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The Infrared Spectrum of Cobalt Carbonyl Hydride[1,2]

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The infrared spectrum of $HCo(CO)_4$ has been determined from 2 to 33 μ. The band at 704 cm.$^{-1}$ is associated with a motion involving the hydrogen atom but no evidence was found for an O–H stretching vibration. The spectrum is that of the tetrahedron $Co(CO)_4$ slightly perturbed by the presence of the hydrogen atom and a detailed assignment was made on this basis. The interpretation of the spectrum does not appear to be consistent with earlier models but is consistent with a model in which the hydrogen atom bridges three CO groups.

Metallic carbonyls have long been of interest to chemists inasmuch as they exhibit unique types of chemical bonding. Cobalt carbonyl hydride has intriguing chemical and physical properties,[4] which include its catalytic effect in the oxo process.[5] The structure of this substance, in particular the location and the bonding of the hydrogen atom, has been the subject of much speculation since its isolation.[6a,b] Hieber[7] has proposed that the hydrogen atom is bound as a proton within the core of the cobalt atom forming a "pseudo-nickel" atom. In an electron diffraction study Ewens and Lister[8] found the four CO groups arranged tetrahedrally about the cobalt atom and suggested that the hydrogen was bound to an oxygen atom in the linear arrangement COH. This view was disputed by Hieber, Seel and Schneider[9] who maintained that the OH bond must make an angle of 90° or less with the CO bond.

The infrared spectra of $HCo(CO)_4$ and $DCo(CO)_4$ have been obtained in the interval between 2 and 20 μ.[10,11] It was concluded that none of the observed bands were associated with motion of the hydrogen atom but no attempt was made to make an assignment of the bands to the fundamental modes of vibration. Recent studies[12,13] of the spectra of $Ni(CO)_4$ and $Co(CO)_3NO$ show that the stretching and bending vibrations of the CO units against the metal atom occur in these molecules between 17 and 33 μ. Besides this region, absorption due to fundamentals would be expected near 5 μ (observed) and beyond 100 μ (not observed). These molecules are isoelectronic with $HCo(CO)_4$. Thus one expects the presence of infrared bands for the hydride just beyond the limits of the earlier study. By extending the investigation to 35 μ, it might be possible to obtain sufficient data to permit a detailed frequency assignment to be made, which, in turn, could provide structural information relating to the hydrogen atom. This paper reports such a study.

Experimental

The $HCo(CO)_4$ was prepared by the reactions

$$2CoO + 10CO \longrightarrow Co_2(CO)_8 + 2CO_2 \qquad (1)$$

$$3Co_2(CO)_8 + 12Py \longrightarrow 2[Co(Py)_6][Co(CO)_4]_2 + 8CO \qquad (2)$$

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[1] Based in part upon the Ph.D. thesis of Charles Magee, Purdue University, December, 1954.

[2] Presented before the Division of Physical and Inorganic Chemistry at the Cincinnati Meeting of the American Chemical Society, April, 1955.

[3] National Science Foundation Fellow, 1952–1954.

[4] J. S. Anderson, *Quart. Rev.*, **1**, 331 (1947).

[5] I. Wender, R. Levine and M. Orchin, THIS JOURNAL, **72**, 4375 (1950).

[6] (a) W. Hieber, *Angew. Chem.*, **49**, 463 (1936); (b) G. W. Coleman and A. A. Blanchard, THIS JOURNAL, **58**, 2160 (1936).

[7] W. Hieber, *Die Chemie*, **55**, 25 (1942). See also the model for $Fe(CO)_4H_2$ in W. Hieber and F. Leutert, *Z. anorg. Chem.*, **204**, 745 (1932)

[8] R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **35**, 681 (1939).

[9] W. Hieber, F. Seel and H. Schneider, *Chem. Ber.*, **85**, 647 (1952).

[10] H. Sternberg, I. Wender, R. Friedel and M. Orchin, THIS JOURNAL, **75**, 2717 (1953).

