would be favored by the steric constraint. Note that the steric constraint does *not* prevent efficient photosubstitution chemistry in fluid solution. Since the source of the activation energy of this process is not yet understood, the significance of this is unclear.

A final interesting point is that chelate constraints appear to have much smaller effects upon emission maxima for Rh(III) complexes; e.g., $Rh(NH_3)_6^{3+}$ and $Rh(en)_3^{3+}$ emission maxima[1c,24] differ by only ~700 $cm^{-1}$. Conceivably, unrestricted equilibrium excited-state distortions are larger for the first-row transition series species, hence more subject to ligand or lattice perturbation. But excited-state distortions appear to be exceptionally large for[8] $Co(CN)_6^{3-}$, relative to $Co(NH_3)_6^{3+}$, so the comparison may not be fair.

**Acknowledgment.** We thank Dr. S. J. Milder, J. S. Connelly, and K. L. Marsh for assistance with certain experiments and for helpful comments. Assistance of Dr. S. F. Rice with certain explosions is also acknowledged. Access to equipment in the laboratories of Prof. Harry B. Gray of the California Institute of Technology, Prof. Michael Grätzel of the Ecole Polytechnique Fédérale, Lausane, Switzerland, and Dr. John S. Connolly of the Solar Energy Research is acknolwedged; as individuals, we most gratefully thank those of the above with whom we have collaborated.

---

[24] DeArmond, M. K.; Hillis, J. E. *J. Chem. Phys.* **1971**, *54*, 2247.

---

Contribution from the Department of Chemistry,
University of California, Santa Barbara, California 93106

# The Transition Metal–Carbon Monoxide Bond

RALPH G. PEARSON

*Received June 28, 1984*

The concept of absolute electronegativity is used to show that the transition metal acts as a Lewis base and that carbon monoxide is a Lewis acid in the neutral metal carbonyls. This means that $\pi$-bonding dominates, though some $\sigma$-bonding will be induced. The values of $\chi$, the absolute electronegativity, and $\eta$, the absolute hardness, are calculated for a number of metal atoms in their low-spin valence states. From these values the amount of electron density transferred from the metal to each CO is calculated. The resulting values are shown to be approximately proportional to $\bar{D}_0$, the mean bond strength, as predicted.

Recent work has developed the concepts of absolute electronegativity, $\chi$,[1] and absolute hardness, $\eta$.[2] The definitions are

$$\chi_S = -(\partial E/\partial N)_Z = -\mu_S \qquad \eta_S = \tfrac{1}{2}(\partial^2 E/\partial N^2)_Z \tag{1}$$

where $E$ is the electronic energy of a molecule S, $N$ is the number of electrons, and $Z$ is a fixed set of nuclear charges. The absolute electronegativity is also equal to the electronic chemical potential, $\mu$, with change in sign. The operational (and approximate) definitions are

$$\chi_S = \tfrac{1}{2}(I_S + A_S) \qquad \eta_S = \tfrac{1}{2}(I_S - A_S) \tag{2}$$

where $I_S$ is the ionization potential of S and $A_S$ is the electron affinity. The absolute electronegativity is the same as the Mulliken value.

We assume that, for small changes in $N$, we can write

$$\mu_S = \mu^0{}_S + 2\eta_S(\Delta N_S) \tag{3}$$

If we have two chemical species, A and B, that are allowed to react, there will be a shift of electrons from the less electronegative molecule, B, to the more electronegative molecule, A. The condition of equilibrium is that the chemical potentials, $\mu_A$ and $\mu_B$, become equal.[2] This leads to a shift in charge, $\Delta N$, from B to A

$$\Delta N = (\chi^0{}_A - \chi^0{}_B)/2(\eta_A + \eta_B) \tag{4}$$

Equation 4 is only an approximation, since it is based on (3), which ignores terms in $(\Delta N)^2$ and so on. This means that the hardness, $\eta$, is considered as a constant. This is not quite valid, especially for anions, where $\eta$ changes rapidly as charge is transferred. The chemical potential is also a function of external fields, so that if A (or B) is charged, this will affect $\mu_B$ (or $\mu_A$) as a function of the distance.[3] Also, covalent bonding can also lower the energy even when $\Delta N = 0$, as for the reaction of two identical atoms.[4]

In spite of these shortcomings, (4), or some elaboration of it, has often been used to estimate the ionic character of chemical bonds.[5] It has the great virtue (and weakness) of containing a minimum number of parameters to characterize the chemical behavior of a molecule. Values of $I_S$ are becoming available for more and more molecules. Values of $A_S$ are still few in number. In fact for most molecules, the electron affinity cannot be detected. In such cases, $A_S$ is set equal to zero, meaning that $E$ is a minimum when the extra electron is at infinity.

The chemical potential and the absolute electronegativity are molecular properties and not orbital properties. However, in considering the transfer of electrons from B to A, it becomes necessary to consider the electrons as coming from definite occupied orbitals in B and going into definite empty orbitals in A. This defines the relative orientations of A and B to give the greatest possible overlap between these frontier orbitals.[6] Also, $\mu_S$ and $\chi_S$ are state functions, and while ground states are most often considered, sometimes it is useful to consider valence states or excited states, particularly for the reactions of atoms.

