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Infrared spectroscopic studies of the reactions between $Co_2(CO)_8$, H_2 and D_2*

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Abstract

The reaction of $Co_2(CO)_8$ with D_2 does not have as product the expected $DCo(CO)_4$ only but gives rise to a mixture of $DCo(CO)_4$ and $HCo(CO)_4$. This phenomenon, observed also with other metal carbonyl hydrides, was explained by the fact that the reaction-vessel walls were covered by a polymeric layer of water which caused a very fast exchange with the deuterium in $DCo(CO)_4$, and hence this was the source of hydrogen in the formation of $HCo(CO)_4$. In this present work, we attempt to obtain alkane solutions of $DCo(CO)_4$ with very high deuteride content in order to study the spectral and chemical properties of this elusive compound. In concentrated solutions of $DCo(CO)_4$, having only traces of $Co_2(CO)_8$, an absorption band at 2048 cm^{-1} was observed, and attributed to a C–O stretching fundamental mode of $DCo(CO)_4$. This band corresponds to the 2052 cm^{-1} band found in $HCo(CO)_4$. In both cases it can be assigned to the a_1 mode in which the axial and equatorial CO groups stretch out of phase. Another band, the total symmetric ν(C–O) mode at 2116.3 cm^{-1}, is only 0.4 cm^{-1} lower in energy than the corresponding band of $HCo(CO)_4$. The extinction coefficients for several significant absorption bands of $DCo(CO)_4$ were calculated. The high pressure IR spectroscopic analysis, previously applied to calculate cobalt carbonyl concentrations in a three-component system, has proven itself to be quite accurate in the present case as well. Using the quantitative data obtained, the equilibrium constants for the reaction between $Co_2(CO)_8$ and D_2 were obtained. Finally, the effect of the presence of H_2O or D_2O on $H/DCo(CO)_4$ mixtures was studied and compared to the exchange with H_2 and D_2 in the gas phase.

Introduction

Several mononuclear and polynuclear cobalt carbonyl complexes have been either proven or postulated to play key roles in important homogeneous catalytic reactions (e.g. hydroformylation, hydrogenation, carboxylation, etc.). Of these cobalt carbonyls, the one most fundamentally involved in the mechanistic steps of these reactions seems to be the cobalt carbonyl hydride, $HCo(CO)_4$. This complex may be obtained *in situ* in the catalytic mixture by the reaction of $Co_2(CO)_8$ with H_2 at elevated $p(H_2)$. During the course of our study of the 'stoichiometric hydroformylation' reaction [1], it became necessary to perform experiments utilizing high-pressure D_2, instead of H_2, in order to facilitate the clarification of some key steps in the mechanism of this reaction [2]. Previously, Piacenti and co-workers [3] reported some results concerning the deuteroformylation reaction without, however, presenting explicitly the IR spectroscopy characteristics of $DCo(CO)_4$.

The reaction of $Co_2(CO)_8$ with D_2 does not generate exclusively the expected $DCo(CO)_4$ as a product, but gives rise to a mixture of $DCo(CO)_4$ and $HCo(CO)_4$. Several groups, in the past 25 years, have tried to synthesize a pure $DCo(CO)_4$ compound, but in all cases, whether in the gas phase [4] or in the solid state [5], the formation of $DCo(CO)_4$ was always accompanied by the formation of $HCo(CO)_4$. Cotton and Wikinson were the first to report that the spectroscopic study of $DCo(CO)_4$ is severely hindered by the extremely fast D → H exchange of this compound with adsorbed water present in the equipment used [5]. Kaesz and co-workers [6] observed a similar easy D → H exchange for $DMn(CO)_5$ and $D_4Os_4(CO)_{12}$, whereas for $D_4Ru_4(CO)_{12}$ the deuteride proved less susceptible to loss of deuterium. This phenomenon was explained by the fact that the walls of the vessel in which the reaction was carried out (glass, stainless steel, etc.) were covered by a monolayer of water which caused a very fast exchange with the deuterium in $DCo(CO)_4$, and this