[11] R. Friedel, I. Wender, S. Shufler and H. Sternberg, *ibid.*, **77**, 3951 (1955).

[12] W. F. Edgell and E. Shull, *J. Chem. Phys.*, to be submitted.

[13] W. F. Edgell and C. Magee *ibid.*, in press.

$$[Co(Py)_6][Co(Co)_4]_2 + H_2SO_4 \longrightarrow 2HCo(CO)_4 + [Co(Py)_6]SO_4 \quad (3)$$

Py = pyridine

The dicobalt octacarbonyl was prepared by a modification suggested to us by Brimm and Lynch.[14] Carbon monoxide was added to a slurry of CoO and hexane to a pressure of 3300 p.s.i. The temperature was raised to 170° and the autoclave vigorously shaken for 2 hours. The dark solution was decanted and filtered quickly to remove particles. $Co_2(CO)_8$ could be precipitated immediately by cooling the solution to −80° but this gave small crystals which readily decomposed to pyrophoric cobalt when dry. Larger crystals were grown by maintaining the solution at 0° for a day. When collected and dried, these crystals could be kept for months if not exposed to the air for long periods of time. Reactions 2 and 3 were carried out as indicated elsewhere.[15] The cobalt carbonyl hydride was collected in a trap at liquid nitrogen temperatures and stored at −80°.

The infrared spectrum was obtained in 10-cm. cells at pressures up to 40 mm. In addition a one-meter cell was used with pressures as high as 30 mm. for the region between 2 and 15 μ. NaCl, CaF_2 and KBr prisms were employed in a Perkin-Elmer Model 21 spectrophotometer to study the region between 2 and 20 μ. For wave lengths to 33 μ, KBr and CsBr prisms were used in a spectrometer built around a Perkin-Elmer Model 99 monochromator. The envelopes of the bands near 5 μ were examined with a LiF prism in this instrument. The frequency calibrations were made with the following reference gases[16]: H_2O, CO_2, CO, HCl, HBr and CH_4. The hydride decomposed during the runs, the reaction being rapid at the higher pressures. Decomposition products, $Co_2(CO)_8$, $Co_4(CO)_{12}$, etc., deposited on the windows and mirrors of the cells. To determine which bands properly belong to $HCo(CO)_4$, a run was repeated at periodic intervals for each filling of the cell and the spectrum of the *empty* cell taken before and after each filling. The infrared spectrum is shown in Figs. 1 and 2 and the frequencies are collected in Table I.

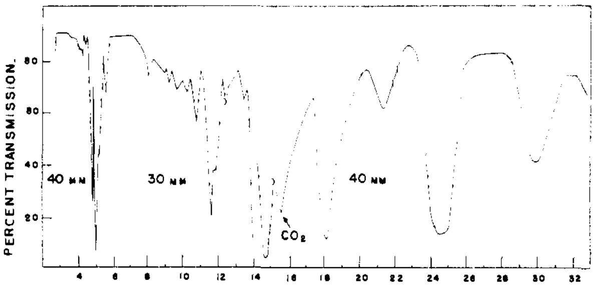

Fig. 1.—The infrared spectrum of $HCo(CO)_4$.

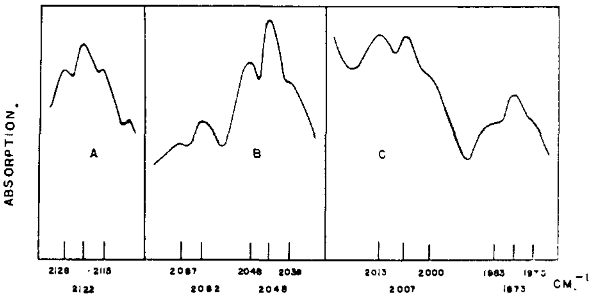

Fig. 2.—The infrared spectrum of $HCo(CO)_4$ in 5 μ region obtained with LiF prism.

