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MEAN ENTHALPY OF DISRUPTION TO VALENCE STATE FOR HOMOLEPTIC TRANSITION METAL CARBONYLS. A REASSESSMENT

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Summary

The data necessary for an estimation of ΔH^{*}, the enthalpy of disruption of an M—CO bond to products in their valence states, is reexamined in the light of the high energy factored force field model (for force constants), the results of SCF—MO calculations of electron configuration and charge, and recent thermochemical experiments. It is shown that, for the metals Cr, Mn, Fe, Co and Ni, the value of ΔH^{*} is effectively constant (365 ± 10 kJ mol^{-1}). The consequences of this are discussed briefly. An attempt has been made to extend this treatment to carbonyls of the 4 *d* and 5 *d* metals.

Introduction

Many years ago, Cotton, Fischer and Wilkinson [1], considered the important problem of the magnitude of the enthalpy of disruption of a bond between a metal, M, and carbon monoxide to form products in the valence state and in the gas phase. Although, as we shall show, their general conclusions, namely that the enthalpy is approximately 350 kJ mol^{-1} and that the generally accepted picture of bonding in transition metal carbonyls is acceptable on the basis of bond energetics are correct, the information which has come to hand in recent years, about the 3 *d*-transition metal carbonyls in particular, seems to justify a reinvestigation of the problem.

At the time of the original study [1] (1958), no thoroughly reliable C—O stretching force constants were known, even for the mononuclear carbonyls of

TABLE 1

FORCE CONSTANTS K(CO) (N m^{-1}), MEAN ENTHALPY OF DISRUPTION $\overline{T}$ (kJ mol^{-1}), AND LIGAND VALENCE REORGANISATION ENERGY, ΔH^{M}_{CO*} (kJ mol^{-1}) FOR 3 d-TRANSITION METAL CARBONYLS

	K_{eq} ^{b}	K_{ax} ^{b}	$\overline{K}$ ^{b}	Ref.	$\overline{T}$ [3] (kJ mol^{-1})	ΔH^{M}_{CO*} (kJ mol^{-1})
$Ni(CO)_4$			17.246	5	146.9 ± 1.3	49.2
$Co_2(CO)_8$ ^{a}	17.02	17.12	17.05	6	136.0 ± 3.3	60.6
$Fe(CO)_5$	16.57	16.95	16.72	7	117.6 ± 1.7	79.7
$Mn_2(CO)_{10}$	16.500	16.308	16.462	8,9	99.2 ± 1.7	94.7
$Cr(CO)_6$			16.472	10	107.5 ± 1.7	94.1

[a] Bridged form. [b] 10^2 Nm^{-1}.

ing force constants for these molecules because this quantity should be more strictly related to $\overline{T}$. Unfortunately this information is not available because of the grave uncertainties in the correct assignment of the ν(MC) and δ(MCO) frequencies in the 600—300 cm^{-1} region, especially for the binuclear compounds $Mn_2(CO)_{10}$ and $Co_2(CO)_8$. Moreover, the extensive mixing of these two vibrational modes prohibits the application of the same force field that has been used in the ν(CO) region.

For a diatomic molecule, the dissociation energy D (kJ mol^{-1}) is given by the expression

$$D = \frac{\omega^2 CN}{4\ \omega x} \qquad (1)$$

in which ω is the harmonic frequency, ωx is a vibrational constant which is a

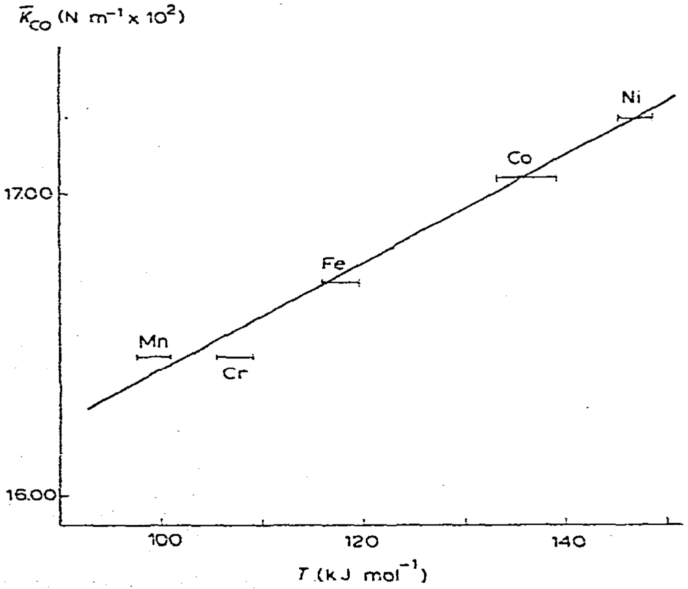

Fig. 2. Variation of the mean CO bond stretching force constant $\overline{K}$(CO) (10^2 Nm^{-1}) for the homoleptic metal carbonyls $M_n(CO)_m$, with the enthalpy of disruption to ground state products, T (kJ mol^{-1}).

