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# THERMOCHEMICAL AND SPECTROSCOPIC STUDIES OF BONDING IN ORGANOTRANSITION METAL CARBONYLS*

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## X-ray photoelectron spectroscopy

The change in the binding energy of the core electrons of carbon monoxide when it is complexed to a metal may provide information on the charge distribution in metal carbonyls. The results of measurements [1] of the core electron ionisation potentials of a number of binary first row metal carbonyls and their derivatives in the gas phase are given in Table 1. The C 1*s* spectrum of $Ni(CO)_4$ is shown in Fig. 1 as an example of the type of spectrum observed.

As the results in Table 1 show, in every case both the carbon and oxygen 1*s* ionisation potential values of the complexed CO are less than the corresponding values in free CO by approximately 2.5 eV. If this shift is taken as a reflection of the change in charge distribution between free and complexed CO, then the measurements suggest superior $\pi$-acceptor character of the coordinated ligand in contrast to the weaker $\sigma$-donor function of the ligand; in short, that back bonding from the metal to the CO ligand is dominant.

TABLE 1

EXPERIMENTALLY DETERMINED BINDING ENERGIES (eV) OF METAL CARBONYLS IN THE GAS PHASE

| Compound | C 1*s*(CO) | O 1*s*(CO) | Metal $2p_{3/2}$ |
|---|---|---|---|
| CO | 296.2 | 542.6 | |
| $Cr(CO)_6$ | 293.5 | 539.6 | 581.8 |
| $Mn(CO)_5H$ | 293.6 | 539.8 | 647.3 |
| $Mn(CO)_5CH_3$ | 293.7 | 540.1 | 646.9 |
| $Mn(CO)_5COCF_3$ | 294.0 | 540.0 | 647.4 |
| $Fe(CO)_5$ | 293.7 | 539.8 | 715.3 |
| $Co(CO)_3NO$ | 293.7 | 539.9 | 786.0 |
| $Ni(CO)_4$ | 294.0 | 539.9 | 860.6 |

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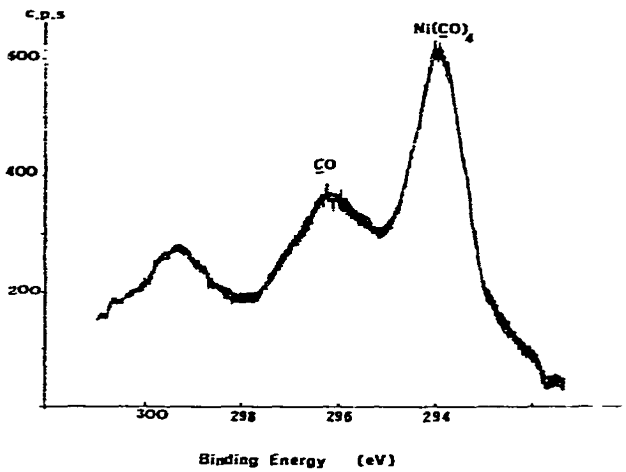

Fig. 1. Gas phase photoelectron spectrum of C 1*s* region of $Ni(CO)_4$ + CO.

The results show that the shift on coordination is not significantly influenced either by the metal atom or by the nature of other substituents attached to the metal, unless these are highly electronegative. As Fig. 1 shows, the spectra of these metal carbonyls in the gas phase also contain the satellite peaks, which were observed in solid state spectra, to high binding energy of the principal C 1*s* and O 1*s* ionisations. This shows that the valence excitation to a virtual orbital (shake-up process) in the hole state of the ion is not uniquely a feature of the solid state of these complex compounds. The remarkable intensity of the shake-up satellites is to be seen as a consequence of the dominant $\pi$-overlap between metal and ligand.

