

HYBRIDIZATION IN CARBON MONOXIDE

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Abstract—Qualitative molecular orbital descriptions of N_2 and CO are given and compared, with special emphasis on hybridization of s and $p\sigma$ orbitals. The principle that orbitals combining to form a strong bond must have comparable energies makes it likely that the atomic orbital of carbon involved in the σ bond in CO has predominantly s character, and leads to a lone pair on carbon with predominant p character. These arguments lead to a straightforward interpretation of the chemical properties of CO and N_2 , and are in agreement with conclusions implied in, but not specifically brought out by more elaborate MO treatments.

THE isoelectronic molecules, nitrogen and carbon monoxide, have strikingly similar physical properties, yet a myriad of reactions are possible with the latter¹ while the homonuclear nitrogen is essentially inert. In molecular orbital theory, the ten valence electrons of each compound are represented by the configuration $(1\sigma)^2(2\sigma)^2(3\sigma)^2\pi^4$, which is consistent with the presence of lone pair electrons on each of the atoms of both molecules, and a triple bond between the joined atoms. Careful molecular orbital calculations are available for both molecules,^{2,3} and the difference in their behavior is interpretable from these complete treatments. However, the difference can very readily be illustrated by means of energy level diagrams constructed on the basis of a much simpler, qualitative molecular orbital discussion, with special emphasis on hybridization; the conclusions will be shown to be in agreement with those from the more exact quantitative treatment.

In the case of nitrogen, the symmetry of the molecule requires that each MO be symmetrical, i.e. made up of equal contributions from the two atoms. The energy level diagrams for the isolated atoms are given at the extreme right and left in Fig. 1(a). In the cylindrical field of the molecule, the p_z and s orbitals of each of the nitrogen atoms (calling the bond axis the z axis) belong to the same symmetry species and can accordingly be mixed (hybridized). The hybridization leads to an energy level scheme in which each atom has two π orbitals and two σ orbitals, as shown in the second and fourth columns in Fig. 1(A). The σ orbitals can be represented by $\sigma_1 = s \cos \alpha + p_z \sin \alpha$ and $\sigma_2 = s \sin \alpha - p_z \cos \alpha$. The value of α can only be determined by a minimization of the total energy of the molecule but qualitative conclusions can be drawn without detailed calculations.

The hybridization of the s and one p orbitals results in two new levels, one (σ_2) below the p level of the isolated atom and one (σ_1) above the s level of the isolated atom. The admixture of the s orbital to the p_z orbital greatly increases the bonding power of σ_2 but is accompanied by a corresponding admixture of p character to the s orbital to form σ_1 . Since σ_1 contains two electrons, and σ_2 only one, this hybridization involves a net expenditure of energy equivalent to the promotion of the appropriate

¹ M. Orchin and I. Wender, *Catalysis* (Edited by P. H. Emmett), Vol. V. Reinhold, New York (1957).

² C. W. Scherr, *J. Chem. Phys.* **23**, 569 (1955).

³ R. S. Sahní, *Trans. Faraday Soc.* **49**, 1246 (1953).

fraction of one electron from an s to a p orbital. Experience teaches that, in the words of Mulliken, "a little hybridization goes a long way", so that only a small admixture of s character greatly increases the bonding power of σ_2 , and at the same time involves not too great an expenditure of promotion energy. Consequently it can be concluded that σ_2 will be predominantly a p_z orbital with some admixture of s character, and conversely, σ_1 will be predominantly an s orbital with some admixture of p_z character.

In the case of carbon monoxide, since the atomic orbitals of the two atoms which

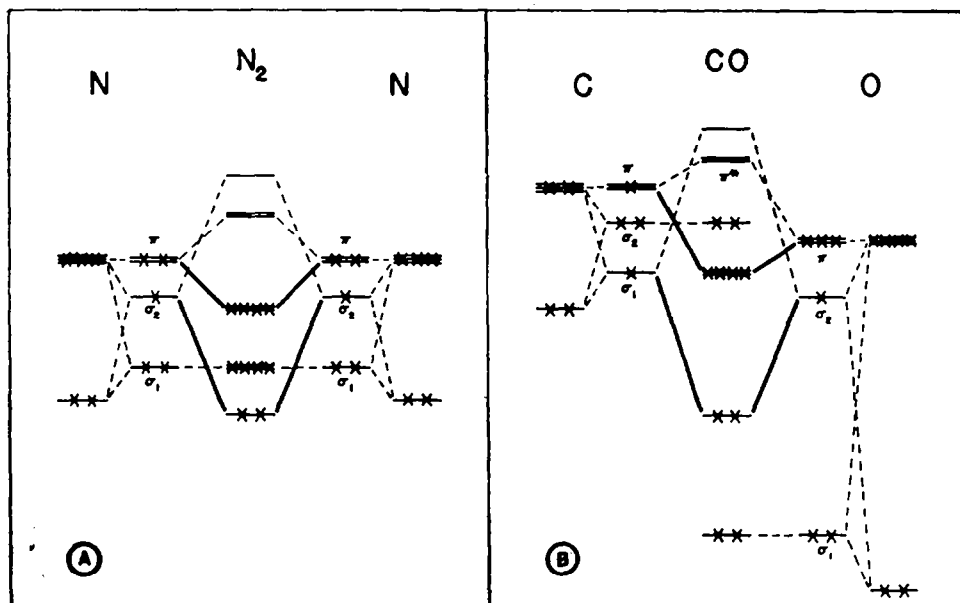


FIG. 1. Energy level diagrams for (A) N₂ and (B) CO.