Discussion

In discussing the vibrations of cobalt carbonyl hydride it will be convenient to picture a hypothetical $Co(CO)_4$ skeleton in which all the CO groups are equivalent. The approximate description of the vibrations expected of such a group is found in Table II. Only the F_2 vibrations would be infrared active. When a hydrogen atom is brought up, it perturbs this structure. As a consequence inactive vibrations may become active and degenerate vibrations may split into two or more modes, depending upon the symmetry of the resulting structure. The results of this perturbation are shown in Fig. 3 for the models of Heiber,[7] Ewens and Lister[8] and Hieber, Seel and Schneider[9] (known as I, II and III hereafter). All vibrations are active in I, II and III except the A_2 modes. In these models, as a rough approximation, the hydrogen atom will move with the atom to which it is attached in the skeletal vibrations. Besides these modes, there will be a stretching (A_1) and bending (E) of the Co–H group in I, a stretching (A_1) and bending (E) of the O–H group in II and a stretching of (A^1) and two bendings (A^1, A^{11}) of the O–H group in III.

TABLE I

THE INFRARED SPECTRUM OF $HCo(CO)_4$

ω(cm.$^{-1}$)	I	Assign.	ω(cm.$^{-1}$)	I	Assign.
4153	w	$\nu_2 + \nu_{8b}$	1930	w	$2\nu_{10} + \nu_7$
4107	w	$\nu_{8a} + \nu_{8b}$	1863	w	$2\nu_{10} + \nu_4$
4076	w	$2\nu_{8b}$	1818	w	$2\nu_{10} + \nu_6$
2746	w	$\nu_{8b} + \nu_{10}$	1631	w	$3\nu_7$
2661	w	$\nu_2 + \nu_7$	1524	w	$2\nu_6 + \nu_{10}$
2615	w	$\nu_{8a} + \nu_7$	1242	w	$\nu_7 + \nu_{10}$
2527	w	$\nu_{8a} + \nu_4$	1149	w	$2\nu_6 + \nu_1$
2453	w-	$\nu_2 + \nu_1$	1081	w	$2\nu_7$
2211	w	$\nu_2 + \nu_5$	1031	w	$\nu_1 + \nu_{10}$
2123	s	ν_2	983	w	$3\nu_1$
2107	w	$\nu_{8b} + \nu_3$	943	w	$\nu_6 + \nu_7$
2067R			870	m-	$\nu_1 + \nu_7$
2062Q	vs	ν_{8a}	850	m-	$\nu_{9a} + \nu_7$
2048R			803	w	$2\nu_6$
2043Q	vvs	ν_{8b}	787	w	$\nu_1 + \nu_4$
2038P			752	w-	$\nu_{9b} + \nu_7$
2013R			703	s	ν_{10} or ν_{11}
2007Q	s-	$\nu c^{13} - 0$	541	s	ν_{7a}, ν_{7b}
2000P			467	m	ν_4
1978	m	$\nu c^{13} - 0$	403	s	ν_{6a}, ν_{6b}
			330	m	ν_1

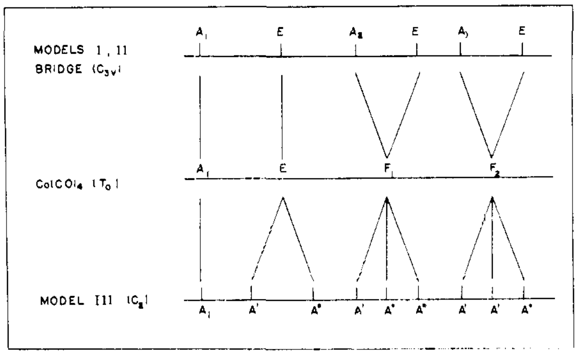

Fig. 3.—Correlation of vibrations of various models of $HCo(CO)_4$ with those of the $Co(CO)_4$ skeleton.

$Ni(CO)_4$ serves as a rough experimental model for the unperturbed $Co(CO)_4$ skeleton while $Co(CO)_3NO$ shows the results of a substantial C_{3v} per-

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[14] E. O. Brimm and M. Lynch, Jr., private communication.

