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.

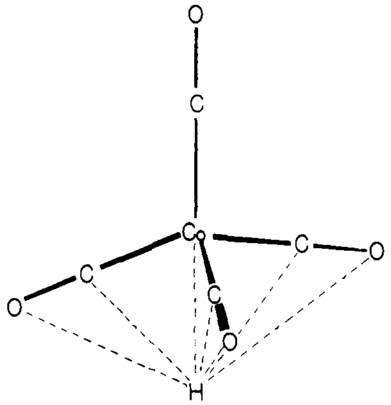

Fig. 5.—The bridge model of $HCo(CO)_4$. (Bond orders are not shown. Heavy lines indicate strong covalent bonding and dotted lines weak covalent bonding.)

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.

Acknowledgment.—Thanks are due to Drs. E. Brimm and M. Lynch, Jr., for stimulating discussions and to Dr. R. Friedel and Prof. H. Gutowsky for information in advance of publication. One of us (C.M.) thanks the National Science Foundation for a fellowship during 1952–1954. The support of the Atomic Energy Commission through contract AT(11-1)-164 with the Purdue Research Foundation is gratefully acknowledged.

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

RECEIVED JANUARY 25, 1956

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

(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**, 745 (1932).

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

atom, completing the 3d shell, and that the proton is bonded linearly to a CO group through the lone pair of electrons of the oxygen atom. The CO groups are bonded *via* the hybridized $4s4p^3$ orbitals of the cobalt atom. This view was disputed by Hieber, Seel and Schneider,[5] who maintained that the OH bond must make an angle of 90° or less with the CO bond.

Edgell, Magee and Gallup[6] have interpreted the infrared spectrum[6–8] of cobalt carbonyl hydride as being inconsistent with these models. They point out that the present knowledge of the spectrum is consistent with a model in which the hydrogen atom forms a bridge between three CO groups and the cobalt atom in a structure of C_{3v} symmetry. It is the purpose of this note to show that this structure is plausible, *i.e.*, that a basis for it exists in valence theory and to clarify, qualitatively, the nature of the bonding of the hydrogen atom in such a model.

The Starting Orbitals.—The beginning point for this treatment is the C_{3v} symmetry of the model. The proposed spatial arrangement of the atoms[7] is shown in Fig 1. The four CO groups are bonded to the cobalt atom in part by σ-bonds, utilizing the sp^3 hybridized 4s4p orbitals of this atom and the (s-p) lone pair electrons of the carbon atoms. As in other metal carbonyls these bonds are presumed to have some double bond character as a result of resonance with structures of the type Co=C=O. The π-bonds involve 3d orbitals of the cobalt and p orbitals of the carbon atoms.

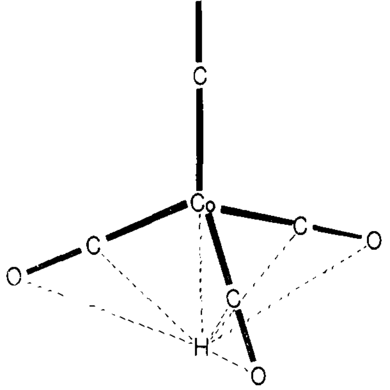

Fig. 1.—The bridge model of $Co(CO)_4H$.

The orbitals may be classified in terms of the C_{3v} symmetry of the molecule. Those designated as A_1 are symmetric to rotation of 120° or 240° about the figure axis of the molecule and to reflection through the three planes of symmetry. Orbitals of type A_2 or E are not symmetric to one or more of the above operations. This classification is important because only orbitals of the same symmetry may overlap to form bonds. The hydrogen 1s orbital, hereafter called ϕ_H, is of type A_1. Since we are primarily concerned with the bonding of the hydrogen atom, we shall restrict our attention to orbitals of this symmetry. The orbitals involved in σ-bonding are considered localized and not available for the bonding of the hydrogen atom. However, the cobalt $3d_{z^2} = \phi_{Co}$ orbital shown in Fig. 2 has the required symmetry. One molecular orbital formed from a p orbital of each of the three symmetrically equivalent carbon atoms is of type A_1. As seen in Fig. 3 the axis of greatest electron density of each p orbital is oriented to intersect the figure axis of the molecule. A similar molecular orbital may be formed from the p orbitals of the oxygen atoms. In the LCAO approximation these are