An important feature of measurements of core electron ionisation potentials is the opportunity they afford for the independent validation of sophisticated molecular orbital calculations, and consequently of the pattern of atomic charge distribution derived from such calculations. As an example of this approach, Table 2 contains information [2] concerning the chromium complexes $[Cr(\eta\text{-}C_6H_6)_n(CO)_{6-3n}]$ ($n = 1,2$). The agreement between experiment and

TABLE 2

SHIFT OF CARBON 1*s* BINDING ENERGY (eV) AND CALCULATED CHARGE FOR $[Cr(arene)(CO)_3]$

| | Shifts | | | | | |
|---|---|---|---|---|---|---|
| | $C_6H_6$ | | CO | | Calculated charge at carbon | |
| | exp. | calc. | exp. | calc. | $C_6H_6$ | CO |
| $C_6H_6$ | 0 | 0 | | | −0.24 | |
| $Cr(\eta\text{-}C_6H_6)_2$ | −0.2 | −0.9 | | | −0.45 | |
| $Cr(\eta\text{-}C_6H_6)(CO)_3$ | 0.5 | 0.5 | −4.1 | −2.9 | −0.39 | −0.03 |
| $Cr(CO)_6$ | | | −2.5 | −0.3 | | 0.23 |
| CO | | | 0 | 0 | | 0.37 |

calculation is satisfactory, at least with regard to the sign of the shift in binding energy. The consistent underestimate of the magnitude of the shift in binding energy on coordination of CO in these compounds calculated by ab initio methods may reflect on the application of Koopmans' theorem in this situation. The calculated charges given in Table 2 confirm the empirical interpretation of changes in binding energy. The benzene ligand in $[Cr(\eta\text{-}C_6H_6)_2]$ is more negatively charged than free benzene. In $[Cr(\eta\text{-}C_6H_6)(CO)_3]$ the electron density on the benzene ligand is less than in $[Cr(\eta\text{-}C_6H_6)_2]$ and is transferred through the chromium atom to the carbonyl ligands. The carbonyl ligands in $[Cr(\eta\text{-}C_6H_6)(CO)_3]$ are more negatively charged than in $Cr(CO)_6$. In this way it is possible to place familiar results on a more secure and internally consistent base.

## Microcalorimetry

The constant reference in the literature to the differing strength of bonds in organotransition metal complexes is almost without any quantitative substantiation. In an attempt to correct this situation we have started on a programme of microcalorimetric measurements. The results of these studies do not pretend to provide values of the very highest accuracy presently attainable by macro-scale combustion calorimetry, but they offer a basis for application on a wide scale and are sufficiently precise for most purposes.

Studies [3] on binary metal carbonyls have led to the values of the mean bond dissociation energy or bond enthalpy contribution given in Table 3, from which certain simple empirical relations between $\bar{T}$ (terminal M—CO bond), $\bar{B}$ (bridging M—CO bond, $\frac{1}{2}[M_2(\mu^2\text{-}CO)]$) and $\bar{M}$ (metal—metal bond) may be developed for polynuclear metal carbonyls thus,

$$\bar{B} \sim 0.5\,\bar{T} \tag{1}$$

$$\bar{M} \sim 0.68\,\bar{T} \tag{2}$$

TABLE 3

BOND ENTHALPY CONTRIBUTIONS IN METAL CARBONYLS[a]

| | Cr | Mn | Fe | Co | Ni |
|---|---|---|---|---|---|
| $\bar{T}$ | 108 | 99 | 118 | 136 | 147 |
| $\bar{M}$ | | 67 | 80 | 92 | |
| $\bar{B}$ | | | 64 | 58 | |
| | Mo | | Ru | Rh | |
| $\bar{T}$ | 152 | | 172 | 166 | |
| $\bar{M}$ | | | 117 | 114 | |
| | W | Re | Os | Ir | |
| $\bar{T}$ | 178 | 187 | 192 | 190 | |
| $\bar{M}$ | | 128 | 130 | 130 | |

[a] Values in kJ $mol^{-1}$ to nearest whole number. $\bar{T}$ is the terminal M—CO bond enthalpy. $\bar{M}$ is the M—M bond enthalpy. $\bar{B}$ is the bridging M—CO bond enthalpy.

These relations can be extended if the enthalpy of sublimation of the metal, $\Delta H_f^0$ (M, g) is considered. This leads to the following set of empirical relations,

$$\overline{\mathrm{T}} \sim (0.28 \pm 0.04)[\Delta H_f^0(\mathrm{M,g})] \quad (3)$$

$$\overline{\mathrm{M}} \sim 2/n[\Delta H_f^0(\mathrm{M,g})] \quad (4)$$

where $n$ is the coordination number of the metal M in the bulk metal. To achieve consistency between relation 2 and relations 3 and 4 for a 12 coordinate face-centred cubic metal, that is, for most of the metals which form polynuclear carbonyl compounds, relation 2 should be modified at this time to be $\overline{\mathrm{M}} \sim (0.64 \pm 0.04)\overline{\mathrm{T}}$.