[15] H. W. Sternberg, I. Wender, R. A. Friedel and M. Orchin, THIS JOURNAL, **75**, 2717 (1953).

[16] A. Downie, M. Magoon, L. Purcell and B. L. Crawford, *J. Opt. Soc. Am.*, **43**, 941 (1953).

TABLE II

APPROXIMATE DESCRIPTION OF VIBRATIONS

	Co(CO)$_4$ Skeleton				HCo(CO)$_4$-Bridge model					
	A$_1$	E	F$_2$	F$_1$	A$_1$	E	A$_1$	E	A$_2$	E
δCo–(CO)[a]		ν_3	ν_5			ν_3	ν_{5a}	ν_{5b}		
νCo–(CO)	ν_1		ν_6		ν_1		ν_{6a}	ν_{6b}		
δC–O		ν_4	ν_7	ν_9		ν_4	ν_{7a}	ν_{7b}	ν_{9a}	ν_{9b}
νC–O	ν_2		ν_8		ν_2		ν_{8a}	ν_{8b}		
$\omega_H(\|\|)$					ν_{11}					
$\omega_H(\perp)$						ν_{10}				

[a] δ = bending, ν = stretching, (CO) = this group moves as a unit, ω_H (||) = motion of hydrogen parallel to C$_3$ axis, etc.

turbation. Thus their frequencies,[12,13] which are plotted in Fig. 4, provide a key to the skeletal modes in HCo(CO)$_4$. A comparison with the data of Table I shows a striking correlation. The bands at 330 and 403 cm.$^{-1}$ correspond to ν_1 and ν_6 (see Table II) found at 381 and 423 cm.$^{-1}$ in Ni(CO)$_4$. The bands at 467 and 541 cm.$^{-1}$ correspond to the bending vibrations of the CO groups ν_4 and ν_7 found at 461 and 540 cm.$^{-1}$ in Ni(CO)$_4$. When compared with Co(CO)$_3$NO, 330 and 467 cm.$^{-1}$ in the hydride go over to 309 and 467 cm.$^{-1}$ in the nitrosyl and 403 and 541 cm.$^{-1}$ split into 391 plus 441 and 481 plus 564 cm.$^{-1}$, respectively. These correlations are shown in Fig. 4. Those frequencies in HCo(CO)$_4$ which arise from infrared inactive vibrations in Ni(CO)$_4$ are weak, while those corresponding to active modes are strong. It can be said that the perturbation of the tetrahedral Co(CO)$_4$ skeleton by the hydrogen atom in the hydride is great enough to make all modes allowed by the symmetry active, but not to split the degenerate modes in this region enough to be observable under the moderate resolution available here.

Although not apparent in Fig. 1 the strong band at 5 μ is doubled. This is more clearly seen in the trace of this region under the higher resolution obtained with the LiF prism in the double-pass spectrometer, Fig. 2. Here the PQ and R branches are seen for the 2043 cm.$^{-1}$ band and the Q and R branches for the band centering at 2062 cm.$^{-1}$. These values correspond very closely to the F$_2$ C–O stretching vibration found in Ni(CO)$_4$ at 2057 cm.$^{-1}$. In addition the bands at 2122 and 2043 have almost the same position and relative intensities as the C–O stretching vibrations in Co(CO)$_3$NO. It is concluded that 2122, 2043 and 2062 cm.$^{-1}$ correspond to C–O stretching vibrations in HCo(CO$_4$). The remaining bands in this region have relative intensities and frequency patterns similar to the bands found in Ni(CO)$_4$ and Co(CO)$_3$NO.