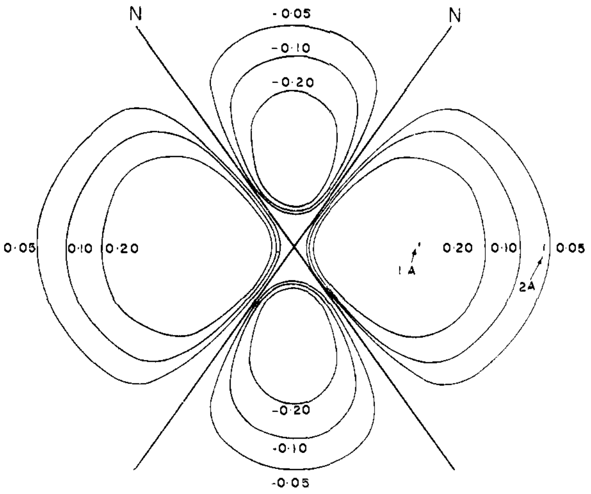

Fig. 2.—The cobalt $3dz^2 = \phi_{Co}$ orbital.

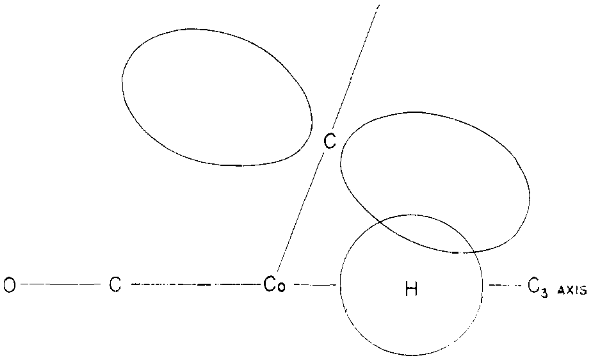

Fig. 3.—The orientation of the carbon p orbital in ϕ_C.

$$\phi_C = \frac{1}{\sqrt{3}}\{p_C(1) + p_C(2) + p_C(3)\}$$

$$\phi_O = \frac{1}{\sqrt{3}}\{p_O(1) + p_O(2) + p_O(3)\}$$

If one electron is placed in each of the four A_1 orbitals, there are just enough electrons left to fill the bonding orbitals discussed above and the remaining atomic orbitals. The electronic configuration corresponding to single bonds between the cobalt and carbon atoms is

$$[Co{:}KL(3s)^2(3p)^6(3d)^8][C{:}K]_4[O{:}K(2s)^2]_4$$
$$(\sigma_1{}^2\pi_1{}^4)_3(\sigma_1{}^2\pi_1{}^2)\sigma_2{}^8\ \phi_{Co}\phi_C\phi_O\phi_H$$

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

[6] W. F. Edgell, C. Magee and G. Gallup, THIS JOURNAL, **78**, 4185 (1956).

[7] H. Sternberg, I. Wender, R. Friedel and M. Orchin, *ibid.*, **75**, 2717 (1953).

[8] R. Friedel, I. Wender, S. Shufler and H. Sternberg, *ibid.*, **77**, 3951 (1955). Some implications of the short wave length spectrum were discussed in references (7) and (8) but no conclusions were reached regarding the location and bonding of the hydrogen atom.

Here σ_1 and π_1 refer to bonds between the carbon and oxygen atoms and σ_2 and π_2 to bonds between the cobalt atom and the carbon atoms. Resonance of the double bond $\sigma_1{}^2\pi_1{}^2$ between the three symmetrically equivalent CO groups is implied. Similar configurations may be written corresponding to various amounts of double bonding between the cobalt and carbon atoms. For example with two double bonds one has

$$[\mathrm{Co:KL(3s)^2(3p)^6(3d)^4}]\,[\mathrm{C:K}]_4[\mathrm{O:K(2s)^2}]_2[\mathrm{O:K(2s)^2(2p)^2}]_2$$
$$(\sigma_1{}^2\pi_1{}^4)(\sigma_1{}^2\pi_1{}^2)_3\ \ \sigma_2{}^8\pi_2{}^4\ \phi_{\mathrm{Co}}\phi_{\mathrm{C}}\phi_{\mathrm{O}}\phi_{\mathrm{H}}$$

The problem of the bonding of the hydrogen atom is thus reduced to the question of how the four orbitals, $\phi_{\mathrm{Co}}\phi_{\mathrm{C}}\phi_{\mathrm{O}}\phi_{\mathrm{H}}$, combine to form bonds.

