid A previously treated with HCl at room temperature. Since it is well known that HCl is dissociatively chemisorbed on the alumina at room temperature (*19*), it is hard to decide whether or not chlorine is also adsorbed on platinum. If there is no chlorine on platinum the shift observed could be attributed to a carrier effect (*33*). In order to elucidate the problem, we made the following experiment: solid B was treated with HCl at room temperature and then evacuated at 200°C. In this case it is well accepted that the carrier still retains an important amount of chloride ions (*20*). A subsequent adsorption of CO gave the initial band at 2065 cm^{-1} as for bare platinum, which rules out the possibility of a carrier effect.

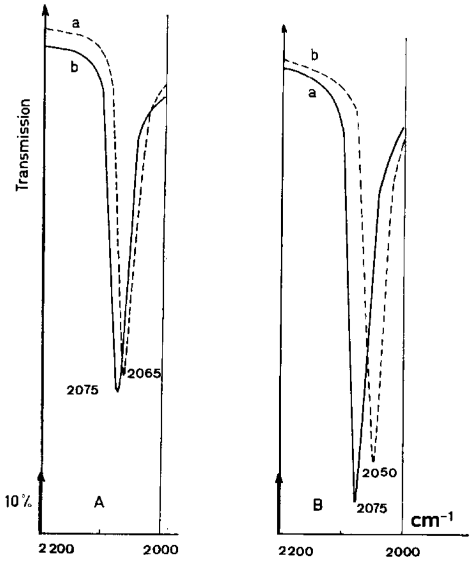


FIG. 4. Adsorption of hydrogen chloride on Pt/Al$_2$O$_3$: A (a) solid B; (b) after introduction of 50 Torr HCl at room temperature. B (a) Solid B after treatment under 50 Torr of HCl at 300°C during 30 min; (b) after desorption of HCl at 200°C during 4 h.

The ν(CO) shift from 2065 to 2075 cm^{-1} is due to the interaction of CO with HCl adsorbed on platinum. It is probably a dissociative chemisorption as it has already been observed in the case of HCl adsorption on Fe, Ni, Pd, Ag and Pb films (*21*) for temperatures higher than 30°C. Therefore, chlorine must be bonded to platinum and its electron acceptor properties decrease the back donation of platinum electrons to the antibonding orbital of CO, which results in an increase of the ν(CO) frequency. The interaction between platinum and chlorine does not proceed significantly through the carrier but directly on the platinum crystallite.

b. Oxygen. Interaction between oxygen in excess and a platinum surface completely covered with CO, followed by a vacuum treatment at room temperature, gave bands at 2120, 1640, 1480, and 3600 cm^{-1}. The last three bands have been attributed to carbonates and to bicarbonated species resulting from the interaction of OH group of the alumina with CO$_2$ (*22*) produced by the reaction:

$$\mathrm{Pt_S\text{-}CO + O_2\ (g) \longrightarrow Pt_S\text{-}O + CO_2\ (ads)}$$

The 2120 cm^{-1} band was also obtained when CO was adsorbed on an oxygen covered platinum surface. Its intensity could be greatly enhanced when many cycles (O$_2$, CO, O$_2$ . . .) or (CO, O$_2$, CO . . .) were performed on platinum (Fig. 5). Hydrogen adsorption on this oxygen treated solid decreased the intensity of the band