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was the source of the formation of $HCo(CO)_4$. A thorough and painstaking attempt to obtain high $DCo(CO)_4$ concentrations has been made by Wilson [7]. He heated his reaction vessel to more than 200 °C, evacuated it for extended periods and washed it with D_2O or D_2O vapors. In spite of this very meticulous handling, he obtained gas samples containing mainly $DCo(CO)_4$ and traces of $HCo(CO)_4$, but could not produce $HCo(CO)_4$-free samples. In spite of these experimental difficulties, Edgell *et al.* succeeded in measuring the IR spectra of gaseous $HCo(CO)_4$ and $DCo(CO)_4$ (with traces of the hydride present) by the use of a 5 m gas cell [8–10]. They observed the Co–H stretching frequency at 1934 cm^{-1} and the Co–D stretching frequency at 1396 cm^{-1}. They assigned these bands based on their mutual absence in the corresponding spectra and on the ν_H/ν_D ratio being reasonably near the theoretical values. These authors discuss the easy exchange of $DCo(CO)_4$ with adsorbed H_2O as well.

We have obtained alkane solutions containing $DCo(CO)_4$ by two independent routes: (a) by the direct reaction of $LiCo(CO)_4$ with gaseous DCl [11], and (b) by the high pressure thermal equilibrium reaction of $Co_2(CO)_8$ with D_2. High deuteride concentrations could be reached only when the equipment has been handled in a manner similar to that of Wilson in order to minimize the amount of water adsorbed on the walls of the reaction vessel, but in all cases we obtained a mixture of $DCo(CO)_4$ and $HCo(CO)_4$.

Therefore, before studying the properties and behavior of $DCo(CO)_4$, we had to develop a method by which we should be able to calculate simultaneously the concentrations of $DCo(CO)_4$ and $HCo(CO)_4$ in solution. As was the case with the three-component system analysis [12], the high pressure IR spectroscopic method provides us with accurate results.

Results and discussion

Analysis of the ν(C–O) and ν(Co–H/D) bands in HCo(CO)₄ and DCo(CO)₄

The high pressure reaction in n-hexane (or isooctane) as solvent, yielded a $(H/D)Co(CO)_4 + Co_2(CO)_8$ mixture, corresponding to the equilibrium composition and containing at most 90% $DCo(CO)_4$ (with 10% $HCo(CO)_4$) even when 100% D_2 gas has been used for the reaction. This high deuteride concentration could only be reached when the equipment has been thoroughly flushed with D_2O prior to the experiment.

A careful examination of the position of the highest energy absorption band in both compounds, the total symmetric ν(C–O) mode, reveals that the cobalt carbonyl hydride, $HCo(CO)_4$, absorbs at 2116.7 cm^{-1} [4], while the cobalt carbonyl deuteride, $DCo(CO)_4$, exhibits a low energy shift for that same band of only 0.4 cm^{-1}, as shown in Fig. 1. This band has been proven, therefore, to be diagnostically useless.

The dicobalt octacarbonyl + $(H/D)Co(CO)_4$ equilibrium solutions showed the presence of an unknown band at 2048 cm^{-1}, but the close neighborhood of the most intensive $Co_2(CO)_8$ band, the 2046/2042 cm^{-1} doublet [13], rendered the unequivocal assignment of this band impossible. However, when the deuteride was prepared by the $LiCo(CO)_4$ method [11], and the deuteride solution contained only very low concentrations of $Co_2(CO)_8$, this 2048 cm^{-1} band could be identified as a C–O stretching fundamental of $DCo(CO)_4$. This band clearly corresponds to the one observed at 2052 cm^{-1} in $HCo(CO)_4$, and should be assigned to the a_1 mode in which the axial and the equatorial CO ligands stretch out-of-phase [14]. Figure 2 (a) and (b) shows the spectra of a hexane solution of $DCo(CO)_4$ containing traces of $HCo(CO)_4$ as well. A freshly prepared $DCo(CO)_4$ solution (Fig. 2(a)) reveals an intensive band at 2048 cm^{-1} (band II) and only a negligible amount of $HCo(CO)_4$ (a shoulder at 2052 cm^{-1}, band I), most likely formed by D → H exchange in the IR cell. A repeated scan of the same solution (Fig. 2(b)) reveals a higher $HCo(CO)_4$ content, as seen from the increase of the 2052 cm^{-1} band (band I). Note that the 2032 cm^{-1} band is present at the same frequency for both compounds.