Overlap and Energy Considerations.—A criterion for the tendency of two orbitals ϕ_A and ϕ_B to form a bond is the degree of overlapping measured by the integral

$$S = \int \phi^{*}_{A}\,\phi_{B}\,dv$$

These have been calculated for the integrals of interest to this problem. Slater atomic orbitals were used throughout and values taken from tables of overlap integrals[9] where possible. Corrections were made for the fact that the hydrogen atom does not lie on the symmetry axis of the p orbitals in evaluating S_{HC} and S_{HO}. Figure 4 shows these quantities as a function of the Co–H distance along the C_3 axis. The salient feature of this diagram is the fact that the hydrogen overlap integrals all have maxima at a Co–H distance just short of 2 Å. Thus one would expect the hydrogen to be located near this position. A second feature is the relatively large value of the $\phi_{\mathrm{H}}\phi_{\mathrm{C}}$ overlap and the relatively small value of the $\phi_{\mathrm{H}}\phi_{\mathrm{O}}$ overlap.

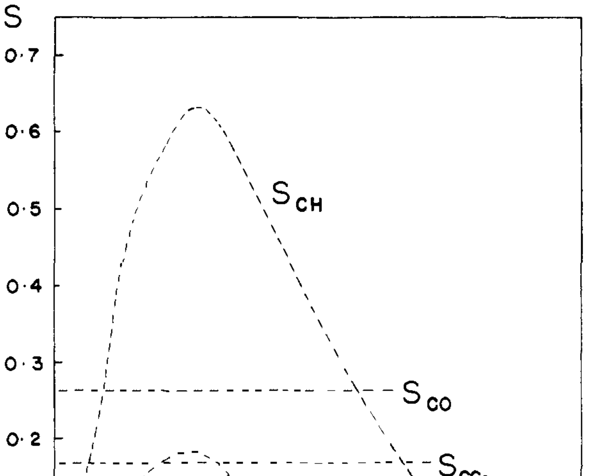

Fig. 4.—The overlap integrals.

If all other things were equal, Fig. 4 would suggest that the primary bonding is between the hydrogen and the carbon atoms with smaller contributions due to bonding between carbon and oxygen atoms, cobalt and carbon atoms and hydrogen and cobalt atoms. However, maximum covalent bonding between two orbitals takes place when the energy of the electron in each orbital is equal. As the energy difference of the two orbitals increases, the mixing of the orbitals and the shift in the energy levels decreases, and the bond is formed with increasing charge transfer. This factor is important here.

To obtain accurate energy levels is beyond the scope of the present work. Approximate energies suffice, however, for the purpose of obtaining a qualitative description of the hydrogen binding. The energy values for the hydrogen and cobalt electrons are taken from appropriate spectroscopic term values of the atoms. In the spirit of the type of approximations being made here, the energy terms involving carbon atoms or oxygen atoms of different CO groups are dropped. One is led to approximate the energy of an electron in ψ_{C} or ψ_{O} by that of the p electron of the carbon or oxygen atom. These values are given in column one and two of Fig. 5. It is seen that the small overlapping of ϕ_{H} with ϕ_{O} will be utilized to the fullest extent while the effect of the larger $\phi_{\mathrm{H}}\phi_{\mathrm{C}}$ overlap will be reduced by that energy difference. It is clear that any tendency to covalent bonding between the cobalt and the hydrogen atom must be weak.

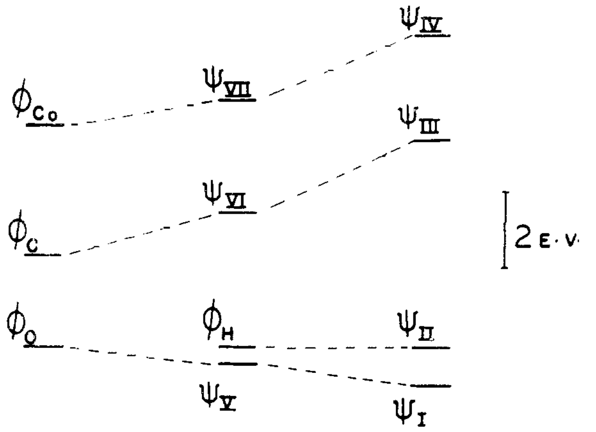

Fig. 5.—The approximate location of the atomic, free radical and molecular orbitals in cobalt carbonyl hydride.