measure of the anharmonicity of the oscillator, N is Avogadro's number (6.022×10^{23}) and C is a conversion factor ($1\ \mathrm{cm}^{-1} = 19.924 \times 10^{-24}$ J), so that CN is equal to 11.998 J mol^{-1}. The observed mean stretching frequency ν, the mean harmonic frequency ω and the anharmonicity ωx for the diatomic species NO, CN, CO and N_2 are given in Table 2. A plot of x vs. ω for these four molecules is shown in Fig. 3.

The stretching frequencies, ν observed by some of us [4—10] and by Jones [12] for the metal carbonyls which concern us here and for $Co(CO)_3NO$, together with Jones' values of the harmonic frequency, ω, in the molecules he has investigated are also shown in Table 2. It is then possible to interpolate the values of ω on the graph (Fig. 3) and in this way to obtain estimates of x. An alternative approach to the evaluation of x, is to note that the ratio ν/ω is constant (0.986 ± 0.003) to a good approximation where both are known precisely, so that ω can be obtained from the value of ν for $Co_2(CO)_8$ and $Mn_2(CO)_{10}$, and then the value of x is derived from Fig. 3. The results of this approach are given in Table 2. The last column of Table 2 shows that ωx is nearly constant (13.16 ± 0.01).

From these observations, that $\nu/\omega = 0.986$ and that $\omega x = 13.16$, it is possible to transform equation 1 so that we have

$$D = 0.2342\, \bar{\nu}^2 \ \mathrm{J\ mol^{-1}}$$

Now, the stretching frequency ν and the force constant, K for carbon monoxide are related by the expression

$$\nu = (K\mu)^{1/2}/2\, c\pi \ \mathrm{cm^{-1}}$$

where μ is the reduced mass and c is the velocity of light, so that

$$D = 0.05855\, K\mu(\pi c)^{-2} \ \mathrm{J\ mol^{-1}}$$

(where K is substituted in units of mdyn/Å = $10^2\ \mathrm{Nm^{-1}}$) which emphasises the

TABLE 2

ESTIMATION OF ANHARMONICITY CONSTANTS x AND HARMONIC FREQUENCIES, ω (cm^{-1}) FOR 3 d-TRANSITION METAL CARBONYLS

	$\bar{\nu}_{obs}$ [c]		ω [a]	$\bar{\nu}/\omega$		$10^3\ x$ [a]		ωx
NO	1876		1904	0.9853		7.337		13.97
CN			2068			6.354		13.14
CO	2143.2		2170	0.9876		6.203		13.46
N_2	2330		2359	0.9877		6.130		14.46
	[b]	[c]	[c]	[c]	ω(calcd.) [d]	$10^3\ x$ [c]	$10^3\ x$(calcd.) [e]	ωx(calcd
$Ni(CO)_4$	2065.6	2065.1	2096.4	0.9851	2093.9	6.290	6.297	13.18
$Co_2(CO)_8$	2054.2				2082.3		6.318	13.15
$Co(CO)_3NO$	2057.3	2067.0	2090.5	0.9888	2085.4			
$Fe(CO)_5$	2033.7	2029.7	2054.7	0.9878	2061.5	6.403	6.380	13.15
$Mn_2(CO)_{10}$	2017.8				2045.4		6.435	13.16
$Cr(CO)_6$	2018.2	2017.7	2052.0	0.9833	2045.8	6.410	6.430	13.15
Mean value				0.9865 [f]				13.16 [g]

[a] Herzberg [11]. [b] Bor [4—10]. [c] Jones [12]. [d] $\bar{\nu}^{b}/0.9865$. [e] By interpolation on Fig. 3. [f] For all values shown. [g] For five values of $M_m(CO)_n$ only.