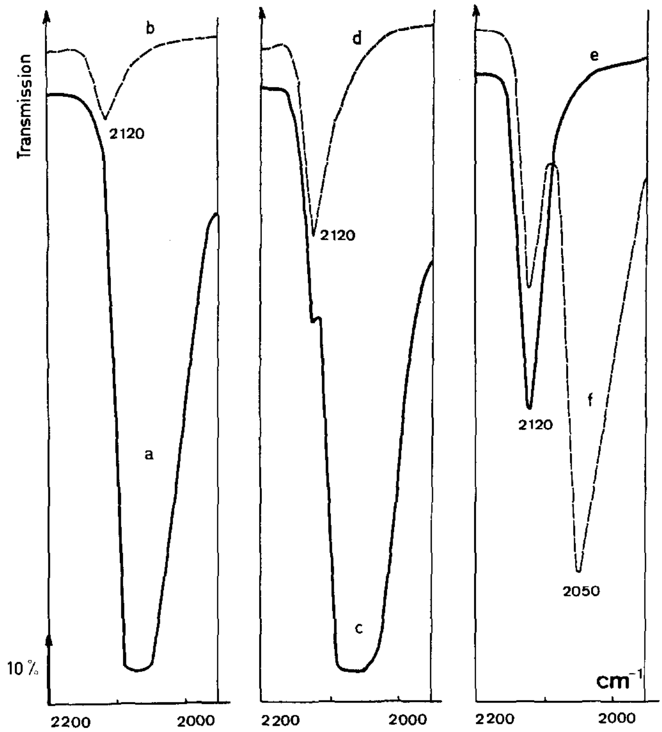
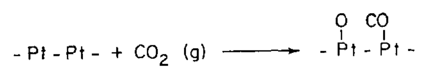


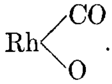
FIG. 5. Oxidation with oxygen of carbon monoxide adsorbed on Pt/Al_2O_3: (a) Solid A + CO at 25°C, evacuated at 25°C. (b) Introduction of O_2 (P = 20 Torr) at 25°C, evacuated at 25°C. (c) Introduction of CO (P = 20 Torr) followed by a desorption at room temperature. (d) Oxidation by oxygen, under vacuum at 25°C. (e) Solid obtained after a second cycle (c) + (d). (f) Introduction of 50 Torr of hydrogen at room temperature.

at 2120 cm^{-1}. The peak was wholly erased by an hydrogen treatment at 150°C, and it was replaced by the 2050 cm^{-1} band (Fig. 5). This 2120 cm^{-1} band is very likely due to a Pt–CO species interacting with an oxygen atom. In this case again the question rises to know whether or not there is a "long distance effect." The answer seems to be given by the following experiment. CO_2 adsorption on solid A gave a CO band close to 2050 cm^{-1} (and another band weaker at 1880 cm^{-1}), which corresponds to a dissociative adsorption of CO_2, probably according to the reaction



$$-Pt-Pt- + CO_2\ (g) \longrightarrow -\overset{O}{\overset{|}{Pt}}-\overset{CO}{\overset{|}{Pt}}-$$

A similar model has been advanced by Blyholder *et al.* (*23*) for CO_2 adsorption on iron which produces Fe–CO and Fe–O species.

The CO frequency is not modified by the oxygen atom adsorbed on an adjacent platinum atom. Therefore, we must consider that, in the case of the 2120 cm^{-1} band, the oxygen atom is bonded to the same platinum atom as CO; this has already been postulated by Garland *et al.* (*24*) in the case of rhodium, who observed a frequency at 2120 cm^{-1} for the species  $Rh\langle^{CO}_{O}$. Heyne and Tompkins (*25*) also mentioned a peak at 2120 cm^{-1} when carbon monoxide is introduced on platinum previously treated with oxygen at 300°C. They ascribed it to a carbonyl group adsorbed on a Pt^{2+} ion: this is not significantly different from our interpretation since Pt^{2+} could represent the formal oxidation state of platinum in the case of a surface of platinum oxide. Still, this interpretation corresponds to a decrease of the electronic density of the platinum.

Consequently, the weakening of the Pt–CO bond resulting from the interaction with an oxygen atom does not involve the collective properties of the metal: it is rather a localized phenomenon between oxygen and CO adsorbed on the same platinum atom.

c. Interaction between phosgene and platinum. The surface reaction between phosgene and alumina has already been studied in the range of temperature 0–200°C (*20*). When the alumina is highly dehydrated, the reaction proceeds by exchange of one surface oxygen atom for two chlorine atoms with formation of gaseous CO_2. For aluminas with high hydroxyl content, $COCl_2$ reacts with OH groups and produces HCl and CO_2.