The most striking feature resulting from this comparison between the ν(C–O) spectra of $HCo(CO)_4$ and $DCo(CO)_4$ is the insensitivity of the highest-energy ν_1^{CO} (a_1 mode) and the most intensive 2032 cm^{-1} (e mode) bands to H → D exchange, while the ν_2^{CO} (a_1 mode) band seems to be quite sensitive to this exchange and undergoes a significant shift. The very low sensitivity of the higher a_1 band (ν_1^{CO}) towards H → D exchange

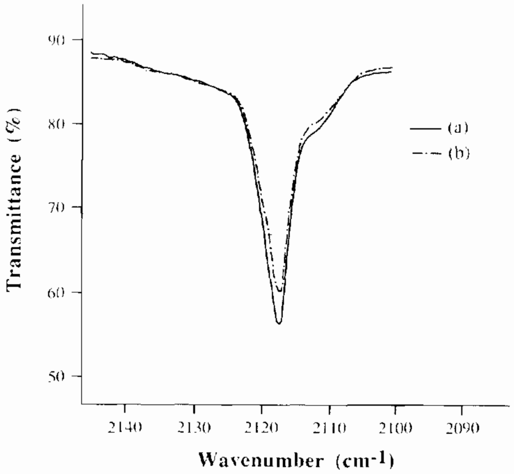

Fig. 1. IR spectra of the total symmetric ν(C–O) stretching mode of $HCo(CO)_4$ (a) and $DCo(CO)_4$ (b) in the 2090–2140 cm^{-1} spectral region.

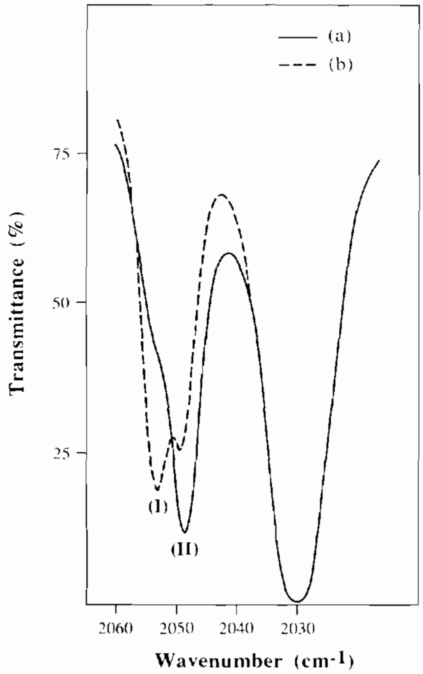

Fig. 2. IR spectra of the ν(C–O) stretching mode of a hexane solution of $DCo(CO)_4$ containing traces of $HCo(CO)_4$: (a) the spectrum of a freshly prepared $DCo(CO)_4$ solution which exhibits only a shoulder at 2052 cm^{-1} (band I which is assigned to $HCo(CO)_4$); (b) a repeated scan (after ~10 min) of the same solution which shows an increase in this band, attributed to an increase in $HCo(CO)_4$ concentration.

and the higher sensitivity of the lower mode (ν_2^{CO}) of the same species, suggests that with ν_1^{CO} only a very low Co–H (or Co–D) character is mixed, but with ν_2^{CO}, the mixing with the stretching of the Co–H (or Co–D) internal coordinates is stronger. This difference in coupling within species a_1 can be attributed to the fact that the ν_2^{CO} mode involves principally the axial CO group and hence the vibrational resonance with the Co–H vibrator is more dominant in this case. An analogous behavior was observed by Braterman *et al.* [6] for the $HRe(CO)_5/DRe(CO)_5$ couple, where the shift of the higher energy a_1 mode was only 0.3 cm^{-1} upon H→D substitution, whereas a frequency shift of 5.7 cm^{-1} was observed for the axially dominated lower a_1 mode (ν_2^{CO}).