Electron transfer leads to an energy lowering, given by[2]

---

[1] Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801. See also: Iczkowski, R. P.; Margrave, J. L. *J. Am. Chem. Soc.* **1961**, *83*, 3547.

[2] Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.

[3] Nalewajski, R. F. *J. Am. Chem. Soc.* **1984**, *106*, 944.

[4] Pritchard, H. O. *J. Am. Chem. Soc.* **1963**, *85*, 1876.

[5] Hinze, J.; Whitehead, M. A.; Jaffe, H. H. *J. Am. Chem. Soc.* **1963**, *85*, 148. Iczkowski, R. P. *J. Am. Chem. Soc.* **1964**, *86*, 2329. Huheey, J. E. *J. Phys. Chem.* **1965**, *69*, 3284. Jolly, W. L.; Perry, W. B. *J. Am. Chem. Soc.* **1973**, *95*, 5442.

[6] Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049.

$$E = -(\chi^0_A - \chi^0_B)^2/4(\eta_A + \eta_B) \tag{5}$$

Note in (4) and (5) that electronegativity differences drive the electron transfer and the sum of hardness parameters inhibits it. The hardness is the resistance of the chemical potential to change in the number of electrons. That is, $2\eta_S = (\partial\mu_S/\partial N)_Z$.

Equation 5 gives only a part of the energy change in the reaction between A and B, since the ionic bonding and parts of the covalent bonding are not included, as already indicated. Nevertheless, it seems that (4) can be useful in estimating the strength of bonding between Lewis acids and bases:

$$A + {:}B = A{\cdot}B \tag{6}$$

Formation of the complex A·B consists of partial transfer of a pair of electrons from B to A, which then allows for the formation of a coordinate covalent bond.

If we assume that A and B are neutral, then we can also assume that the strength of the covalent bond will be proportional to $\Delta N$, which will usually be small. If necessary, we can make corrections for the charges that are developed on A and B and also for any dipoles originally present. The most useful results will be obtained when a series of similar acids, or bases, are compared in their reactions with a common substrate. The relative values of $\Delta N$ should then be a measure of relative bond strengths.

A suitable example for testing these ideas is the reaction of the transition-metal atoms with carbon monoxide:

$$M(g) + nCO(g) = M(CO)_n(g) \tag{7}$$

The bonding in the metal carbonyls is usually considered to be a symbiotic blend of $\sigma$- and $\pi$-bonding. In $\sigma$-bonding, CO acts as the Lewis base and the metal atom is the Lewis acid. In $\pi$-bonding, the roles are reversed.

While anions are almost always Lewis bases and cations are almost always Lewis acids, neutral molecules are ambiguous. Usually they can function as both. One great advantage of the electronegativity concept is that we can usually decide which of two molecules is A and which is B.

There have been a number of ab initio calculations of Ni(CO)$_4$, Fe(CO)$_5$, and Cr(CO)$_6$.[7] Unfortunately, there is little agreement as to how much $\sigma$- and how much $\pi$-bonding there is. For example, in Ni(CO)$_4$ the best $\pi$-bonding orbitals would be of e species, but these have been calculated to be entirely d orbitals of the metal.[7b] Even Cr(CO)$_6$, where other evidence suggests the greatest amount of $\pi$-bonding, is sometimes calculated to be almost entirely $\sigma$-bonded.[7d] When one considers that total electronic energies in these molecules are of the order of 2500 au, whereas energy changes due to bonding are on the order of 0.5 au, the difficulty of analyzing the bonding changes becomes evident.

The general acid–base reaction (6) may also be analyzed by using semiempirical VB[8] or MO[9] methods. The parameters that occur are the ionization potential of the base, the electron affinity of the acid, and exchange or overlap integrals. The products, A·B, may also be called donor–acceptor, or charge-transfer, complexes. Usually the calculations are used to explain the absorption spectra of these complexes. In principle, bonding energies can also be calculated, but this has rarely been done.

## Calculations

A number of heats of formation have been measured for mononuclear and polynuclear metal carbonyls.[10] These enable us to calculate the heats of reaction 7 for several metals. The polynuclear metal carbonyls are more complicated because of metal–metal bonding and the presence of bridging carbonyls. However we can add the dinuclear carbonyls, if we know the metal–metal bond strengths:

$$M_2(CO)_{2n}(g) = 2M(CO)_n(g) \tag{8}$$

In this way we can add Mn(CO)$_5$ and Co(CO)$_4$ to the list.

Dividing $\Delta H$ for reaction by $n$ gives $\bar{D}_0$, the mean M–CO bond energy. Some additional data come from the activation energies for dissociation of one CO from M(CO)$_n$.[11] These energies will be less than $\bar{D}_0$ always. The nonexistence of certain metal carbonyls may also be taken as evidence that $\bar{D}_0$ is rather small.