Phosgene adsorption at room temperature on solid A gave a band at 2075 cm^{-1} (Fig. 6) which must be attributed to a Pt–CO species interacting with a chlorine atom (see paragraph *C*.a.).

When phosgene was adsorbed on solid A at 200°C the spectrum presented various bands situated at 2190, 2135, and 2090 cm^{-1} (Fig. 6). The 2190 cm^{-1} band, eliminated under vacuum at room temperature, is due to CO adsorbed on the alumina (*7*). The carbon monoxide would be produced by the thermal decomposition of $COCl_2$ on platinum. The 2090 cm^{-1} band corresponds to a species irreversibly adsorbed at room temperature; it was eliminated under oxygen at 25°C and can be attributed to a Pt–CO species interacting with chlorine atoms. The 2135 cm^{-1} band was not erased under O_2 at 300°C. Upon treatment under hydrogen between 200 and 500°C, this band was progressively removed and replaced by a peak situated around 2075 cm^{-1}. The intensity of the 2135 cm^{-1} band was significantly enhanced upon treatment of the solid with CO. The attribution of this band is possible if we refer to the ν(CO) frequency of the carbonyl complexes of platinum such as $(Pt\,CO\,X_2)_2$. This ν(CO) frequency, which depends upon the electron acceptor properties of the (ligand) *X*, varies from 2146 cm^{-1} for $X = Cl$ to 2122 cm^{-1} for $X = I$. Therefore, we can ascribe the 2135 cm^{-1} band to a platinum complex arising from the dissociative chemisorption of phosgene at moderate temperature (200°C):

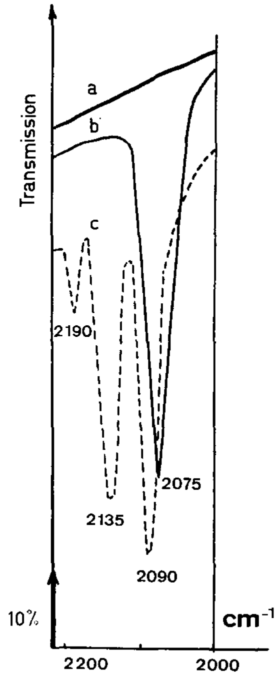
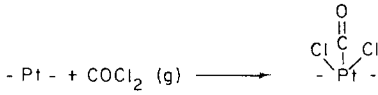
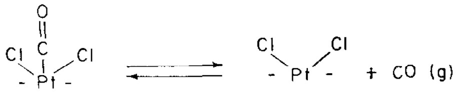


FIG. 6. Adsorption of phosgene on Pt/Al_2O_3: (a) solid A, (b) introduction of 10 Torr $COCl_2$ at 25°C, (c) after heating at 200°C during 2 hr.



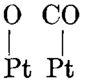
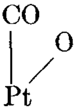
This complex is able to decompose according to the reaction:

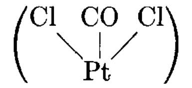
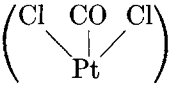


The equilibrium is displaced to the left under CO. The same complex decomposes under hydrogen with formation of hydrogen chloride adsorbed on platinum and alumina.

Although our results cannot be summarized in a single theory, the simple model of a σ and π bond between CO and the platinum is able to explain the direction of the shift and its extent when various compounds are interacting with chemisorbed CO.

When Lewis bases are adsorbed on platinum, by means of a donor–acceptor bond, the back donation of *d* electrons of platinum increases and the ν(CO) frequency decreases. This is a "long distance" interaction which implies that the collective properties of the crystallite play an important role; the ν(CO) frequency is a witness of the electronic density of the crystallite.