When Edgell and Summitt [10] measured the spectrum of gaseous $HCo(CO)_4$ with a 5 m gas cell, a weak band observed at 1934 cm^{-1} was attributed to the Co–H stretching mode. When we measured the spectrum of a very concentrated hexane solution of $HCo(CO)_4$ with the purpose of identifying the same stretching band in solution, two, rather than one, very weak broad bands were observed in this region, at 1960 and 1930 cm^{-1}, as shown in Fig. 3. The unequivocal identification of the band at 1930 cm^{-1} as a Co–H stretching mode was possible by the direct comparison with the spectrum

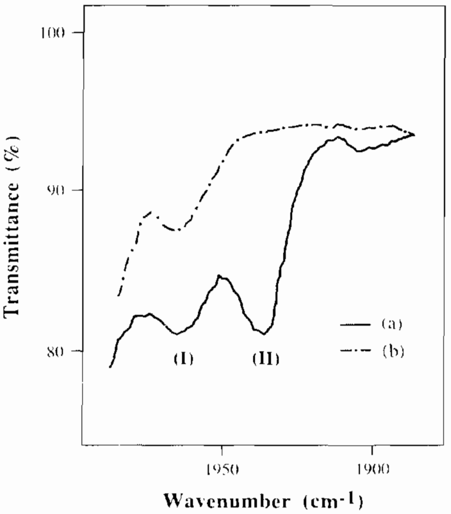

Fig. 3. IR spectra of the Co–H stretching mode region: (a) a concentrated (concentration of about 100-times greater than the one used for scanning the C–O stretching bands) hexane solution of $HCo(CO)_4$; (b) a concentrated hexane solution of $DCo(CO)_4$.

of a concentrated hexane solution of $DCo(CO)_4$ in which this band was absent. The 1960 cm^{-1} band, on the other hand, was present also in the deuteride spectrum with the same shape and intensity as in the hydride spectrum. With high probability this band is due to a negative combination (difference band) with a low frequency fundamental mode. The very low intensity of the ν(Co–H) band can be explained, in our opinion, by assuming that the dipole moment arising from the Co–H stretching displacement is mostly cancelled by the local vibrating dipole moment of the $Co(CO)_4$ group, i.e. the slight ν(C–O) displacement of the axial CO ligand *trans* to the Co–H band. The two dipole moment components should hence have opposite sign.

The direct observation of the analogous Co–D band in an alkane solution was not successful. This band can be expected around 1390 cm^{-1} (observed at 1397 cm^{-1} in the vapor phase [10]), and the strong absorption of the alkane solvents used in this study interferred in this spectral region.

The extinction coefficients of $DCo(CO)_4$ at 2116 and 598 cm^{-1}

Since, as we have shown in the previous section, the position of the highest energy absorption band of $HCo(CO)_4$ and $DCo(CO)_4$ is separated only by 0.4 cm^{-1}, and taking into consideration the resolution of IR instruments applicable to solutions, we may confidently approximate that both absorptions overlap. Therefore, in a solution containing both the hydride and the deuteride, the intensity of the 2116 cm^{-1} band will be the sum of the individual intensities of each compound at this frequency. However, even though at the beginning of these studies we were tempted to assume that the extinction coefficient of $DCo(CO)_4$ at 2116 cm^{-1} was the same as that of $HCo(CO)_4$ [12], we developed a short calculation method in order to check this important point.