We need $\chi_M$ and $\eta_M$ for the metal atoms, and also $\chi_{CO}$ and $\eta_{CO}$. The ionization potential of CO is 14.01 eV, and the electron affinity is zero.[12] Both $\chi$ and $\eta$ for CO are then calculated to be 7.00. The ground-state values of $\chi_M$ and $\eta_M$ are readily calculated[2] and are all less than 7.0.

The ground-state metal atoms are all high spin, whereas the metal carbonyls are low spin, with all electrons paired up in d orbitals, as far as possible. Therefore, the logical valence state should be a low-spin d$^k$ configuration.[14] $I$ and $A$ should be the energies of processes

$$M(d^k) \rightarrow M^+(d^{k-1}) + e^- \quad I \tag{9}$$

$$M(d^k) + e^- \rightarrow M^-(d^k s) \quad A \tag{10}$$

The reason for adding the electron to an s orbital in (9) has been discussed before.[15] It presupposes that $\sigma$-bonding, in which CO donates the electrons, involves primarily an s orbital on the metal.

For comparison, the nonexistent carbonyls Cu$_2$(CO)$_6$, Ag$_2$(CO)$_6$, and Au$_2$(CO)$_6$ are included. For these metals the valence states are necessarily taken to be d$^{10}$s:

$$M(d^{10}s) \rightarrow M^+(d^9 s) + e^- \quad I \tag{11}$$

$$M(d^{10}s) + e^- \rightarrow M^-(d^{10}s^2) \quad A \tag{12}$$

The electron is ionized from the d shell because these are the $\pi$-bonding electrons.

Except in a few cases, the anions and cations are not the ground states for the charged species. Therefore, corrections must be made for all three species M, M$^+$, and M$^-$. The general procedure has been indicated previously[14b,15a] but will be reviewed here.

For M and M$^+$ the first correction will be from the high-spin ground-state configuration to the high-spin valence-state configuration. The necessary data are available in Moore's tables of atomic energy levels,[16] for most, but not all, transition metals. The second correction is the spin-pairing energy, $\Delta$. This is conveniently done by using the tables of Ballhausen.[17] For convenience, the formulas in terms of the Racah parameters, $B$ and $C$, are given for various numbers of d electrons:

$$\begin{gathered} d^4\!: \ \Delta = 6B + 5C \qquad d^5\!: \ \Delta = 15B + 10C \\ d^6\!: \ \Delta = 5B + 8C \qquad d^7\!: \ \Delta = 7B + 4C \\ d^8\!: \ \Delta = 12B + 3C \end{gathered} \tag{13}$$

---

[7] (a) Hillier, I. H.; Saunderson, V. R. *Mol. Phys.* **1975**, *30*, 1735. (b) DeMuynk, J.; Viellard, A. *Theor. Chim. Acta* **1973**, *28*, 241. (c) Jansen, H. B.; Ros, P. *Theor. Chim. Acta* **1974**, *34*, 85. (d) Johnson, J. B.; Klemperer, W. G. *J. Am. Chem. Soc.* **1977**, *99*, 7132. (e) Braga, M.; Larsson, S.; Leite, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 3867. (f) Bursten, B. E.; Freier, D. G.; Fenske, R. F. *Inorg. Chem.* **1980**, *19*, 1810. (g) Sherwood, D. E.; Hall, M. B. *Inorg. Chem.* **1983**, *22*, 93. (h) Guenzberger, D.; Saitovitch, E. M. B.; DePaoli, M. A.; Manela, H. *J. Chem. Phys.* **1984**, *80*, 735.

[8] Mulliken, R. S.; Person, W. B. *Annu. Rev. Phys. Chem.* **1962**, *13*, 107.

[9] Pearson, R. G. *J. Chem. Phys.* **1949**, *17*, 969. Gray, H. B.; Beach, N. A. *J. Am. Chem. Soc.* **1963**, *85*, 244.

[10] Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71.

[11] For reviews of this subject see: Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557. Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113.

[12] Rempt, R. D. *Phys. Rev. Lett.* **1969**, *22*, 1034.

[13] Ray, N. K.; Samuels, L.; Parr, R. G. *J. Chem. Phys.* **1979**, *70*, 3680.

[14] (a) Cotton, F. A.; Fischer, A. K.; Wilkinson, G. *J. Am. Chem. Soc.* **1956**, *78*, 5168. (b) Skinner, H. A.; Summer, F. H. *J. Inorg. Nucl. Chem.* **1957**, *4*, 245.

[15] (a) Nyholm, R. S. *Proc. Chem. Soc., London* **1961**, *273*. (b) DeKock, R. L. *Inorg. Chim. Acta* **1976**, *19*, L27.

[16] Moore, C. E. *Natl. Bur. Stand. (U.S.), Circ. No. 467*, **1957**, *2*; **1958**, *3*. The lowest term of a given configuration is taken.

[17] Ballhausen, C. J. "Introduction to Ligand Field Theory"; McGraw-Hill: New York, 1962; Tables 4-5 and 4-7, pp 76 and 80.

