A Mössbauer Investigation of Some Iron Carbonyl Compounds

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In recent years, the structure and Mössbauer spectra of iron carbonyl compounds have attracted much interest.¹⁻³ Also in this laboratory, work has been carried out in order to elucidate the relative strength of σ - and π -bonds in iron carbonyl compounds; this has involved the same assumptions as in the investigation of substituted dinitrosyl dicarbonyl iron compounds.⁴ The investigated compounds of the general formula $\text{Fe}(\text{CO})_3\text{L}_2$ are all assumed to have the structure of a rigid trigonal bipyramid with the substituents in the axial positions. This structure is based on IR and X-ray crystal investigations.^{5,6} The non rigid structure obtained by NMR^{1,7,8} is assumed to exist only in solutions. The Mössbauer parameters were determined by Elron Mössbauer equipment on the solid compounds wafered between polyethylene at approximately 80 K and a commercial source of ⁵⁷Co in platinum was used. All the investigated compounds were prepared according to literature methods.

From the experimental data summarized in Table 1 it follows that there is a rather great variation in the quadrupole splitting, whereas the variation in the isomer shift is very small (as normal for similar iron compounds).

As the investigated compounds are all uncharged, the variation in the quadrupole splitting should be explained by differences in the bonding properties of the ligands. Furthermore the L-ligands will give the greatest contribution to this variation. The contribution from the carbonyl groups is rather small judging from

the variation in the force constants for the CO-group where the discrepancies are almost within the accuracy of the applied force field.⁹ Moreover, the variation in the bonding of the carbonyl groups will be levelled to some extent since both the bonding and the antibonding E' -orbitals are filled. (The notation used here is consistent with the character table given by F. A. Cotton²⁰). Using the normally accepted assumptions for approximate calculations of the electric field gradient (EFG) for transition elements, only the 3d electrons are considered, as the overwhelming contribution to EFG comes from these orbitals.¹⁰ In such cases we have for the quadrupole splitting:

$$\Delta E_Q \propto n(d_{x^2-y^2}) + n(d_{xy}) - n(d_{z^2}) - \frac{1}{2}[n(d_{xz}) + n(d_{yz})] \quad (1)$$

where n represents the orbital occupancy. In the compounds $[\text{Fe}(\text{CO})_3\text{L}_2]$ with constant bonding to the " CO_3 "-moiety this expression can be rewritten

$$\Delta E_Q \propto K' - \sigma_L - \frac{1}{2}(K'' - \frac{1}{2}\pi_L + K'' - \frac{1}{2}\pi_L) = K - \sigma_L + \frac{1}{2}\pi_L \quad (2)$$

where σ_L represents the amount of charge transferred to the d_{z^2} orbital by σ -bonding (to L) and π_L represents the amount of charge transferred to the ligand π -orbitals (on L) from the E'' -orbitals (i.e. d_{xz} and d_{yz}).

In the following discussion it will be assumed that $\Delta E_Q > 0$ for all compounds in Table 1;² referring to eqn. (2), this means that $K > 0$.

As we only have one equation to characterize the σ - and π -bonding properties of the ligands, it is necessary to incorporate earlier results regarding the ligands¹¹⁻¹³ in order to achieve some qualitative values for the bond strengths (bond strength will refer to the magnitude of the MO coefficient in LCAO description).

The ligands triphenylarsine and triphenylstibine are characterized by the greatest quadrupole splittings and these ligands must [following eqn. (2)] have the weakest σ -bond or/and the strongest π -bond. These ligands have been investigated by IR-spectroscopy and ¹²¹Sb-Mössbauer spectroscopy and the results are interpreted in that way that the two ligands have rather poor π -acceptor capacities and therefore they must be characterized by a very weak σ -donor capacity (at least regarding donation to the d_{z^2} -orbital). The ligands triphenylphosphite and -phosphine are situated in the middle of the observed quadrupole splitting scale and have very close values of the quadrupole splitting. We must therefore suspect that these ligands have stronger σ -bonds than the arsine and stibine homologues and further more that values of $(\sigma_L - \frac{1}{2}\pi_L)$ for the two ligands must also be close.

Table 1. Data for $\text{Fe}(\text{CO})_3\text{L}_2$ -compounds.

L	$\sigma^{a,b}$ mm/S	$\Delta E_Q^{b,d}$ mm/S	$k_{\text{COeq}}^{c,e}$ mdyn/Å
$\text{As}\phi_3$	0.20	3.20	14.5
$\text{Sb}\phi_3$	0.19	3.16	14.5
$\text{P}\phi_3$	0.16	2.63	14.3
$\text{P}(\text{O}\phi)_3$	0.15	2.61	15.1
$\text{P}(\text{C}_6\text{H}_5)_3$	0.15	2.31	14.2
$\text{P}(\text{OCH}_3)_3$	0.12	2.28	14.8
$\text{P}[\text{N}(\text{CH}_3)_2]_3$	0.15	2.27	14.4
$\text{CN}\phi$	0.16	2.03	14.8

^a Isomer shift relative to sodium nitroprusside.