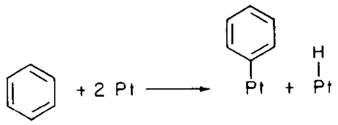
When electron acceptor compounds interact with chemisorbed CO by means of a σ bond, the back donation of *d* electrons decreases so that the ν(CO) frequency increases. However, in contrast with Lewis bases, the effect is detected only when the interaction is localized. Indeed, with  $\begin{array}{cc} O & CO \\ | & | \\ Pt & Pt \end{array}$ surface complex, we have no shift of the ν(CO) band whereas with the species  $\begin{array}{ll} CO & \\ | & O \\ | \diagup & \\ Pt & \end{array}$ the shift is very significant.

Besides, the replacement of the 2135 cm^{-1} band  $\left(\begin{array}{ccc} Cl & CO & Cl \\ \diagdown & | & \diagup \\ & Pt & \end{array}\right)$ by the 2075 one, upon hydrogen treatment, is not a progressive shift. The discontinuity suggests strongly a very localized interaction which does not involve collective properties of the metal. In species such as  $\left(\begin{array}{ccc} Cl & CO & Cl \\ \diagdown & | & \diagup \\ & Pt & \end{array}\right)$ for which the highest shift is observed ($\Delta\nu = 75$ cm^{-1}), platinum involved in this surface complex might have lost its metallic character.

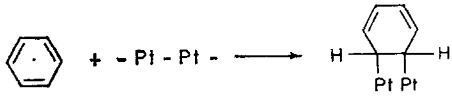
D. Application to Catalysis: Benzene Adsorption on Platinum

We have seen in the preceding parts of the paper that the position of the ν(CO) frequency is able to supply information about the nature of the bond between the adsorbed species and the catalyst, provided these species do not displace carbon monoxide from the surface.

Concerning benzene adsorption on platinum (*27*) many hypotheses have been postulated in order to explain the results obtained for benzene hydrogenation or benzene-deuterium exchange. Farkas and Farkas (*28*) propose a dissociative chemisorption of benzene:



Horiuti and Polanyi (*29*) postulate that the unsaturated hydrocarbon chemisorbs by the opening of the double bond:



Garnett (*30*) was the first to propose a π complex adsorption. In this case, in contrast with the classical dissociative theory, there is a "net flow of charge" towards the platinum. There is no experimental proof, so far, in favor of any one of these hypotheses; it is for this reason that we undertook the study of the interaction between benzene and platinum by means of the ν(CO) frequency shift.

Benzene adsorption at room temperature on solid B, followed by evacuation at the same temperature shifted the ν(CO) band from 2065 to 2025 cm^{-1} (Fig. 7). The peaks of small intensity (around 3,000 cm^{-1}) are due to benzene chemisorbed on alumina or platinum. The treatment of the sample under hydrogen instantaneously produced two bands at 2990 and 2840 cm^{-1} attributed to cyclohexane which was easily desorbed under vacuum at room temperature. Besides, the ν(CO) frequency recovered almost its initial value (2055 cm^{-1}).

The shift of the ν(CO) frequency from 2065 to 2025 cm^{-1} is a proof of the flow of charge towards platinum when benzene is adsorbed; this shift is therefore a strong