There remains one strong infrared band at 703 cm.$^{-1}$ which is unassigned. Comparison with the spectra of Ni(CO)$_4$ and Co(CO)$_3$NO shows that all the skeletal vibrations expected in this region have already been assigned to observed frequencies. Moreover no skeletal vibration is expected with so high a frequency.[17] Therefore the 703 cm.$^{-1}$ band must arise from a vibration involving the hydrogen atom! This assignment is strongly supported by recent infrared data[11] on the Co(CO)$_4^-$ ion which shows a strong band at 555 cm.$^{-1}$ but *none* corresponding to the 703 cm.$^{-1}$ of the hydride. The 555 cm.$^{-1}$ band is just what is expected from the above assignment since it corresponds to the F$_2$ (infrared active) C–O bending vibration ν_7 of the tetrahedral ion.

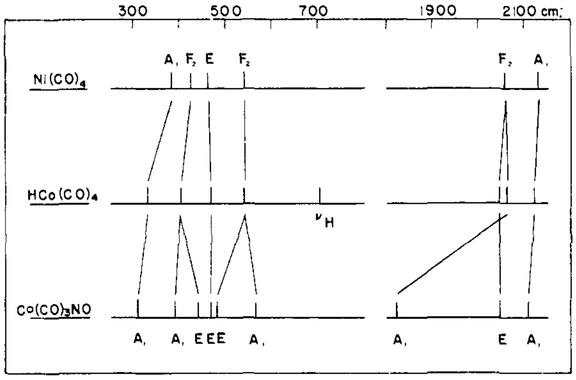

Fig. 4.—Correlation of the vibrations of HCo(CO)$_4$ with those of Ni(CO)$_4$ and Co(CO)$_3$NO.

No strong infrared band remains unassigned in the spectrum of cobalt carbonyl hydride. In particular no band was found which could be associated with an O–H stretching vibration although the spectrum was examined from 2 to 15 μ with a one meter cell at pressures up to 30 mm.

This information may be compared with that expected from the several models for cobalt carbonyl hydride. The fact that the hydrogen atom perturbs the tetrahedral Co(CO)$_4$ skeleton enough to make inactive frequencies active but not to split degenerate modes (observably) in the intermediate frequency region from 330 to 540 cm.$^{-1}$ is consistent with all of the above models. But when the perturbation at the same time results in a substantial splitting of the C–O stretching vibrations, one is led to the conclusion that the hydrogen atom is associated with one or more C–O groups. This is consistent with models II and III but not with I.

Gutowsky and co-workers[18] have measured the proton magnetic resonance spectrum of this molecule and found a chemical shift of -1.55 with regard to the hydrogen in water. This means a high electron density about the hydrogen and indicates that vibrations of the hydrogen atom should give rise to intense infrared bands. This is the case for the band at 703 cm.$^{-1}$. Therefore the absence of a band in the O–H region should be accepted at face value; the data are also inconsistent with models II and III.[19]

The agreement is not too bad between the data and the expectations of a model with a weak bond formed by d-s overlap between the cobalt and hydrogen atoms.[20] When a hydrogen atom is placed in such a position near a face of the Co(CO)$_4$ tetrahedron, substantial overlapping also occurs between its s-orbital and the p-orbitals of the three

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[17] The C–O stretching vibrations near 2000 cm.$^{-1}$ are not reerred to in this statement.

[18] H. S. Gutowsky, private communication.

[19] The bond would presumably be formed by the overlap of the hydrogen s-orbital and the oxygen (s-p)-orbital in model II and the hydrogen s-orbital and an oxygen p-orbital in model III. These would be expected to form reasonably strong covalent bonds.

[20] The difference between this and Hieber's model (I) lies in the position of the hydrogen on the face of the Co(CO)$_4$ tetrahedron with little "penetration" of the cobalt electron cloud.

carbon atoms and to a smaller extent the p-orbitals of the three oxygen atoms. Thus, bonding should also take place with the atoms of the three CO groups. In the general case such bonding would be described by an eight-centered molecular orbital but it is convenient to speak of the hydrogen as forming a *bridge* between the several atoms involved. The bridge model is shown in Fig. 5. One extreme of this model limits the covalent bonding of the hydrogen atom to bonding with the cobalt atom and the other extreme to bonding with the CO groups. While the relative amounts of these two types of covalent bonding in the molecule is a matter for conjecture at present, a simplified M. O. calculation favors that involving the CO groups. In any event the hydrogen is expected to be weakly bound to the $Co(CO)_4$ skeleton.