^b Quadrupole splitting. ^c Calculated as in Ref. 9.

^d ± 0.02 mm/S. ^e ± 0.2 mdyn/Å.

As it is known from IR-¹⁵ and Mössbauer-spectroscopy⁴ that $\text{P}(\text{OC}_6\text{H}_5)_3$ has stronger π -bonds than $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{OC}_6\text{H}_5)_3$ must also have stronger σ -bonds in order to fulfill eqn. (2).

Also, the ligands tributylphosphine, trimethylphosphite, and tris(methylamino)phosphine have close quadrupole splitting values and must [according to eqn. (2)] have the same value of $(\sigma_L - \frac{1}{2}\pi_L)$. According to IR-spectroscopy¹⁵ the π -strengths should vary in the order $\text{P}(\text{OCH}_3)_3 > \text{P}(\text{C}_4\text{H}_9)_3 > \text{P}(\text{N}(\text{CH}_3)_2)_3$ and the σ -strength should show a similar variation. This variation is confirmed for $\text{P}(\text{C}_4\text{H}_9)_3$ and $\text{P}(\text{N}(\text{CH}_3)_2)_3$, since the aminophosphine has the smaller basicity¹⁷ and therefore should exhibit the weakest σ -bonding. The relative strong σ - and π -bonding of trimethylphosphite is confirmed by Mössbauer-spectroscopy of other iron compounds.¹⁸ The last compound in Table 1, CNC_6H_5 , is characterized by a pronounced low quadrupole splitting and must according to eqn. (2) have very strong σ -bonding and/or weak π -bonding. The smallness of the quadrupole splitting suggests that both mechanisms are in work. This is confirmed by IR-spectroscopic investigations¹⁹ which reveal that the C-N stretching frequency of the complexed isocyanide ligand is higher than the frequency of the uncomplexed ligands. This suggests that the σ -bonding is stronger than the π -bonding as σ -bonding will tend to raise and π -bonding to lower the frequency.

In conclusion, it is found that the σ -bond strength decreases in the following sequences:

The π -bond strength shows also variations but in general it has not been possible to calculate qualitative values for π -bond strengths.

It is generally assumed^{3,11,12,21} that there is a correlation between σ -donor and π -acceptor properties of ligands. From the present work it follows that this is not always the case.

1. Cullen, W. R., Harbourn, D. A., Liengme, B. V. and Sams, J. R. *Inorg. Chem.* 8 (1969) 1464.
2. Clark, M. G., Cullen, W. R., Garrod, R. E. B., Maddock, A. G. and Sams, J. R. *Inorg. Chem.* 12 (1973) 1045.
3. Carroll, W. E., Deeney, F. A., Delawey, J. A. and Lalor, F. J. *J. Chem. Soc. Dalton Trans.* (1973) 718.
4. Mosbæk, H. and Poulsen, K. G. *Acta Chem. Scand. A* 28 (1974) 157.
5. Cotton, F. A. and Parish, R. V. *J. Chem. Soc.* (1960) 1440.
6. Kelbourn, B. T., Raeburn, V. A. and

- Thompson, D. T. *J. Chem. Soc. A* (1969) 1960.
7. Mann, B. E. *Chem. Commun.* (1971) 1173.
8. Akhtar, M., Ellis, P. E., MacDiarmid, A. G. and Odum, J. D. *Inorg. Chem.* 11 (1972) 2917.
9. Dalton, J., Paul, I., Smith, C. and Stone, F. G. A. *J. Chem. Soc. A* (1968) 1199.
10. Harris, C. B. *Inorg. Chem.* 7 (1968) 1517.
11. Graham, W. A. G. *Inorg. Chem.* 7 (1968) 315.
12. Angelici, R. J. and Malone, M. D. *Inorg. Chem.* 6 (1967) 1731.
13. Stewart, R. P. and Freichel, P. M. *Inorg. Chem.* 7 (1968) 1942.
14. Delbeke, F. T., Claeys, E. G. and van der Kelen, G. P. *J. Organometal Chem.* 28 (1971) 391.
15. Horrocks, W. D. and Taylor, R. C. *Inorg. Chem.* 2 (1963) 723.
16. Bowen, L. H., Garrou, P. E. and Long, G. G. *Inorg. Chem.* 11 (1972) 182.
17. Thorsteinson, E. M. and Basolo, F. J. *Amer. Chem. Soc.* 88 (1966) 3929.
18. Libbey, E. T. and Bancroft, G. M. *J. Chem. Soc. Dalton Trans.* (1974) 87.
19. Cotton, F. A. and Zingales, F. J. *Amer. Chem. Soc.* 83 (1961) 351.
20. Cotton, F. A. *Chemical Applications of Group Theory*, Interscience, New York 1965.
21. Bigorgne, M. J. *Inorg. Nucl. Chem.* 26 (1964) 107.

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