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PYRIDINE INDUCED DISPROPORTIONATION REACTION OF $Co_2(CO)_8$ IN THF: HOMONUCLEAR ION PAIRS AND DIHYDROGEN ACTIVATION

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Summary

The IR spectra of the $Co^{2+}/Py/Co(CO)_4^-$ system in THF reveal complex associative phenomena. Three kinds of homonuclear ion pairs were distinguished by means of variable temperature IR spectroscopy. Under the conditions in which these associative equilibria exist cobalt(II) is reduced by dihydrogen to cobalt($-$I) under 1 atm of syngas at room temperature.

Introduction

Close relationships have been observed between ion pairing and reactivity of carbonylmetallates [1]. Our attention in this field is directed to homonuclear ion pairs (HNIP) containing the same transition metal in both the anion and the cation. In the case of cobalt under suitable conditions we were able to observe directly association equilibria between Co^{2+} and $Co(CO)_4^-$, i.e. the products of the water-induced disproportionation of $Co_2(CO)_8$ (I) in THF. Electron transfers from the anion to the cation occur readily, as shown by the existence of equilibrium 1 at room temperature or below [2].

$$\tfrac{3}{2}Co_2(CO)_8 \xrightleftharpoons{H_2O,\ THF} Co^{2+} + 2\ Co(CO)_4^- + 4\ CO \qquad (1)$$

It is noteworthy that unsaturated organic substrates and simple molecules can be involved in these electron transfers, Co^{2+}, $Co(CO)_4^-$, olefins, CO and dihydrogen being converted to acylcobalt tetracarbonyls at room temperature and atmospheric pressure (eq. 2) [3].

$$Co^{2+} + 2\ Co(CO)_4^- + \tfrac{1}{2}H_2 + 5\ CO + \text{olefin} \xrightarrow{1\ \text{atm},\ 23^\circ C} (CO)_4CoC(O)R + Co_2(CO)_8 \qquad (2)$$

Reaction 2 is relevant to a better understanding of the role played by cobalt carbonyls in the dihydrogen activation required for the formation of acyls, which are possible intermediates in the catalytic hydroformylation of olefins.

More generally, the HNIP-promoted activation of dihydrogen may constitute an important aspect of metal carbonyl chemistry. The present paper describes the properties of $[CoPy_6][Co(CO)_4]_2$ (II), [4] in THF, and presents evidence that $Co^{2+}/Co(CO)_4^-$ HNIP are involved in the reduction of cobalt(II) to cobalt(−I) by dihydrogen at room temperature and atmospheric pressure.

Experimental

Unless otherwise stated, all manipulations were carried out under prepurified argon.

Infrared spectra were recorded on a Perkin–Elmer 983 model spectrophotometer; absorptions due to THF were automatically subtracted. Variable temperature measurements were carried out by means of a Specac apparatus in an 0.1 mm CaF_2 cell.

Chemicals. Tetrahydrofuran (THF) and pyridine (Py) were obtained from Prolabo Co., THF was distilled from $LiAlH_4$ and Py from CaH_2 after 48 h of reflux. $Co_2(CO)_8$ (I) was purchased from Strem Chemicals and sublimed (38°C/0.1 mmHg). H_2, CO and a 1/1 mixture thereof were pure gases supplied by Rivoira Co..

$[CoPy_6][Co(CO)_4]_2$, (II). The compound was prepared as described in ref. 4. Prolonged drying of the product under vacuum results in loss of pyridine and darkening.

Reaction of II with syngas. 1.2 g (1.37 mmol) of II were dissolved in 100 ml of THF and the resulting green solution was stirred under 1/1 syngas at atmospheric pressure and room temperature (20–28°C). Gas absorption took place, and the colour became red orange during 30 h. Anhydrous LiCl (1.5 g) was then added to the stirred solution which turned pale yellow as a colourless precipitate separated. The solid was filtered off, washed with 20 ml of THF, dissolved in water, and titrated potentiometrically against 0.10 *N* NaOH. The shape of the titration curve was consistent with the neutralization of PyHCl. The end point was reached after the addition of 37 ml of base (90% yield based on eq. 4).