The Bonding Orbitals.—The molecular orbitals governing the binding of the hydrogen atom are of the form

$$\psi_i = \Sigma\, a_{ij}\,\phi_j$$

where the ϕ_j are the four A_1 orbitals discussed above. Of course, there are four ψ_i which are to be classified as bonding, antibonding and possibly non-bonding. The coefficients a_{ij} were chosen by the variational method, which leads to the secular equation for the energies of the ψ_i orbitals

$$|H_{jk} - ES_{jk}| = 0$$

In carrying out the calculations, the following approximations were made

$$H_{jj} = E_j,\ S_{jj} = 1$$

$$H_{jk} = \left(H_{jj} + H_{kk} + \frac{e^2}{2R_{jk}}\right) S_{jk}$$

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(9) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

E_j is the energy of an electron in the ϕ_j orbital and the S_{jk} are the overlap integrals (both discussed above). R_{jk} is the distance between an atom of the kind associated with ϕ_j and one associated with ϕ_k. All integrals between non-adjacent atoms were set equal to zero. Two calculations were made, one for a Co–H distance of 2 Å. and the other with the hydrogen at infinity. The latter gives the energies and orbitals of a cobalt carbonyl radical *predisposed* to bond with the hydrogen atom and which is written as $Co(CO)_4{}^{\mp}$. The orbital energies obtained in the latter case are shown in column two of Fig. 5 while the orbitals themselves are

bonding:

$$\psi_V = 0.356\phi_C + 0.846\phi_O + 0.010\phi_{Co}$$

antibonding:

$$\psi_{VI} = 0.867\phi_C - 0.558\phi_O + 0.316\phi_{Co}$$

antibonding:

$$\psi_{VII} = 0.478\phi_C - 0.223\phi_O - 0.965\phi_{Co}$$

In the state of lowest energy, two electrons are found in ψ_V and one in ψ_{VI}.

The energies of the four orbitals of $Co(CO)_4H$ are found in column three of Fig. 5 while the corresponding orbitals are

bonding:

$$\psi_I = 0.416\phi_C + 0.396\phi_O + 0.612\phi_H + 0.005\phi_{Co}$$

non-bonding:

$$\psi_{II} = 0.005\phi_C - 1.000\phi_O + 0.625\phi_H - 0.001\phi_{Co}$$

antibonding:

$$\psi_{III} = 0.413\phi_C - 0.209\phi_O - 0.390\phi_H + 0.857\phi_{Co}$$

antibonding:

$$\psi_{IV} = 1.000\phi_C - 0.074\phi_O - 0.633\phi_H - 0.548\phi_{Co}$$

The approximate nature of these values should be stressed; they serve to give a qualitative picture of the bonding. In the ground state of the molecule, two electrons are found in ψ_I and two in ψ_{II}. Figures 6 and 7 show the contours of these orbitals on the CoCOH plane. Here one can see the sharing of the electron pair in ψ_I between the hydrogen atom and the carbon atoms, between the carbon and oxygen atoms, and, to some extent, between the hydrogen atom and the oxygen atoms. The electron pair in ψ_{II} is concentrated on the oxygen atoms and the hydrogen atom with a node between them. Such an arrangement may be described as a hydrogen bridge between the atoms involved. This qualitative calculation puts most of the covalent bonding of the hydrogen atom to the CO groups.

The charge distribution may be calculated from the squares of the coefficients appearing in the equation for each occupied orbital. Of the two electrons in ψ_I, slightly more than one is associated with the hydrogen atom while slightly less than $^1/_6$ of an electron appears on each of the three carbon and oxygen atoms involved in the bonding. Of the two electrons in ψ_{II}, slightly more than $^1/_2$ an electron appears on the hydrogen atom while slightly less than $^1/_2$ an electron is on each of the three oxygen atoms. While additional contributions to the charge on the carbon, oxygen and cobalt atoms are made from the rest of the bonding, the total charge on the hydrogen atom is given by the above. Thus 1.6 electrons is associated with the hydrogen atom, and it is surrounded by a sheath of negative charge.