form the sigma bond need not be equivalent, their relative energies must also be considered. It is well-known that two atomic orbitals form a strong bond only if their energies are fairly close. Inspection of Fig. 1(B), which gives the energy level diagram, shows that this criterion of similar energies in CO can only be met if σ_1 of carbon interacts with σ_2 of oxygen to form the sigma bond. As a result, the lone pair of the carbon atom in :C≡O: will be in a σ_2 orbital and have largely p_z character and the lone pair of the oxygen atom will be in σ_1 , and have largely s character.⁴ The ionization potential of the carbon lone pair is thus quite low, making it a relatively basic lone pair. This relatively high energy level of the lone pair and the fact that it is largely p in character and thus strongly directional must be responsible for the many reactions in which carbon monoxide acts as a nucleophile. The ionization potential of the oxygen lone pair is relatively high and these electrons are thus unavailable chemically; further, the orbital has predominantly s character, and is accordingly not strongly directional. The lone pair electrons on the nitrogen atoms in N₂ are similar to those of the oxygen atom in CO. These facts explain why the reactivity

⁴ This assignment is diametrically opposite to that made by W. Moffitt, *Proc. Roy. Soc. A* **196**, 524 (1949) who assumed that the orbital involved in forming the σ bond is essentially sp^3 hybridized, and hence the orbital containing the lone pair on carbon has 75 per cent s character.

of carbon monoxide resides on the carbon atom and is so much greater than that of nitrogen.

The energy level diagram of CO further serves to explain the reactivity of carbon monoxide toward nucleophilic reagents (e.g. RO^-) as well as the unusual ability of carbon monoxide to accept back-donation from filled d orbitals in transition metal carbonyls. The lowest unoccupied orbital is a π^* orbital ($c_C p\pi_C - c_O p\pi_O$). Inspection of the MO diagram shows that this orbital lies much closer to the $p\pi$ orbitals of the isolated carbon atom than those of the isolated oxygen atom, and hence receives a predominant contribution from the carbon $p\pi$ orbital and a much smaller contribution from the corresponding oxygen orbital, i.e. $c_C > c_O$. Accordingly, nucleophilic attack occurs exclusively on carbon, and overlap of the π^* orbital with a $d\pi$ orbital of a metal is favorable because in the $\int d\pi_{\text{Metal}} \pi_{\text{CO}}^* d\tau = \int d\pi_{\text{Metal}} (c_C p\pi_C - c_O p\pi_O) d\tau = c_C \int d\pi_{\text{Metal}} p\pi_C d\tau - c_O \int d\pi_{\text{Metal}} p\pi_O d\tau$ the last integral is small and multiplied by a small coefficient, and $\int d\pi_{\text{Metal}} p\pi_C d\tau$ is large and multiplied by a large coefficient. The relatively low energy of the π^* orbital further contributes to its acceptor ability and electrophilic character.

To test these qualitative conclusions using the data available for these molecules,^{2,3} it is necessary to transform the non-localized orbitals into equivalent or localized orbitals. Unfortunately this transformation involves some arbitrary decisions and considerable calculation and consequently only rough approximations will be used here. Sahni has transformed his orbitals of CO into a set of "localized" orbitals.³ From his data it can be estimated that the lone pair orbital localized predominantly on the oxygen atom has about 22 per cent p character and the orbital localized predominantly on carbon approximately 68 per cent p character. An approximate transformation of Scherr's $3\sigma_p$ and $2\sigma_u$ orbitals leads to equivalent, largely localized, but non-orthogonal orbitals corresponding roughly to the two nitrogen lone pairs. At the nitrogen atom on which each of these equivalent orbitals is predominantly localized, the orbital has approximately 29 per cent p character. Thus the qualitative conclusions regarding hybridization shown in Fig. 1 are borne out by use of the more quantitative calculations in the literature.

A further difference between nitrogen and carbon monoxide is that, upon ionization, the bond strength and internuclear distance in the former decreases whereas in CO both increase.⁵ The schematic energy level diagram for N_2 in Fig. 1(A), in which the highest occupied orbital is a bonding π -orbital is consistent with the observed bond-weakening effect of ionization. However, Scherr's calculations which take account of interaction of all σ orbitals show that the highest occupied orbital is one of the lone pair orbitals ($3\sigma_p$). Only on the basis of quantitative calculations could one decide whether in N_2^+ the sequence of levels would be retained or whether the π -level would lie above $3\sigma_p$. The schematic diagram of Fig. 1(B) for CO has the lone pair orbital of carbon as the highest occupied orbital and hence removal of an electron would not lead to any bond-weakening. Furthermore, ionization, which according to Fig. 1(B) occurs essentially at the carbon atom would increase the electron affinity of this atom and hence lower its energy levels and permit a more even distribution of the bonding π electrons between C and O, thereby strengthening the bond.

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⁵ L. H. Long and A. D. Walsh, *Trans. Faraday Soc.* 43, 342 (1947).