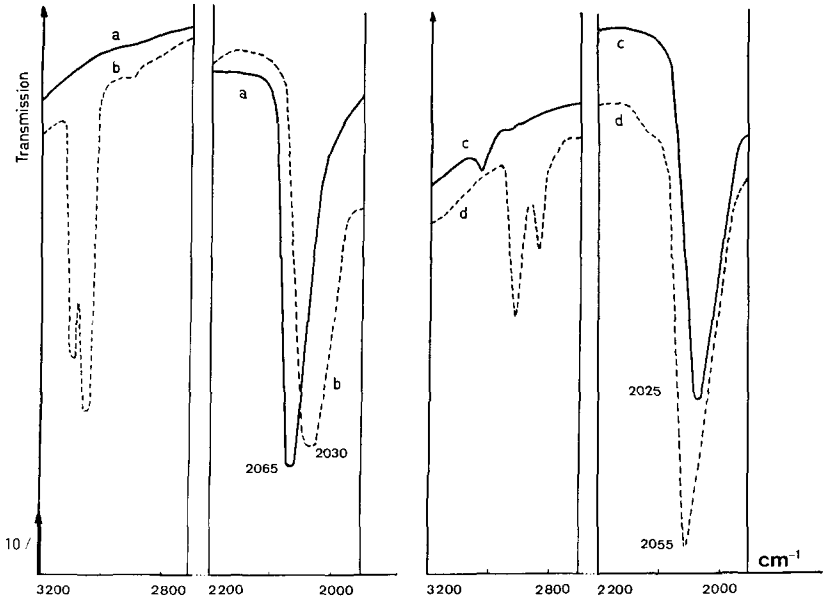


FIG. 7. Adsorption of benzene on Pt/Al_2O_3: (a) solid B, (b) introduction of 30 Torr C_6H_6 at 25°C, (c) under vacuum at 25°C, (d) introduction of 100 Torr of hydrogen at room temperature.

support in favor of the π complex adsorption model proposed by Garnett and rules out the classical dissociative mechanisms. We have verified that the dissociative adsorption of H_2 on platinum had almost no influence on the ν(CO) vibration.

The shift of the ν(CO) frequency is the best way to determine the nature of the bond between benzene and platinum: the direct investigation of the ν(CH) vibrations of the adsorbed hydrocarbon is not very sensitive due to the low extinction coefficient of these vibrations. As a matter of fact, in π-arene complexes such as Cr $(CO)_3\pi$–C_6H_6 (*31*), the bands of the aromatic ring are much weaker than those of CO. The fact that we did not observe bands due to adsorbed C_6H_6 is not a proof of the loss of aromatic character (*32*).

E. Conclusion

The ν(CO) vibration of CO adsorbed on platinum is very sensitive to the extent of the back bonding: the shifts of frequency give very useful information on the overall flow of charge resulting from the chemisorption of compounds on the platinum crystallites.

Chemisorption of Lewis bases increases the electronic density of the metal which results in a shift of the ν(CO) frequency toward low wave numbers. This process involves the collective properties of the crystallite.

The fixation on platinum of electron acceptor elements such as chlorine or oxygen decreases the electronic density of the metal. However, in contrast with Lewis bases, this kind of interaction seems to be localized and does not involve the electronic collective properties of the metal.

The shift of the ν(CO) vibration when benzene is adsorbed on platinum has shown a net flow of charge from benzene to platinum; this is a proof of the existence of a π complex between benzene and platinum, as the intermediate state in benzene hydrogenation.

As a conclusion, the shift of the ν(CO) frequency, upon the subsequent adsorption of various compounds, seems to be an interesting tool to determine the type of bonding of adsorbed phases, and we will apply this "technique" to the study of various catalytic reactions on metals, or interactions of metals with carriers (*33*).