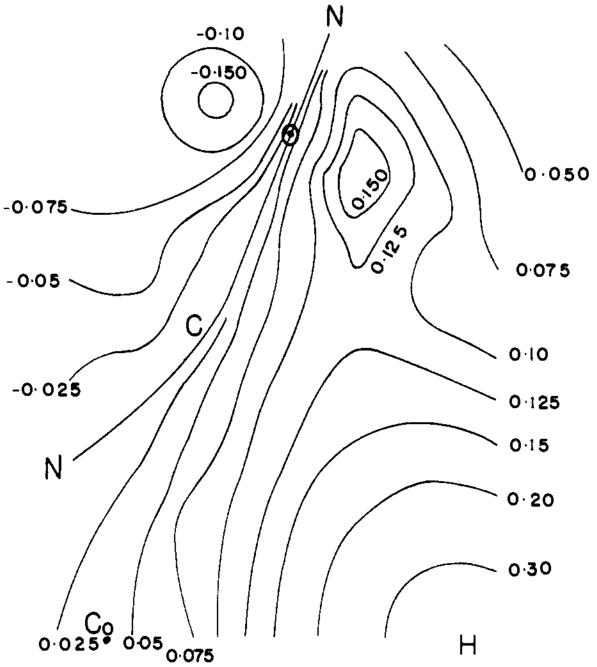

Fig. 6.—The covalent bonding molecular orbital ψ_I in cobalt carbonyl hydride.

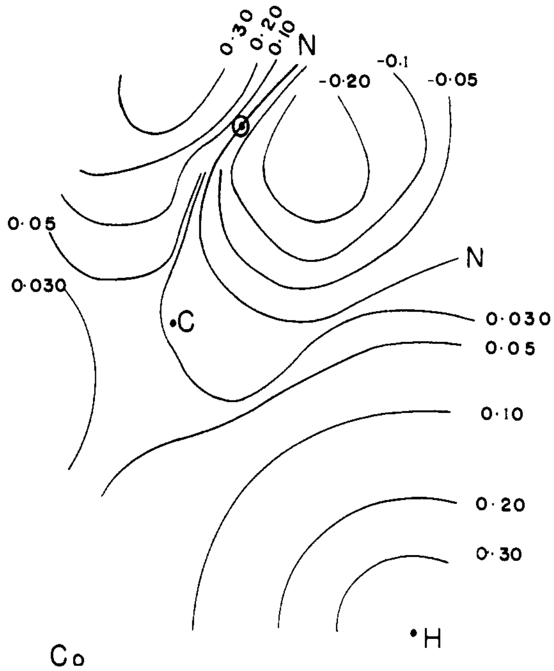

Fig. 7.—The non-bonding molecular orbital ψ_{II} in cobalt carbonyl hydride.

The above picture would be more satisfying to some if it could be represented in the valence bond picture through a set of resonating structures. This is very awkward to do (as is CO itself) if the usual unhybridized meanings are given to the bonds and the formal charge distribution found in the customary manner. Structures I, II and III below are obtained by using the hybridization discussed by Coulson[10a] and Moffit[10b] for CO. Charge transfer

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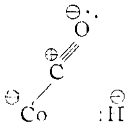
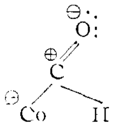
(10) (a) C. A. Coulson, "Valence," Clarendon Press, Oxford, 1952, p. 212; (b) W. Moffit, *Proc. Roy. Soc.* (*London*), **196A**, 524 (1949).

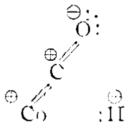
upon bond formation produces a charge on each atom of the sign which is circled. Only one CO group is shown. I is formed by putting the four CO groups tetrahedrally about the cobalt atom in its sp^3 orbitals. The negative charge on the cobalt atom is reduced by the transfer of the d electron to the hydrogen atom on the C_3 axis.



I



II



III

Structure II may be obtained from I by removing an electron pair from one CO π bond and placing it in the p orbital of the oxygen followed by bond formation between the p orbital of the carbon and the s orbital of the hydrogen using the electron pair previously on the hydrogen. Of course there are three resonating structures like II. Structure III enters into the resonance composite to counter-act the negative charge on the cobalt atom in structures I and II.

Comparison with Experiment.—The bonding found for the bridge model is in qualitative agreement with the substantiated experimental facts now known for $Co(CO)_4H$. It predicts a diamagnetic molecule. The weak covalent bonding of the hydrogen atom agrees with the ease of decomposition to form H_2 and $Co_2(CO)_8$. The large negative charge on the hydrogen atom calls for the large negative chemical shift found by Gutowsky and co-workers[11] in the proton magnetic resonance spectrum. And an interesting prediction may be made about the CO stretching vibration in $Co(CO)_4^-$, which may be described as having two electrons in ψ_V and two in ψ_{VI} followed by the delocalization of the charge. This latter process will not change the general character of the orbitals. Since ψ_{VI} is antibonding with regards to the CO bond, one expects the frequency of the CO stretching vibration in $Co(CO)_4^-$ to be less than those in $Co(CO)_4H$. The experimental values for $Co(CO)_4H$ are[6] 2122, 2043 and 2062 cm.$^{-1}$ while the value for $Co(CO)_4^-$ is[8] 1883 cm.$^{-1}$, in striking agreement with theory.