Table I. Properties of Transition-Metal Atoms (eV)[a]

| metal | $\chi$(gs) | $I$(vs) | $A$(vs) | $\chi$(vs) | $\eta$(vs) |
|---|---|---|---|---|---|
| V | 3.64 | 3.48 | 0.9 | 2.24 | 1.24 |
| Cr | 3.76 | 4.05 | 0.9 | 2.47 | 1.58 |
| Mn | 3.72 | 5.29 | 0.9 | 3.10 | 2.19 |
| Fe | 4.03 | 4.11 | 1.0 | 2.55 | 1.55 |
| Co | 4.26 | 7.15 | 1.1 | 4.12 | 3.04 |
| Ni | 4.44 | 5.80 | 1.2 | 3.50 | 2.30 |
| Cu | 4.48 | 10.44[b] | 1.23 | 5.84 | 4.61 |
| Mo | 3.92 | 5.15 | 1.2 | 3.18 | 1.98 |
| Ru | 4.24 | 5.88 | 1.2 | 3.54 | 2.34 |
| Pd | 4.44 | 8.20 | 1.3 | 4.8 | 3.5 |
| Ag | 4.44 | 12.43[b] | 1.30 | 6.87 | 5.57 |
| Pt | 5.6 | 8.33 | 2.4 | 5.3 | 2.9 |
| Au | 5.8 | 11.10[b] | 2.3 | 6.71 | 4.4 |

[a] gs = ground state; vs = valence state, $d^k$ or $d^ks$. [b] Electron removed from d shell.

A number of $B$ and $C$ values for gaseous metal atoms and cations are given by Figgis.[18] Note that, in using (13) for $d^5$ and $d^6$, the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals are empty. For $d^7$ and $d^8$, the $d_{z^2}$ orbital is empty. The $d_{xy}$ orbital is half-filled in $d^7$, and $d^4$ has the $(d_{xy})^2(d_{xz})(d_{yz})$ configuration. The low-spin states do not correspond to observable spectroscopic states, in general.

The metal anions present a problem since the promotion energies are not available from atomic spectroscopy. The ground-state configurations of $M^-$ are all ($d^ks^2$) high spin. Two procedures were used to estimate the valence-state values of $A$. The first was developed by Nyholm.[15a] The ionization potentials of an isoelectronic sequence, such as Cu, $Zn^+$, and $Ga^{2+}$, were found. A plot of $I$ against the charge can be extrapolated to give a value for $Ni^-$. More accurately, a quadratic equation in charge can be used. For $Cr^-$, the values of $I$ for Mn, $Fe^+$, and $Co^{2+}$, all in the low-spin ($d^6s$) configuration, are available. Less information is available for the other metals. However Zollweg[19] has shown that plots of $I$ vs. $k$ for the $d^ks$ configuration form smooth curves for a series of adjacent metal atoms or ions of the same charge. This locates the electron affinities of Fe, Co, and Mn rather closely, since Cr and Ni are known. The same procedures can be used for the second and third transition series with somewhat less certainty.

By these methods, it was possible to calculate $I$, $A$, $\chi_M$, and $\eta_M$ for a number of metal atoms in their valence states. The values obtained are listed in Table I, along with ground-state electronegativities. The values of $A$ for Ni, Pd, and Pt are the same as those found by Nyholm.[15a] The values of $I$ for Cr, Fe, and Ni agree with those calculated by Nyholm within 0.1 eV. For several third transition series metals, such as W and Re, there were not enough data to find the promotion energies.

The values of $\chi_M$ are all less than 7.0, and we can conclude that CO is the Lewis acid and the metals act as Lewis bases. Accordingly, $\pi$-bonding will be more important than $\sigma$-bonding. The latter is not excluded, since as d-electron density is transferred to CO, $\chi_M$ will increase and $\chi_{CO}$ will decrease. At equilibrium there will be a single value of $\chi$ for the molecule.[13] Because of the initial imbalance, there must be more $\pi$-bonding than $\sigma$-bonding. It should be noted that the M–CO interaction is somewhat special in that both $\sigma$- and $\pi$-bonding can operate efficiently with the same orientation of reactants. This is not always the case.

We are now ready to calculate $\Delta N$, the number of electrons transferred from the valence state of the metal to $n$ coordinated carbonyl ligands. For several molecules of base B, eq 4 must be modified:

$$\Delta N/n = (\chi^0_{CO} - \chi^0_M)/2(\eta_{CO} + n\eta_M) \qquad (14)$$

This form is suitable for evaluating the electrons per bond, which should be proportional to $\bar{D}_0$. A large value of $\Delta N/n$ means more $\pi$-bonding, which then leads to more $\sigma$-bonding. The charges that develop are also favorable to bonding.

The results of using (14) are given in Table II, along with the experimental values of $\bar{D}_0$ and the heat of activation for the dissociation of the first CO molecule from the metal carbonyl. Also listed are the force constants, $F_{CO}$, for the CO stretch in the compounds. Several unstable, or unknown, metal carbonyls are also included in Table II.