Results and discussion

As pointed out by Hieber [4], II is red orange in the solid state but its THF solutions are green. The IR spectrum of solid II as a Nujol mull shows a single broad band at 1880 cm^{-1} indicative of an essentially unperturbed $Co(CO)_4^-$ in T_d symmetry [5]. However, the Co stretching region of an IR spectrum of II in THF obscured by various bands which change their relative intensity on varying the temperature or concentration: owing to association with Co^{2+}, the symmetry of $Co(CO)_4^-$ is reduced and HNIP are apparent. Each different kind of HNIP is expected to have its own spectrum [6]. The observed spectrum for II under specific conditions is the sum of the spectra from the various types of HNIP present. In order to interpret the nature of these cation–anion interactions the spectrum of each type of HNIP must be distinguished. This was achieved by studying the IR spectra of an 0.014 *M* THF solution at 10° intervals in the range 230–340 K. In addition to the 1887 cm^{-1} band attributable to unperturbed $Co(CO)_4^-$, three groups of bands

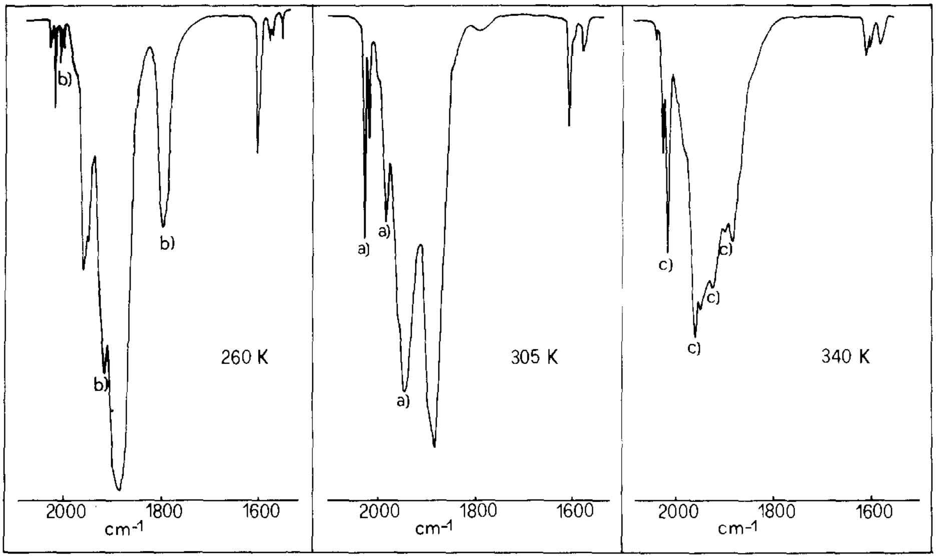
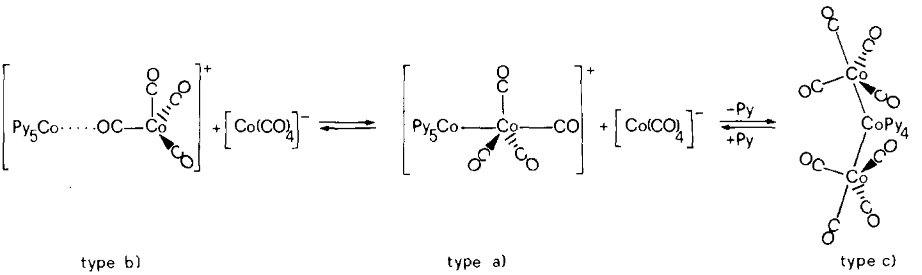


Fig. 1. The infrared spectra of II, 0.014 *M* in THF. 260–340 K.

were found to change their intensities with temperature in a parallel way within each group and therefore they were attributed to three different types of HNIP. The group (a) of bands (2059(m), 1986(m) and 1947(s) cm^{-1}) progressively disappear at both high and low temperatures, and reach a maximum at 305 K (Fig. 1, middle).