One crucial assumption is made in this work, that bond enthalpy contributions are transferable from one system to another. This means that for example, $\overline{\mathrm{T}}$ remains unchanged in $[\mathrm{Cr}(\eta\text{-}C_6H_6)(CO)_3]$ from its value in $\mathrm{Cr(CO)_6}$. In the same way we assume that the bond enthalpy contribution of $[\mathrm{Cr}(\eta\text{-}C_6H_6)]$ in the same compound is unchanged from its value in $[\mathrm{Cr}(\eta\text{-}C_6H_6)_2]$. There is some experimental evidence in favour of this assumption, but the limits within which it is valid have yet to be determined. Furthermore, it has been necessary to assume "reasonable" values of the heats of sublimation of many compounds, pending their direct determination [5].

If exact transferability of $\overline{\mathrm{T}}$, $\overline{\mathrm{M}}$ and $\overline{\mathrm{B}}$ values is accepted as a valid assumption, it is possible to derive [4] the bond enthalpy contributions of various coordinated organic ligands as shown in Table 4. These figures show that in general the bond enthalpy contribution is dependent upon substituents, upon the metal and upon aromatic character. Thus, whereas in general arene—metal bonds are stronger than metal—CO bonds, the latter are stronger than olefin—metal bonds. Table 4 also emphasises the point of the argument that transition metal—carbon

TABLE 4

BOND ENTHALPY CONTRIBUTIONS OF COORDINATED ORGANIC LIGANDS AND RELATED GROUPS[a]

| Bond | Bond enthalpy contribution | Source |
|---|---|---|
| *(a). Arenes and olefins* | | |
| $C_6H_6$—Cr | 180 | $\mathrm{Cr}(\eta\text{-}C_6H_6)(CO)_3$ |
| 1,3,5-$C_6H_3Me_3$—Cr | 205 | $\mathrm{Cr}(\eta\text{-}C_6H_3Me_3)(CO)_3$ |
| $C_6Me_6$—Cr | 251 | $\mathrm{Cr}(\eta\text{-}C_6Me_3)(CO)_3$ |
| $C_7H_8$—Cr | 155 | $\mathrm{Cr}(\eta\text{-}C_7H_8)(CO)_3$ |
| $C_6H_6$—Co | 255 | $\mathrm{Co_4}(\eta\text{-}C_6H_6)(CO)_9$ |
| 1,3,5-$C_6H_3Me_3$—Co | 280 | $\mathrm{Co_4}(\eta\text{-}C_6H_3Me_3)(CO)_9$ |
| $C_2H_4$—Fe | 96 | $\mathrm{Fe(C_2H_4)(CO)_4}$ |
| *(b) Alkyl- and acyl-metal σ-bonds* | | |
| $CH_3$—Mn | 117 | $\mathrm{Mn(CO)_5CH_3}$ |
| $CH_3$—Re | 222 | $\mathrm{Re(CO)_5CH_3}$ |
| PhCO—Mn | 105 | $\mathrm{Mn(CO)_5COPh}$ |
| *(c). Trifluorophosphine complexes* | | |
| $PF_3$—Cr | 107 | $\mathrm{Cr(PF_3)_6}$ |
| $PF_3$—Ni | 147 | $\mathrm{Ni(PF_3)_4}$ |

[a] Values in kJ $\mathrm{mol^{-1}}$ to nearest whole number.

$\sigma$-bonds are not thermodynamically weak and, in the examples chosen, certainly not weaker than the metal—CO bonds in an alkyl metal carbonyl complex. By the same token, there is no evidence that the bond enthalpy contribution of the trifluorophosphine ligand in $M(PF_3)_n$ complexes is greater than $\bar{T}$, so that thermodynamic arguments regarding the particular stability of certain $PF_3$ complexes have no justification.

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