Table II. Bond Energy Data for Metal Carbonyls

| compd | $D_0$,[a] kcal | $\Delta N/n$ | $\Delta H^\ddagger$,[b] kcal | $F_{CO}$,[c] mdyn/Å |
|---|---|---|---|---|
| $Cr(CO)_6$ | 54 | 0.138 | 40 | 16.5 |
| $Fe(CO)_5$ | 59 | 0.151 | 42[d] | 16.7 |
| $Ni(CO)_4$ | 46 | 0.108 | 22 | 17.3 |
| $Mo(CO)_6$ | 56 | 0.101 | 40[d] | 17.3 |
| $Ru(CO)_5$ | $59 > D_0 > 28$ | 0.093 | 28[i] | 16.6[e] |
| $Pd(CO)_4$ | unstable[f] | 0.052 | | 17.6[f] |
| $Pt(CO)_4$ | unstable[f] | 0.046 | | 17.3[f] |
| $Mn_2(CO)_{10}$ | 57[g] | 0.109 | 37 | 16.5 |
| $CO_2(CO)_8$ | 51[h] | 0.075 | 22 | 17.1 |
| $Cu_2(CO)_6$ | unstable | 0.028 | | |
| $Ag_2(CO)_6$ | unstable | 0.003 | | |
| $Au_2(CO)_6$ | unstable | 0.007 | | |

[a] From ref 10, except as indicated. [b] From ref 11, except as indicated. [c] Battiston, G.; Sbrigandello, G.; Bor, G.; Connor, J. A. *J. Organomet. Chem.* 1977, *131*, 445. [d] Lewis, K. E.; Golden, D. M.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 3905. [e] From vibrational spectra, related to $Fe(CO)_5$. [f] Exists in low-temperature matrix. Kündig, E. P.; McIntosh, D.; Moskovits, M.; Ozin, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 7234. [g] Mn–Mn bond energy taken as 37 kcal/mol. Colville, N. J.; Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 2499. [h] Co–Co bond energy taken as 22 kcal/mol. Absi-Halabi, M.; Atwood, J. D.; Forbus, N. P.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 6248. [i] Huq, R.; Poe, A. J.; Chawla, S. *Inorg. Chim. Acta* 1979, *38*, 121.

## Discussion

For the mononuclear metal carbonyls the electronegativities and hardness parameters for the valence states are substantially less than for the ground states. Presumably this is part of the reason for adopting these valence states, since now larger values of $\Delta N/n$ and stronger bonding are possible. Indeed, the calculated values of $\Delta N/n$ show a good correlation with the values of $\bar{D}_0$. The unknown metal carbonyls, such as $Cu_2(CO)_6$, have very small values of $\Delta N/n$. The unstable, but known, carbonyls, such as $Pd(CO)_4$ and $Pt(CO)_4$, have intermediate values. The stable carbonyls have the largest values of $\Delta N/n$, with the magnitudes roughly matching the mean bond strengths.

The radicals $Mn(CO)_5$ and $Co(CO)_4$ have somewhat smaller values of $\Delta N/n$ than expected but are internally consistent. A valence state of $d^{k-1}s$ might be chosen instead of $d^k$. This would affect $Co(CO)_4$ very little but would make both $\bar{D}_0$ and $\Delta N/n$ smaller for $Mn(CO)_5$. The Mn–Mn and Co–Co bond strengths may well be larger than those used in Table II. However, any error is diluted by a factor of 10 for $Mn_2(CO)_{10}$ and a factor of 8 for $Co_2(CO)_8$.

The values of $\Delta N/n$ are also in good inverse relation to those of $F_{CO}$, where known. It is generally agreed that $\pi$-bonding weakens the CO bond and reduces $F_{CO}$. Since the lone pair on CO is in an orbital that is weakly antibonding for C and O, $\sigma$-bonding will also affect the value of $F_{CO}$, but in the opposite direction. This effect must be relatively small, since $CO^+$ has a force constant of 19.5 mdyn/Å, compared to 18.55 mdyn/Å for CO.[20] The electron lost in $CO^+$ comes from the $\sigma$ lone pair on carbon.

There are indications that $\sigma$-bonding can be of importance comparable to that of $\pi$-bonding in some cases. Both $Mn(CO)_6^+$ and $V(CO)_6^-$ are inert to carbon monoxide substitution.[21] The values for the CO stretching frequencies are as

---

(18) Figgis, B. N. "Introduction to Ligand Fields"; Interscience: New York, 1966; Table 3.3, p 52.

(19) Zollweg, R. J. *J. Chem. Phys.* **1969**, *50*, 4251.

(20) Lefebvre-Brion, H.; Moser, C. M. *J. Chem. Phys.* **1966**, *44*, 295.

(21) (a) Hieber, W.; Wollman, K. *Chem. Ber.* **1962**, *95*, 1552. (b) Shi, O.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 71.

follows: $V(CO)_6^-$, $Cr(CO)_6$, $Mn(CO)_6^+$, CO(free), ~1860 $cm^{-1}$; ~2000 $cm^{-1}$; 2090 $cm^{-1}$; 2183 $cm^{-1}$. These figures are usually taken to mean that $\pi$-bonding is very large in $V(CO)_6^-$ and $\sigma$-bonding is dominant in $Mn(CO)_6^+$, which must have rather strong bonds because it is inert. An example of a metal–CO bond that is entirely $\sigma$-bonded may be CO adsorbed on solid ZnO.[22] Here the CO stretch has a value of 2202 $cm^{-1}$, higher than that for free CO.