We conclude that the three bands arise from the same kind of HNIP (type (a)). The frequencies of all these are higher than that of unperturbed $Co(CO)_4^-$ in high dielectric constant solvents, thus indicating that there is a covalent interaction between Co^{2+} and $Co(CO)_4^-$, electron density being donated to Co^{2+} by $Co(CO)_4^-$ [7]. Furthermore the spectrum of type (a) HNIP closely resembles that of the metal-to-metal tight ion pair Tl...$Co(CO)_4$ in low dielectric constant solvents [8a,8b]. On these grounds we assign the structure of Scheme 1 to type (a) HNIP. As noted above, group (a) bands fall in intensity as the solution temperature is lowered, while the 1887 cm^{-1} band increases in intensity and three new absorptions (2018(w), 1918(m) and 1798(m) cm^{-1}) become evident, constituting group (b) bands (Fig. 1, left). These intensity variations show an increased concentration of $Co(CO)_4^-$ in an



SCHEME 1. Equilibria among various types of cobalt HNIP in a THF solution of II under an inert atmosphere.

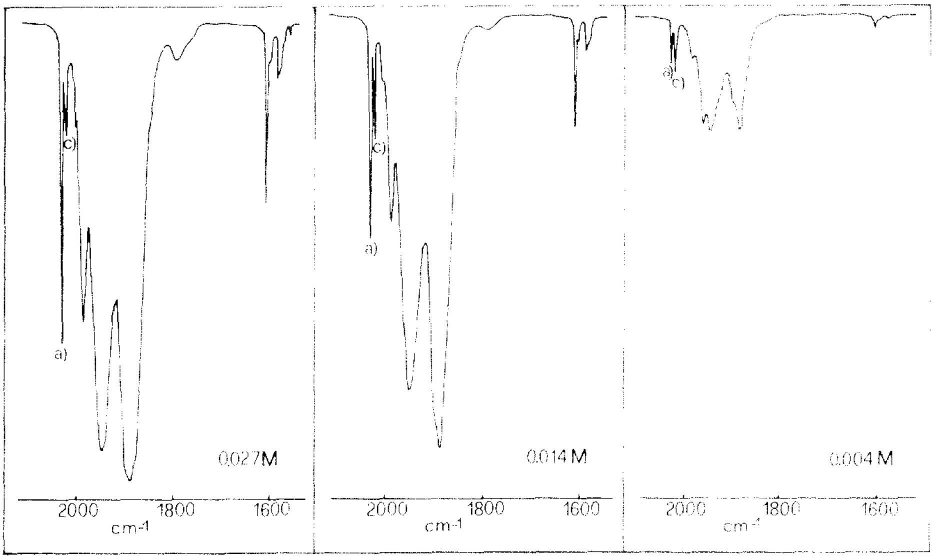


Fig. 2. The infrared spectra of II at 305 K, 0.027–0.004 *M* in THF.

essentially symmetric environment, and the three new absorptions relate to a type (b) HNIP, which presumably involve a Co^{2+}/Co(CO)$_4^-$ association through a carbonyl oxygen; the low frequency band (1798 cm^{-1}) and the two higher frequency bands (2018 and 1918 cm^{-1}) are expected for a Co(CO)$_4^-$ in C_{3v} symmetry, with a CO group interacting directly with the acidic countercation. As the temperature is raised above 305 K, the group (a) bands and the 1887 cm^{-1}absorption both fall in intensity, giving way to bands of a third group (c) (2040(m), 1963(s), 1929(m) and 1903(w) cm^{-1}) (Fig. 1, right). Both type (a) HNIP and unperturbed Co(CO)$_4^-$ are converted into a type (c) HNIP, which therefore has two Co(CO)$_4^-$ anions located in the coordination sphere of Co^{2+} cation. As discussed above for type (a) HNIP, the lack of ν(CO) absorptions at lower frequencies than that of unperturbed Co(CO)$_4^-$ indicates that this kind of association occurs through cobalt atoms, and results in cobalt–cobalt covalent interaction. On the basis of these observations, the equilibria among different HNIP summarized in Scheme 1 can be suggested.