$HCo(CO)_4$ has a well contoured, nicely shaped absorption band at 701 cm^{-1} [7–10], as shown in Fig. 4. This is the δ(Co–H) mode which has an intensity comparable to that of the ν(C–O) symmetric band at 2116 cm^{-1}. A careful examination of the ratio between these two bands for the pure $HCo(CO)_4$ gives the following result

$$R_{HCo(CO)_4} = \frac{A_{701}\ (cm^{-1})}{A_{2116}\ (cm^{-1})} = 0.88$$

The extinction coefficient of $HCo(CO)_4$ at 701 cm^{-1} can be easily calculated on the basis of $\epsilon_{HCo(CO)_4}$ at 2116 cm^{-1} (330±4 mol^{-1} cm^{-1}, ϵ_3 in ref. 5), and the value obtained was $\epsilon_{HCo(CO)_4}(701) = 290 \pm 3$ l mol^{-1} cm^{-1}. Therefore, the concentration of $HCo(CO)_4$ in solution can be directly calculated from the individual band of $HCo(CO)_4$ at 701 cm^{-1}.

A certain intensity, $A_{HCo(CO)_4}(701)$, of the 701 cm^{-1} band of $HCo(CO)_4$, must correspond to an intensity $A_{HCo(CO)_4}(701)/0.88$ for the 2116 cm^{-1} band. If $DCo(CO)_4$ is also present in solution, the intensity of the 2116 cm^{-1} band which is due to the presence of $DCo(CO)_4$ will be the difference between the total intensity of the 2116 cm^{-1} band and the calculated intensity of the 2116 cm^{-1} band of the $HCo(CO)_4$ compound

$$A_{DCo(CO)_4}(2116) = A_{tot}(2116) - A_{HCo(CO)_4}(701)/0.88$$

The concentration of $DCo(CO)_4$ in solution can be calculated using the difference method already employed for the three-component system calculations, a method which can be extended also for more than three components [12]. Table 1 shows the results obtained for concentrated hydride/deuteride solutions which gave rise to intensive bands and therefore increased the precision of our measurements. The average value obtained for the extinction coefficient of $DCo(CO)_4$ at 2116 cm^{-1} is therefore $\epsilon_{DCo(CO)_4}(216) = 478 \pm 55$ l mol^{-1} cm_{-1}. Hence, the extinction coefficient of $DCo(CO)_4$ at 2116 cm^{-1} is by 45% higher than that of $HCo(CO)_4$ at the same wavenumber.

On the basis of the extinction coefficient of $DCo(CO)_4$ at 2116 cm^{-1}, we can now calculate the extinction coefficient of $DCo(CO)_4$ at 598 cm^{-1} [10]. The band of $DCo(CO)_4$ at 598 cm^{-1} is the δ(Co–D) mode which was found to be at 701 cm^{-1} for the δ(Co–H) mode. In experiments where the samples were taken into a high-pressure IR cell containing KBr windows, there was enough energy in the low-frequency range of the spectrum to enable us to scan the 598 cm^{-1} band of the deuteride, as shown in Fig. 5. The measured A_{598}

TABLE 1. The calculated intensities of the 2116 cm^{-1} IR absorption band of $DCo(CO)_4$, the corresponding calculated concentrations of $DCo(CO)_4$ and the resulting values obtained for the extinction coefficients of $DCo(CO)_4$ at 2116 cm^{-1}.

$[DCo(CO)_4] \times 10^3$ (mol/l)	$A_{DCo(CO)_4}(2116)$ (a.u.)	$\epsilon_{DCo(CO)_4}(2116)$ (l mol^{-1} cm^{-1})
1.172	0.0190	456
1.956	0.0359	517
5.136	0.0973	533
7.923	0.1380	490
9.657	0.1589	464
10.255	0.1668	458
11.078	0.1722	438
11.176	0.1853	467