A calculation of the electron transfer in $Mn(CO)_6^+$ and $V(CO)_6^-$ is of some interest, since it illustrates the problems created by charged species. For low-spin ($d^6$) $Mn^+$, $\chi_M$ is calculated to be 11.7 eV and $\eta = 4.3$ eV. The higher value of $\chi$ apparently reverses the direction of electron flow so that CO donates electrons to $Mn^+$ and we have mainly $\sigma$-bonding. However, it is necessary to correct $\chi_{CO}$ for the effect of the positive charge on the metal atom. One way to do this is by a point charge centered on the metal and acting on the center of each CO molecule. In the final product this corresponds to a distance of about 2.5 Å. The potential raises $\chi_{CO}$ by an amount

$$\Delta\chi = 14.43/2.5 = 5.8 \text{ eV} \qquad (15)$$

The correction raises the electronegativity of CO to 12.8 eV, so that electrons again flow from the metal to the ligands. However, it is no longer easy to calculate $\Delta N$. Both the numerator and denominator of (4) will contain Coulombic corrections. It is now advantageous to also add corrections for covalent bonding. These covalent terms are opposite in sign to the Coulombic terms, and similar in magnitude, so that considerable cancellation occurs.

The conclusion that the net transfer is still from metal to CO is of importance. The hypothetical ion $Cu(CO)_4^+$ is unknown, though it would be isoelectronic with $Ni(CO)_4$. The values of $I$ and $A$ for $Cu^+$ are 20.3 eV and 7.70 eV, to be compared with 16.0 eV and 7.40 eV for $Mn^+$. The $\sigma$-bonding should be about the same in the two complex ions, but $\pi$-bonding will be much reduced in the copper case. This factor is responsible for the instability of $Cu(CO)_4^+$. The weak $\sigma$-bonding power of CO is also evidenced by the absence of stable complexes in solution with Lewis acids such as $H^+$, $Mg^{2+}$, and $Al^{3+}$.

For $V(CO)_6^-$, the reactant is $V^-$ in a low-spin $d^6$ state. An estimate from the isoelectronic Cr and $Mn^+$ atoms indicate that this is not a bound state. Thus, as a reactant, $V^-$ would have to be considered as having a negative electronegativity. An alternative would be to consider that the relevant reaction is

$$V(g) + 6CO(g) + e^- = V(CO)_6^-(g) \qquad (16)$$

If we form $V(CO)_6$ first and then add an electron, we can conclude that $\pi$-bonding in $V(CO)_6^-$ is somewhat greater than in the neutral carbonyl. From the data in Table I, the value of $\Delta N/n$ for the latter is calculated as 0.165.

The bond energy in $V(CO)_6$ is not known. This unstable 17-electron molecule is remarkable in that it undergoes ligand substitution by an $S_N2$ mechanism, rather than the $S_N1$ mechanism normally found for metal carbonyls.[21b] The bond energy in terms of $\Delta N/n$ is expected to be strong. However, vanadium would be a $d^5$ atom in its valence state. This suggests that $\Delta N/n$ should be multiplied by a factor of $^5/_6$ to get the true bond strength, as compared to that of $Cr(CO)_6$. Similarly, the hypothetical molecule $Sc(CO)_6$ would be unstable since only three d electrons would contribute to the bonding. Note that a value of $\Delta N$ larger than half the number of d electrons would lead to reduced covalent bonding.

Table III. Stretching Frequencies ($cm^{-1}$) for CO and $N_2$ in Metal Complexes

| | $NiL_4$ | $FeL_5$ | L | $L^{+\,c}$ |
|---|---|---|---|---|
| L = CO | 2051, 2121 | 1994, 2028 | 2183 | 2200 |
| L = $N_2$ | 2174, 2246[a] | 2017, 2111[b] | 2331 | 2191 |

[a] Huber, H.; Kundig, E. P.; Moskovits, M.; Ozin, G. A. *J. Am. Chem. Soc.* 1973, *95*, 332. [b] Barrett, P. H.; Doeff, M.; Parker, S. F.; Pearson, R. G. *Inorg. Chem.*, in press. [c] Reference 20.

As mentioned in the introduction, the fact that $A$ for most molecules must be set equal to zero introduces some uncertainty. One can imagine that negative values of $A$, related, but not equal, to the energies of the lowest empty orbitals, should be used. This idea can be tested by considering the interaction between metal atoms and other molecules, such as $N_2$. As is well-known, dinitrogen forms compounds similar to those of carbon monoxide, but less stable.[24]

The values of $I$ and $A$ for $N_2$ are 15.58 eV and zero, so that $\chi = 7.8$ eV, which is greater than for CO. The orbital energies for the empty $\pi^*$ orbitals are calculated as 0.127 and 0.300 au for CO and $N_2$.[25] The value of $\chi$ says that electrons should flow from the metal to $N_2$. The resulting $\pi$-bonding will be a little stronger for $N_2$ than for CO, if $\chi$ is calculated correctly with $A = 0$. If the orbital energies are important, the $\pi$-bonding will be weaker in the dinitrogen compounds.