As mentioned previously, the gross concentration of II in THF affects these equilibria. At constant temperature (305 K), the IR spectra of concentrated solutions (0.014–0.027 *M*) show that the 2059 cm^{-1} band of the dinuclear type (a) HNIP is more intense than the 2040 cm^{-1} band of the trinuclear type (c) HNIP (Fig. 2, middle and left), while in more dilute solutions (0.004 *M*) the opposite is the case (Fig. 2, right). It appears therefore that as the concentration is increased, Co^{2+} associates preferentially with only one Co(CO)$_4^-$, the formation of the trinuclear type (c) being inhibited. This feature may arise from that HNIP formation when II is dissolved in THF involves release of "free" pyridine in solution as a consequence of substitution by Co(CO)$_4^-$ in the complex cation [CoPy$_6$]$^{2+}$. Thus, in more concentrated solutions a relatively high concentration of "free" pyridine released in the formation of type (a) HNIP hinders formation of type (c) HNIP in accord with the equilibria shown in Scheme 1.

The equilibrium between II and I in THF

Analogies between spectroscopic properties of II in THF and other ion pairs, mainly studied by Edgell and Darensbourg, allowed us to establish the multiplicity and nature of $Co^{2+}/Co(CO)_4^-$ HNIP. We should emphasize that homonuclearity in ion pairs results in a chemistry which cannot be related to Co^{2+} or $Co(CO)_4^-$ separately. Formally, the oxidation state of cobalt atoms in type (c) HNIP can be averaged at zero, and we found that solutions of II in THF behave as though unsaturated cobalt(0) atoms were present.

A 0.014 M solution of II in THF reacts readily with CO at 305 K and P(CO) 520 mmHg, 1.09 mol of CO per mol of II being absorbed in minutes. The reaction can be reversed by pumping away the CO, so that under an inert atmosphere the IR spectrum of the solution is that shown in the middle of Fig. 1, whereas that shown in Fig. 3 is observed under CO at 1 atm of total pressure.

Comparison between the two shows that bands due to type (a) HNIP and to unperturbed $Co(CO)_4^-$ weaken under CO, as new absorptions appear in the 2110–1960 cm^{-1} region and at 1843 and 1828 cm^{-1}, suggesting the presence of products of type $Co_2(CO)_{8-n}Py_n$ ($n = 1, 2$) with edge-bridging CO groups [9a,b]. Since under CO this last class of products can be regarded as being in equilibrium with I, these results suggest that II and I are the two extremes of a series of equilibria, the components of which are indicated in Scheme 2.

$$Co_2(CO)_8 + n\,Py \rightleftarrows Co_2(CO)_{8-n}Py_n + n\,CO$$

$$Co_2(CO)_{8-n}Py_n + \cdot Co(CO)_4 \underset{-CO}{\overset{+Py}{\rightleftarrows}} \underset{\text{type (c)}}{(OC)_4Co\cdots CoPy_4\cdots Co(CO)_4}$$

$$\underset{\text{type (c)}}{(OC)_4Co\cdots CoPy_4\cdots Co(CO)_4} + Py \rightleftarrows \underset{\text{type (a)}}{[Py_5Co\cdots Co(CO)_4]^+} + [Co(CO)_4]^-$$

$$\Big\uparrow\!\Big\downarrow {\scriptstyle +Py}$$

$$[CoPy_6]^{2+} + 2[Co(CO)_4]^-$$

SCHEME 2. Some components of equilibria observed in the $Co^{2+}/Py/Co(CO)_4^-$ system in THF under CO.

Starting from II in THF, as a consequence of the formation of type (c) HNIP and replacement of pyridine by CO, gradual electron transfer from $Co(CO)_4^-$ to Co^{2+} occurs, giving rise to CoL_4 (L = Py, CO) radicals which eventually pair up to form dinuclear species $Co_2(CO)_{8-n}Py_n$. Starting on the other side from I and pyridine, an increasing degree of replacement of CO by pyridine leads to increase in the electron density in $Co_2(CO)_{8-n}Py_n$ species, thus presumably weakening the Co–Co bond for electronic and steric reasons. In order to confirm this view, the direct reaction of I with pyridine in THF was investigated by means of IR spectroscopy. At constant temperature (305 K) and concentration of I (0.021 M), the Py/I molar ratio was varied from 20 to 4 and 1.6. For each molar ratio solutions equilibrated either under CO or under an inert atmosphere and were examined. For reactions under an inert atmosphere or under CO a large excess of pyridine ($Py/I > 20$ molar ratio) induces Hieber's reaction (eq. 3).