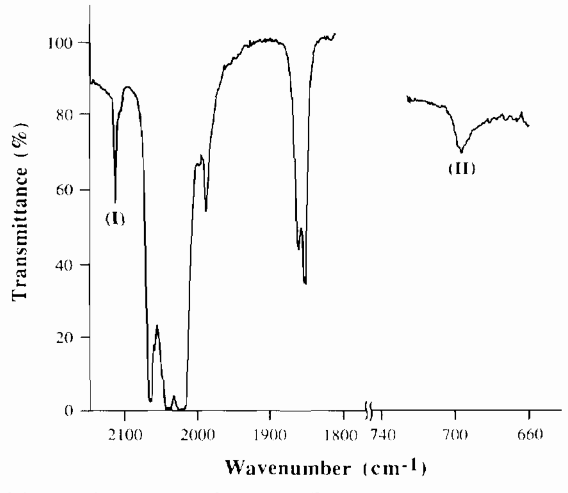

Fig. 4. IR spectra of the totally symmetric ν(C–O) (I) and the δ(Co–H) (II) bands of a hexane solution of $HCo(CO)_4$.

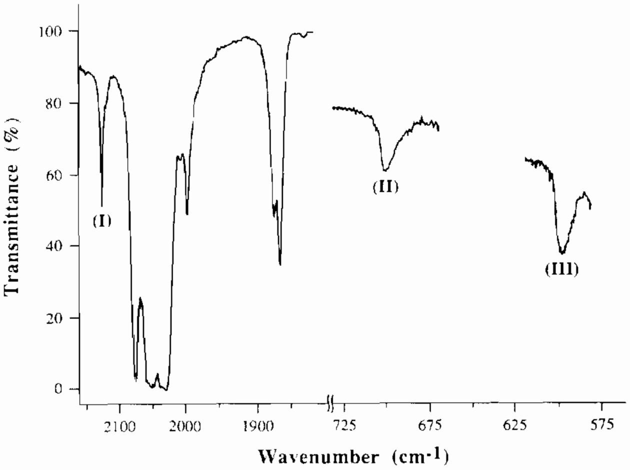

Fig. 5. IR spectra of the totally symmetric ν(C–O) (I) band and of the δ(Co–H) (II at 701 cm^{-1}) and δ(Co–D) (III at 598 cm^{-1}) bands of a hexane solution of $HCo(CO)_4$ and $DCo(CO)_4$.

of $DCo(CO)_4$ was compared to the calculated A_{2116} of $DCo(CO)_4$, and the ratio was found to be

$$R_{DCo(CO)_4} = \frac{A_{598}\ (\mathrm{cm}^{-1})}{A_{2116}\ (\mathrm{cm}^{-1})} = 1.75 \pm 0.05$$

Since the extinction coefficients of the 2116 cm^{-1} total symmetric ν(C–O) band for both $HCo(CO)_4$ and $DCo(CO)_4$ differ only by $\sim 30\%$, we would have expected the extinction coefficients of the δ(Co–H) and δ(Co–D) bands to have similar ratios. Consequently, the ratio A_{598}/A_{2116} of $DCo(CO)_4$ should have been of the same order of magnitude as the ratio A_{701}/A_{2116} of $HCo(CO)_4$ (which was measured to be 0.88). However, this is not the case. The extinction coefficient for the 598 cm^{-1} band of $DCo(CO)_4$ band was calculated to be $\epsilon_{DCo(CO)_4}(598) = 836 \pm 96\ \mathrm{l\ mol^{-1}\ cm^{-1}}$.

The effect of H_2O and D_2O on the hydride/deuteride composition

The exchange of $DCo(CO)_4$ or $HCo(CO)_4$ with H_2 or D_2 in the gas phase is much slower than the exchange with H_2O or D_2O, respectively [15]. This phenomenon is well illustrated in Fig. 6(a)–(c). When a solution containing 90% $DCo(CO)_4$ is placed under a 1:1 gas mixture of H_2:D_2 (within the closed system in which this high $DCo(CO)_4$ concentration was formed), the exchange of the deuterium atom with the hydrogen in the gas phase takes place. A 1:1 $HCo(CO)_4$:$DCo(CO)_4$ composition in solution, which corresponds to the 1:1 composition of H_2:D_2 in the gas phase, is reached after 7 days (Fig. 6(a)). This solution is now treated with an equimolar amount of H_2O dissolved in isooctane. Within 10 min, $HCo(CO)_4$ reaches a concentration representing 77% of the total concentration of both the hydride + deuteride (Fig. 6(b)). The same rapid exchange is observed when introducing equimolar amounts of D_2O dissolved in isooctane (Fig. 6(c)). It is evident, therefore, that $DCo(CO)_4$ and $HCo(CO)_4$ are very sensitive towards traces of water [15], and that obtaining a pure $DCo(CO)_4$ compound without traces of $HCo(CO)_4$ is a very complicated task, even if the reaction is taking place under high D_2 pressure.