References

1. Little, L. H., "Infrared Spectra of Adsorbed Species," Academic Press, London and New York, 1966.
2. Eischens, R. P., and Pliskin, W. A., *Advan. Catal. Relat. Subj.* **10,** 1 (1958); Eischens, R. P., *Accounts Chem. Res.* **5**, 74 (1972).
3. Heyne, H., and Tompkins, F. C., *Trans. Faraday Soc.* **63,** 1274 (1967).
4. Queau, R., and Poilblanc, R., *C. R. Acad. Sci. Paris* **274C,** 337 (1972); Queau, R., and Poilblanc, R., *J. Catal.* **27,** 200 (1972).
5. Primet, M., Basset, J. M., Mathieu, M. V., and Prettre, M., *J. Catal.* **28,** 368 (1973).
6. Bozon-Verduraz, F., Contour, J. P., and Pannetier, G., *C. R. Acad. Sci. Paris* **269C,** 1436 (1969); Contour, J. P., Thesis, Paris (1970).
7. Parkyns, N. D., *J. Amer. Chem. Soc.* **41,** 121 (1966).
8. Cable, J. W., and Sheline, R. K., *Chem. Rev.* **56,** 1 (1956).
9. Blyholder, G. J., *Phys. Chem.* **68,** 2772 (1964); Blyholder, G. J., and Allen, M. C., *J. Amer. Chem. Soc.* **91,** 3158 (1969).
10. Cotton, E. A., and Wilkinson, G., "Advances Inorganic Chemistry," p. 616, Interscience New York, 1962.
11. Jaffe, H. H., and Orchin, M., *Tetrahedron* **10,** 212 (1960).
12. Labarre, J. F., and Leibovici, C., *J. Chim. Phys.* **69,** 404 (1972).
13. Brown, T. L., and Darensbourg, D. J., *Inorg. Chem.* **6,** 971 (1967).
14. Poilblanc, R., and Bigorgne, M., *Bull. Soc. Chim. Fr.* **7,** 1301 (1962).
15. Pichat, P., Mathieu, M. V., and Imelik, B., *J. Chim. Phys.* **66,** 845 (1969).
16. Griffiths, D. W. L., Hallam, H. E., and Thomas, W. J., *Trans. Faraday Soc.* **64,** 3361 (1968).
17. Pichat, P., Mathieu, M. V., and Imelik, B., *Bull. Soc. Chim. Fr.* **8,** 2611 (1969).
18. Singh, S. S., and Sengar, C. B. S., *Israel J. Chem.* **7,** 471 (1969).
19. Tanaka, M., and Ogasawara, S., *J. Catal.* **16,** 157 (1970); Peri, J. B., *J. Phys. Chem.* **70,** 1482 (1966).
20. Basset, J. M., Thesis, Lyon (1969); Basset, J. M., Mathieu, M. V., and Prettre, M., *Rev. Chim. Min.* **5,** 879 (1968); Mutin, R., Basset, J. M., and Prettre, M., *C. R. Acad. Sci. Paris* **273C,** 1704 (1971).
21. Dadiza, Y. M., and Saleh, J. M., *J. Chem. Soc. Faraday Trans.* **2,** 269 (1972).
22. Parkyns, N. D., *J. Chem. Soc.* **A,** 410 (1969).
23. Blyholder, G., and Neff, L. D., *J. Phys. Chem.* **66,** 1464 (1962).
24. Garland, C. W., Lord, R. C., and Troiano, P. F., *J. Phys. Chem.* **69,** 1188 (1965).
25. Heyne, H., and Tompkins, F. C., *Proc. Roy. Soc.* **A292,** 460 (1966).
26. Irving, R. J., and Magnusson, E. A., *J. Chem. Soc.* 2283 (1958).
27. Bond, G. C., "Catalysis by Metals," Academic Press, London and New York, 1962; Germain, J. E., "Catalytic Conversion of Hydrocarbons," Academic Press, London and New York, 1969.
28. Farkas, A., and Farkas, L., *Trans. Faraday Soc.* **35,** 917 (1939).
29. Horiuti, J., and Polanyi, M., *Trans. Faraday Soc.* **30,** 1164 (1934).
30. Garnett, J. L., *Catal. Rev.* **5,** 229 (1971).
31. Adams, D. M., "Metal-Ligand and Related Vibrations," Edward Arnold, London, 1967; Fritz, H. P., and Manchot, J., *Spectrochim. Acta* **18,** 171 (1962); Ibid., *Z. Naturforsch.* **176,** 711 (1962).
32. Erkelens, J., and Eggink-du Burk, S. H., *J. Catal.* **15,** 62 (1969).
33. Dalla Betta, R. A., and Boudart, M., "Proc. Vth International Congress on Catalysis," Palm Beach, 1972, in press.