The question naturally arises as to how a molecule with a negative charged hydrogen can dissolve in water to form a strong acid. This process may be divided into the following steps

$$Co(CO)_4H(g) \longrightarrow Co(CO)_4{\neq}^-(g) + H^+(g) \quad +8.2\text{ e.v.} \quad (1)$$

$$Co(CO)_4{\neq}^-(g) \longrightarrow Co(CO)_4^-(g) \quad -R \quad (2)$$

$$H^+(g) \longrightarrow H^+(aq) \quad -11.4 \quad (3)$$

$$Co(CO_4)^-(g) \longrightarrow Co(CO)_4^-(aq) \quad -1.7 \quad (4)$$

$$Co(CO)_4H(g) \longrightarrow Co(CO)_4^-(aq) + H^+(aq) \quad -4.9 - R \quad (5)$$

The value for the first step was taken from Fig. 5, that for the third is from a tabulation by Latimer[12] and that for the fourth was estimated from values for other negative ions by means of the Born equation for the hydration energy of ions. The second step releases the delocalization energy. Although this quantity is unknown, its exact value does not alter the conclusions. If it is taken as $R = 1$ e.v., the value for the energy released in the solution of $Co(CO)_4H$, step 5, is 5.9 e.v. Any process which releases 135 kcal. of energy has a strong motivation to take place.

Acknowledgment.—The authors gratefully acknowledge the financial support of this work by the Atomic Energy Commission under contract AT-(11-1)-164 with the Purdue Research Foundation.

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[11] H. S. Gutowsky, private report.

[12] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, 1938, p. 22.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

The Raman Spectrum and Thermodynamic Properties of Iron Pentacarbonyl

BY FRANK T. KING AND ELLIS R. LIPPINCOTT

RECEIVED MARCH 13, 1956

A sodium vapor source was used to obtain the Raman spectrum of iron pentacarbonyl. An assignment of frequencies consistent with the trigonal bipyramid structure of $Fe(CO)_5$ was made using this spectrum and the previously reported infrared spectrum. The thermodynamic functions C_p, $(H° - E_0°)/T$, $-(F° - E_0°)/T$, $S°$, $\Delta H_f°$, $\Delta F_f°$ and $\Delta S_f°$ were calculated at 100° temperature intervals from 298.16° to 1000°K. A comparison of the spectral and thermodynamic properties of $Fe(CO)_5$ with those of $Ni(CO)_4$ as well as a calculation of the metal–carbon bond energy shows that the Fe–C metal bonds are stronger than Ni–C bonds. The metal–carbon bonds in $Fe(CO)_5$ and $Ni(CO)_4$ are best regarded as single bonds with only a limited amount of double bond character.

Introduction

A considerable number of structural and spectroscopic studies of the transition metal carbonyls have been made in order to obtain a better understanding of the type of bonding involved.[1–7] The structure of iron pentacarbonyl, $Fe(CO)_5$, is interesting because of the rare occurrence of pentacoördinated compounds. The two possible structures for this compound are the trigonal bipyramid

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[1] For reviews of the metal carbonyls see: J. S. Anderson, *Quart. Rev.*, **1**, 331 (1947); A. A. Blanchard, *Chem. Revs.*, **21**, 3 (1937); W. E. Trout, *J. Chem. Ed.*, **14**, 453 (1937).

[2] R. K. Sheline and K. S. Pitzer, THIS JOURNAL, **72**, 1107 (1950).

[3] B. L. Crawford and P. C. Cross, *J. Chem. Phys.*, **6**, 525 (1938); B. L. Crawford and W. Horwitz, *ibid.*, **16**, 147 (1948).

[4] L. H. Long and A. D. Walsh, *Trans. Faraday Soc.*, **43**, 342 (1947).

[5] R. A. Friedel, I. Wender, S. L. Shufler and H. W. Sternberg, THIS JOURNAL, **77**, 3951 (1955).

[6] N. J. Hawkins, H. C. Mattraw, W. W. Sabol and D. R. Carpenter, *J. Chem. Phys.*, **23**, 2422 (1955).

[7] R. S. Nyholm and L. N. Short, *J. Chem. Soc.*, 2670 (1953).