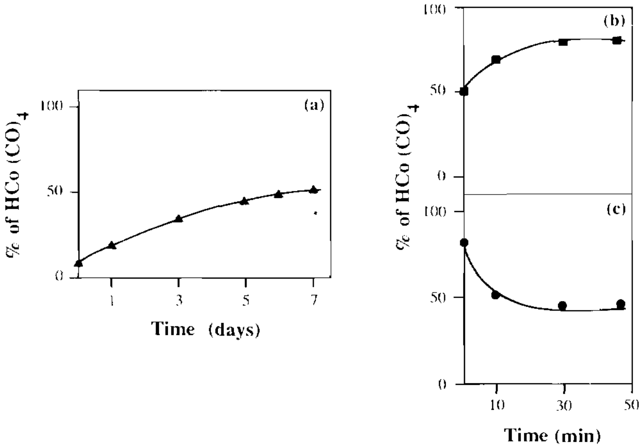

Fig. 6. The isotopic effect of $H/DCo(CO)_4$ with H_2/D_2 or H_2O/D_2O: (a) a 90% $DCo(CO)_4$-containing isooctane solution placed under a high pressure 1:1 H_2:D_2 gas mixture; (b) a 1:1 $HCo(CO)_4$:$DCo(CO)_4$ solution treated with equimolar amount of H_2O dissolved in isooctane; (c) a 77% $HCo(CO)_4$-containing isooctane solution treated with equimolar amount of D_2O dissolved in isooctane.

TABLE 2. Comparison of the equilibrium constants of the reactions between $Co_2(CO)_8$ and H_2 and $Co_2(CO)_8$ and D_2 at one temperature

Compound	T (°C)	$1000/T$ (K)	K_c	$\ln K_c$
$HCo(CO)_4$	64.0	2.967	0.0837	−2.480
$DCo(CO)_4$	63.5	2.971	0.0841	−2.475

Equilibrium constant of the reaction between $Co_2(CO)_8$ and D_2

Since we have been able to reach solutions with relatively high $DCo(CO)_4$ concentrations, we used these solutions for some equilibrium calculations. The calculation was made on a solution containing 90% $DCo(CO)_4$ and 10% $HCo(CO)_4$, and the result compared with the equilibrium constant of $HCo(CO)_4$ alone at the same temperature [16], as shown in Table 2. It seems, and very reasonably so, that the behavior of both compounds does not differ to a considerable extent, and that no thermodynamic isotope effects should be expected. However, these findings do not rule out the possibility that kinetic isotope effects might occur during the formation of these compounds.

Experimental

Synthesis of $DCo(CO)_4$

Direct synthesis of $DCo(CO)_4$

The cobalt carbonyl deuteride, $DCo(CO)_4$, may be synthesized directly by the reaction of $LiCo(CO)_4$ with DCl. The details of the reaction are described by Fachinetti *et al.* [11]. The IR spectra of hexane solutions of $DCo(CO)_4$ prepared in this way were recorded in sealed KBr liquid cells on a Nicolet FTIR model 7000, with a 0.1 cm^{-1} resolution and 1024 scans.

High pressure reaction of $Co_2(CO)_8$ with D_2

1.5757 g $Co_2(CO)_8$ of freshly prepared crystals [17] were dissolved in 600 ml isooctane (pretreated with $LiAlH_4$ and distilled under N_2 atmosphere), to give a 7.68×10^{-3} M solution. The solution was transferred by suction into a 1093 ml stainless-steel autoclave, with exclusion of air. Prior to solution introduction, the autoclave was heated to 200 °C, evacuated at that temperature for extended periods and washed thoroughly with D_2O and D_2O-containing isooctane. The reaction started after the autoclave was pressurized with 60 atm D_2 at 31 °C. The autoclave was equipped with an efficient stirrer and heated by means of a thermostated oil bath. The total pressure was measured with calibrated manometers.