Table III shows vibrational frequency data for two analogous CO and $N_2$ metal complexes. These particular examples for $N_2$ are stable only in low-temperature matrices. However, the same pattern exists for stable $N_2$ complexes and their CO analogues.[26] It can be seen that compared to the case of the free ligand, there is an even greater frequency lowering for $N_2$ than for CO, upon forming a metal complex. This is explained in part by the fact that the $\sigma$ lone pair in $N_2$ is in a bonding orbital, as shown by the data for $N_2^+$. Thus both $\sigma$- and $\pi$-bonding change the stretching force constant in the same direction. The results for $Fe(N_2)_5$ clearly show that there must be substantial $\pi$-bonding, as well as some $\sigma$-bonding.

Unfortunately in neither case can it be decided whether there is more or less $\pi$-bonding for $N_2$ than for CO. The weaker overall bonding in nitrogen complexes is due in part to poor $\sigma$-bonding. The prototype for pure $\sigma$-bonding would be the proton. The proton affinities of CO and $N_2$ are 139 and 114 kcal/mol, respectively.[27] Theoretical calculations indicate about equal amounts of $\pi$-bonding for CO and $N_2$.[7e] The method of Tolman would show the $\pi$-bonding ability to be in the order $CO > PF_3 > N_2 > PCl_3$. This method is based on the CO stretching frequency in $Ni(CO)_3L$ complexes.[28] The final conclusion is that $\chi$ is a reasonably good criterion for electron transfer, even when $A$ is set equal to zero. The energies of the $\pi^*$ orbitals do play some role, however.

It is possible that the electron affinity of CO is as negative as −2.0 eV.[12] This would make $\chi = 6.0$ and $\eta = 8.0$. The amount of electron density transferred would be very much smaller in all cases, if these values are used. Nevertheless, the direction of electron transfer and the relative numbers for the various metals would not be changed. This shows the advantage of comparing a group of similar reactants with a fixed reagent.

---

(22) Strong $\pi$-bonding in metal carbonyl anions is responsible for the acidity of metal carbonyl hydrides. See: Pearson, R. G. *Chem. Rev.*, in press.

(23) D'Amico, K. L.; McFeely, F. R.; Solomon, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 6380.

(24) The Ni–$N_2$ bond energy in $Ni(CO)_3N_2$ has been measured as 10 kcal/mol, compared to 22 kcal/mol for the first Ni–CO bond energy in $Ni(CO)_4$: Turner, J. J.; Simpson, M. B.; Poliakoff, M.; Maier, W. B., II. *J. Am. Chem. Soc.* **1983**, *105*, 3998.

(25) Jorgensen, W. L.; Salem, L. "The Organic Chemists' Book of Orbitals"; Academic Press: New York, 1973; pp 78–79.

(26) Collman, J. P.; Kubota, M.; Vastine, F. D.; Sun, J. Y.; Kang, J. W. *J. Am. Chem. Soc.* **1968**, *90*, 5430.

(27) Hiraoka, K.; Saluja, P. P. S.; Kebarle, P. *Can. J. Chem.* **1979**, *57*, 2159.

(28) Tolman, C. A. *Inorg. Chem.* **1972**, *11*, 3128.

*Inorg. Chem.* **1984**, *23*, 4679–4682

In both $N_2$ and CO, the fact that an antibonding orbital is accepting electrons is more than balanced by the developing metal–ligand $\pi$-bond. The importance of this is underscored by considering the interaction of metal atoms with the noble gases. The ionization potential of argon is 15.76 eV, so that we might naively predict electron flow from the metal to argon. This does not happen, the bonding being only of van der Waals strength.[29] Clearly the accepting orbital of Ar cannot form a bond to the metal, since it is not in the valence shell of the atom. To be an electron acceptor, as G. N. Lewis pointed out years ago, an atom must have a vacant orbital in the valence shell. In a molecule there must also be a vacancy in the valence shell, though the vacant orbital may be antibonding.

It has been shown that any polar molecule with a dipole moment greater than 1.63 D must have a finite, though small, electron affinity.[30] However, the electron in cases such as HF or $H_2O$, is in a very diffuse, Rydberg-like orbital.[31] Such orbitals, presumably, cannot be used to form bonds to the electron donor. A value of $A = 0$ for such polar molecules is probably more useful.

**Acknowledgment.** This work was supported by a grant from the Department of Energy, Contract No. DEA503-765F00034. W. E. Palke and R. G. Parr are thanked for helpful discussions.

(29) McNab, T. K.; Micklitz, H.; Barrett, P. H. *Phys. Rev. B.: Solid State* **1971**, *4*, 3787. Simpson, M. B.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1355.

(30) Crawford, O. H. *Mol. Phys.* **1971**, *20*, 585; **1973**, *26*, 139.