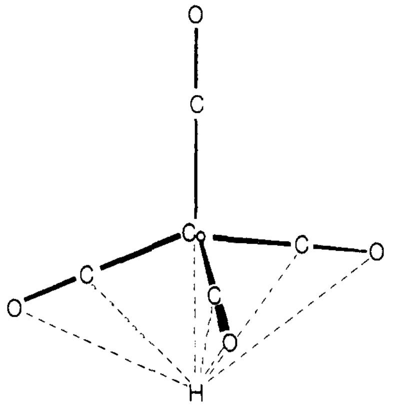

Fig. 5.—The bridge model of $HCo(CO)_4$. (Bond orders are not shown. Heavy lines indicate strong covalent bonding and dotted lines weak covalent bonding.)

The approximate description of the vibrations of the bridge model is given in Table II and their correlation with those of the $Co(CO)_4$ tetrahedron in Fig. 3. An assignment of the observed fundamentals on this basis can be found in Table III. These serve to give a reasonably good representation of the overtone and combination bands in the spectrum, as seen in Table I, despite the fact that values for at least four fundamental frequencies lie beyond the region of observation.

Thus, the infrared spectrum, taken at face value, is not consistent with the previous models for cobalt carbonyl hydride. As now understood, it is consistent with a model in which the hydrogen forms a bridge (Fig. 5).

TABLE III

THE FUNDAMENTAL FREQUENCIES OF $HCo(CO)_4$, CM.$^{-1}$[a]

ν_1	330	ν_{6a}, ν_{6b}	403
ν_2	2122	ν_{7a}, ν_{7b}	541
ν_3	(65)?	ν_{8a}, ν_{8b}	2062, 2043
ν_4	467	ν_{9a}, ν_{9b}	(309 211)?
ν_{5a}, ν_{5b}	(89)?	ν_{10} or ν_{11}	703

[a] Values in parentheses are obtained from combination and overtone bands and are uncertain.

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LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

A Simple M. O. Treatment of the Binding of the Hydrogen Atom in the Bridge Model for Cobalt Carbonyl Hydride

BY WALTER F. EDGELL AND GORDON GALLUP

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It was recently pointed out that the infrared spectrum of cobalt carbonyl hydride was consistent with a model in which the hydrogen atom occupies a bridging position between the three CO groups and the cobalt atom. Such a model is examined here in terms of elementary molecular orbital theory. A basis for the bonding exists and it should be considered as a plausible model. The hydrogen atom bears a negative charge and covalent bonding to the CO groups is stronger than that to the cobalt atom. It is pointed out that this model of cobalt carbonyl hydride gives agreement with the known, substantiated experimental facts.

Introduction

$Co(CO_4)H$ is perhaps the best known example of an unusual class of substances—the metal carbonyl hydrides. Interest in this material is enhanced by the discovery of its catalytic role in the oxo process.[1] Its chemical and physical properties[2] suggest unusual chemical bonding. The structure of this substance, in particular the location and the bonding of the hydrogen atom, has been the subject of much speculation. An early proposal was that of Hieber[3] who suggested that the hydrogen atom is bound as a proton in the core of the cobalt atom, forming a "pseudo nickel" atom. Ewens and Lister[4] studied the electron diffraction of the gas and found the CO groups arranged tetrahedrally about the cobalt atom. For a structure they proposed that the hydrogen atom gives its electron to the cobalt

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[1] I. Wender, R. Levine and M. Orchin, THIS JOURNAL, **72**, 4375 (1950).

[2] J. S. Anderson, *Quart. Rev.*, **1**, 331 (1947).

[3] W. Hieber, *Die Chemie*, **55**, 25 (1942). See also the model for $Fe(CO)_4H_2$ by W. Hieber and F. Leutert, *Z. anorg. Chem.*, **204**, 145 (1932).

[4] R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **35**, 681 (1939).