$$\tfrac{3}{2}Co_2(CO)_8 \xrightarrow[\text{THF}]{\text{excess of pyridine}} [CoPy_6]^{2+} + 2[Co(CO)_4]^- + 4\,CO \tag{3}$$

At a Py/I molar ratio of 4 the IR spectrum of the solution equilibrated under CO

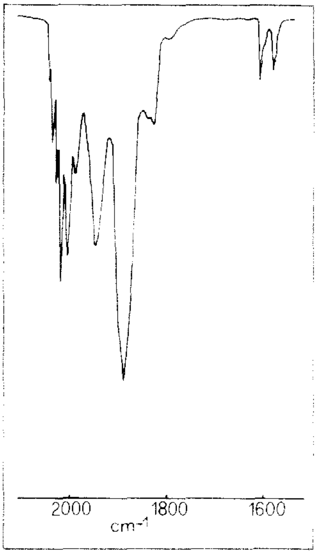


Fig. 3. The infrared spectrum of II 0.014 *M* in THF, equilibrated at 305 K under 520 mmHg CO pressure.

was superimposable on that in Fig. 3, and became that shown in the middle part of Fig. 1, under an inert atmosphere. This confirms that treating II with CO or I with pyridine gives rise to the equilibria shown in Scheme 2, the relative concentrations of the various components being a function of temperature, *P*(CO), and the pyridine and cobalt concentrations. Finally, at a Py/I molar ratio of 1.6 I was found to participate directly in the equilibria of Scheme 2. In the IR spectrum of the solution under Co, a band at 2118 cm^{-1} reveals the presence of unreacted I; under an inert atmosphere this band disappears as absorptions due to type (a) HNIP and unperturbed $Co(CO)_4^-$ grow.

On the basis of these findings it seems that to describe the reaction between I and pyridine as a disproportionation is restrictive, since only the last component of the equilibria in Scheme 2 would be accounted for. In Scheme 2 the sequence of equilibria from I to II provides a suitable mechanism for the base-induced disproportionation of I. At the same time, since for a wide range of cobalt concentrations, Py/I molar ratios, *P*(CO) and temperatures, intermediates were found to be present, the reaction between I and moderate amounts of pyridine cannot any longer be regarded as a disproportionation.

Bases-promoted dihydrogen activation in cobalt carbonyl solutions

It is likely that bases other than pyridine can give rise to a similar chemistry: the water-induced overall equilibrium 1 presumably involves equilibria of the type shown in Scheme 2, with water replacing pyridine. It has already been pointed out that solutions in which equilibrium 1 is operating allow reaction 2 and deuterium exchange with hydrogen atoms of H_2O to occur under mild conditions [10]. We have now observed that dihydrogen activation at room temperature and atmospheric pressure also occurs in solutions in which equilibria of Scheme 2 are present. Upon stirring a 0.014 *M* solution of II in THF under CO/H_2 1/1 at room temperature and atmospheric pressure gas absorption takes place, and in 30 h the colour changes from deep green to red orange. The IR spectrum of the resulting solution is much simpler, the intense band at 1887 cm^{-1} showing unperturbed $Co(CO)_4^-$ to be almost the only carbonyl species present in solution. As for the countercation, the absorption at 1638 cm^{-1} suggests the presence of protonated pyridine [11] while the absence of a 1598 cm^{-1} band indicates that no "free" pyridine is present. The cation PyH^+ was precipitated as PyHCl in 90% yield by adding an excess of LiCl. The overall reaction can therefore be formulated as in eq. 4.

$$[CoPy_6][Co(CO)_4]_2 + 4\ Co + \tfrac{3}{2}H_2 \rightarrow 3[HPy_2]^+ + 3[Co(CO)_4]^- \qquad (4)$$

Formally, the Co^{2+} cation is reduced by dihydrogen under CO to $Co(CO)_4^-$. However, in view of our findings about the nature of II in solution, the dynamic situation represented by the whole set of equilibria in Scheme 2 must be taken into account in reaching a better understanding of reaction 4. The present work may help to explain the apparent inconsistency between the pyridine-induced disproportionation of I and the accelerating effect of moderate amounts of base in dihydrogen activation promoted by cobalt carbonyls [12].

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