(31) Lowe, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 5557. This reference has a good description of the electron affinities of small molecules.

---

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

# Crystal Structures from Powder Data. 1. Crystal Structure of $ZrKH(PO_4)_2$

A. CLEARFIELD,* L. B. McCUSKER, and P. R. RUDOLF

*Received June 4, 1984*

The crystal structure of $ZrKH(PO_4)_2$ was solved from X-ray powder data. Initial positional parameters for the zirconium atom were obtained by solution of the Patterson map prepared with integrated intensities of 47 unambiguously indexed reflections. The remaining atoms were located by Fourier methods, and structure refinement was effected by the Rietveld method using the entire 10–80° data set. Final indicators were $R_F = 0.036$, $R_{wp} = 0.145$, and $R_{wr} = 0.024$. Unit cell parameters obtained from the Rietveld refinement are $a = 9.228$ (1) Å, $b = 5.336$ (1) Å, $c = 16.661$ (1) Å, and $\beta = 114.35$ (1)°. The space group is $P2/c$ with $Z = 4$. The structure can be described as consisting of $\alpha$-zirconium phosphate layers in which adjacent layers are shifted by $^1/_2b$ with respect to the parent compound. Potassium ions lie halfway between the layers and are coordinated by eight oxygen atoms, four from $P–O^-$ and four from the Zr–O–P framework. Bond distances and angles for the non-potassium atoms were comparable to those in $Zr(HPO_4)_2{\cdot}H_2O$ while the K–O interatomic distances ranged from 2.76 (4) to 3.01 (5) Å. The unexchanged hydrogen atoms could not be located.

## Introduction

During the past 15 years increasing sophistication in methods of solving the X-ray phase problem has combined with advanced instrumentation and computer software to make the solution of most small- and medium-sized crystal structures a relatively routine and rapid operation. The structural information that has accumulated through the use of X-ray diffraction studies has been fundamental to our understanding of matter on the molecular level. However, there are many crystalline substances for which single crystals suitable for X-ray structural studies are difficult, if not impossible, to grow. Therefore, the ability to solve structures from X-ray (or neutron) powder data without any prior knowledge of the structure is greatly to be desired.

Our interest in this problem dates back to 1970 when it became apparent that we would not be able to prepare suitable single crystals of ion-exchanged phases of zirconium phosphate. The structure of the $\alpha$-phase, $Zr(HPO_4)_2{\cdot}H_2O$, has been solved[1,2] and shown to be a layered one. The monohydrogen phosphate protons can be exchanged singly, forming half-exchanged and fully exchanged phases, respectively, with alkali-metal cations.[3] Although large single crystals of the acid form can be prepared,[4,5] the crystals shatter and disorder as the layers expand to accommodate the cations. Only in the case of the ammonium ion form, $Zr(NH_4PO_4)_2{\cdot}H_2O$, were suitable single crystals obtained and was the structure solved.[6] This was possible because $NH_3$ intercalates between the layers rather than exchanges.[7]

In our first attempt[8] the integrated intensities were determined by cutting out the area under the peaks on the powder pattern and weighing them. Only umambiguously indexed reflections were treated in this way, yielding 40–50 usable pieces of data. In all cases tried, the position of the zirconium atom could be determined from the Patterson map, and in some instances, phosphorus atom positions could also be derived. The remaining atoms were found by Fourier methods and refinement carried out by a least-squares routine with employment of heavy damping. This work was never published because of the unsatisfactory bond distances and angles obtained. However, it was encouraging in that a starting model had been obtained from no, or little, prior knowledge of the structure.

Since that time great progress has been made in recognizing and overcoming the problems inherent in powder X-ray studies.[9-11] Since the advent of the Rietveld method for

---

(1) Clearfield, A.; Smith, G. D. *Inorg. Chem.* **1969**, *8*, 431.

(2) Troup, J. M.; Clearfield, A. *Inorg. Chem.* **1977**, *16*, 3311.

(3) Clearfield, A. In "Inorganic Ion Exchange Materials"; CRC Press: Boca Raton, FL, 1982; Chapter 1.

(4) Alberti, G.; Torracca, E. *J. Inorg. Nucl. Chem.* **1968**, *30*, 317.

(5) Inoue, Y.; Yamada, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3528.

(6) Clearfield, A.; Troup, J. M. *J. Phys. Chem.* **1973**, *77*, 243.

(7) Alberti, G.; Bertrami, R.; Costantino, U.; Gupta, J. P. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1057.

(8) Duax, W. L.; Clearfield, A., unpublished results.

(9) National Bureau of Standards. "Accuracy in Powder Diffraction"; Block, S.; Hubbard, C. S.; Eds.; U.S. Government Printing Office: Washington, DC, 1980.

(10) Smith, D. K., Barret, C. S., Leyden, D. E., Predecki, P. K., Eds. "Advances in X-ray Analysis"; Plenum Press: New York, 1981; Vol. 24.

(11) Hubbard, C. S.; et al. "Advances in X-ray Analysis"; Plenum Press: New York, 1983; Vol. 26.

0020-1669/84/1323-4679$01.50/0