After 71 h, a 50 ml isooctane solution containing 1.5301 g $Co_2(CO)_8$ was introduced into the autoclave in the following manner. The solution was placed in five small stainless-steel vessels, each of 10 ml in volume, connected in line, and connected to one end of the autoclave. This second solution was then pushed into the main-reaction autoclave by means of an excess pressure achieved by CO. After the transfer of the second solution was complete, the partial CO pressure was maintained at 4 atm and the temperature was raised to 64 °C.

A sampling tube reaching the bottom of the autoclave was connected to a flow-through type high pressure IR cell [18]. Before each spectrum was scanned, the cell was washed with D_2O-saturated isooctane introduced through a three-way valve placed between the autoclave and the cell. Immediately thereafter, the cell was flushed with 10–15 ml of fresh solution from the autoclave by opening a discharge valve placed after the cell. Total pressure was maintained constant in the whole system by simultaneously repressurizing the autoclave with deuterium.

Spectra were scanned by a Perkin-Elmer model 325 grating infrared spectrophotometer. The slit program was 4.5, corresponding to a spectral slit width of 0.87 cm^{-1} at 1900 cm^{-1}. Scanning speed was 5–8 cm^{-1} min^{-1}. Solvent absorption was compensated for by the use of a commercial variable pathlength cell. This variable cell also served as indicator for the cell thickness, which in this case was 0.028 cm at 38 °C.

Special attention was paid to the scanning of the 701 cm^{-1} band of the hydride since due to this band the concentration of the hydride and consequently that of the deuteride were calculated. The solution equilibrated after 450 h and the concentrations of the various cobalt carbonyl species were 1.263 mM $HCo(CO)_4$, 11.176 mM $DCo(CO)_4$, 8.472 mM $Co_2(CO)_8$ and 0.170 mM $Co_4(CO)_{12}$.

H_2O and D_2O influence on hydride/deuteride composition

For this experiment, the equilibrated solution described above was used. As a first step, the D_2 gas was flushed out and collected in a gasometer for further use. Then, the autoclave was pressurized with 80 atm of a 1:1 gas mixture of H_2/D_2. After 7 days, the composition of the hydride species corresponded to the composition of the gas phase. At this point, 50 ml isooctane saturated with H_2O at 40 °C (which corresponds to 0.636 mmol of H_2O), were introduced into the system. The solubility of H_2O in isooctane is 1.8×10^{-3} mol/100 g [19]. The volume of H_2O-saturated isooctane was calculated in such a way as to contain an equimolar amount of water with respect to the hydridic species in the system. The system reached equilibrium after ~ 1 h, when the content of $HCo(CO)_4$ reached 77% of the total hydride species.

The same procedure was subsequently repeated with D_2O. The solubility of D_2O in isooctane is similar to that of H_2O. Since the total amount of hydride decreased because of the removal of samples for IR analysis, only 30 ml of D_2O-saturated isooctane were introduced into the system. The D_2O dissolved in the 30 ml isooctane was equivalent to 0.381 mmol.

Samples were removed at intervals of 10 min the first hour after the addition of the water-containing isooctane, and then, since equilibrium was almost reached during the first hour, sampling was performed once a day for 4 days. The loss of pressure due to sampling was accounted for by repressurizing the system with a 1:1 gas mixture of H_2/D_2. At the conclusion of the experiment, the concentration of the cobalt carbonyl species in the solution present in the autoclave was 1.25 mM $HCo(CO)_4$, 3.13 mM $DCo(CO)_4$, 3.43 mM $Co_2(CO)_8$ and 0.029 mM $Co_4(CO)_{12}$. $DCo(CO)_4$ represented at this time 60% of the hydride + deuteride concentration.

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