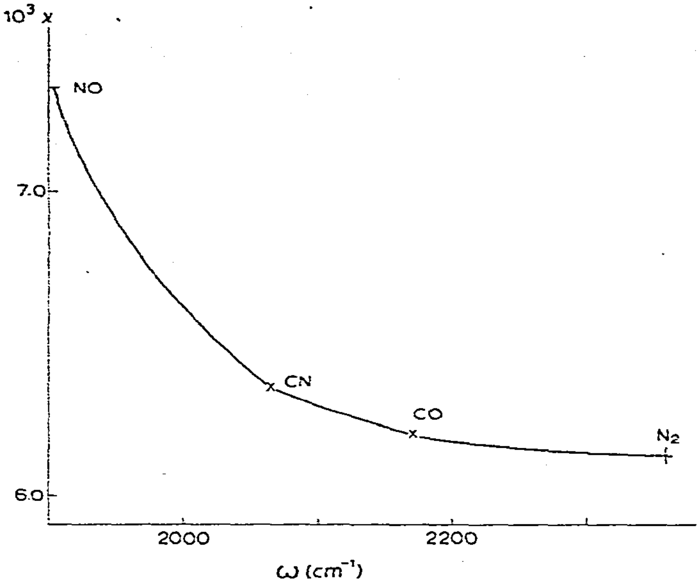

Fig. 3. Variation of x with ω cm^{-1} for NO, CN, CO and N_2 [11].

linear relationship between D and K for these complexes in the range 2100—2000 cm^{-1}. Consequently we may write

$$\Delta H^{M}_{CO*} = D[CO, g] - D[CO, complex]$$
$$= (1049 - 57.97\ K)\ kJ\ mol^{-1}$$

which gives the values shown (±2 kJ mol^{-1}) in Table 1.

Valence state promotion energy of the metal, ΔH_{M*}

The electron configuration of the metal atom in these binary 3 d-metal carbonyls is obtained from calculations the validity of which is reinforced by photoelectron spectroscopic measurements of core and valence ionization potentials.

Ab initio SCF—MO calculations have been carried out for $Cr(CO)_6$, $Ni(CO)_4$ [13,15] and $Fe(CO)_5$ [14]. The metal electron configuration in $[{}^{\cdot}Co(CO)_4]$ is here taken to be the same as that obtained for $[Co(CO)_3NO]$ [15]. The electron configuration of the manganese atom in $Mn_2(CO)_{10}$ has been obtained from SCCC calculations [16].

The valence state promotion energy at the calculated charge was obtained by interpolation between the mean value of the energy of all the multiplet terms of the neutral valence state configuration, d^n with respect to the ground state of the neutral atom ($\Delta E^*_{av}(0)$), and that of the valence state d^{n-1} obtained by ionization of one d-electron, also referred to the ground state of the neutral atom, that is ($\Delta E^*_{av}(+1)$ + IP). These values are related by the equation [17]

$$\Delta E^*_{av}(+1) + I_1 = \Delta E^*_{av}(0) + \mathrm{VOIP}$$

where I_1 is the first ionization energy of M and VOIP is the valence orbital ionization potential.

As an example of this procedure we consider $Ni(CO)_4$, for which the nickel

TABLE 3

ESTIMATION OF VALENCE STATE PROMOTION ENERGY ΔH_{M*} (kJ mol^{-1}) FOR 3 d-TRANSITION METAL CARBONYLS

	q [a]	$M*$ [b]	$\Delta E^*_{av}(0)$	$\Delta E^*_{av}(+1)$	ΔH_{M*}
$Ni(CO)_4$	0.5	$d^{9.1}\ p^{0.4}$	63.4	266.4	164.9
$Co(CO)_4$	0.4	$d^{8.3}\ p^{0.3}$	97.9	275.7	169.0
$Fe(CO)_5$	0.8	$d^{7.2}$	96.9	197.4	177.3
$Mn(CO)_5$	0.3	$d^{6.7}$	139.5	232.1	167.3
$Cr(CO)_6$	0.7	$d^{5.3}$	110.5	180.6	159.6

[a] Calculated charge on metal atom. [b] Valence electron configuration of metal.

valence electron configuration is calculated to be 3 $d^{9.1}$ 4 $p^{0.4}$ and the charge on the nickel is calculated to be +0.5 [13,15]. The neutral configuration of nickel metal is d^{10}, so that

$$\tfrac{7}{12}\, d^n + \tfrac{5}{12}\, (d^{n-1}p) = \tfrac{7}{12}\, d^{10} + \tfrac{5}{12}\, (d^9p) = d^{9.6}\, p^{0.4}$$

and the energy of this configuration, $\Delta E^*_{av}(0)$ (in 1000 cm^{-1} [17])

$$\tfrac{7}{12}\,(14.7) + \tfrac{5}{12}\,(30.2) = 21.16$$

which is distributed among four equivalent carbonyl ligands so that, $\Delta E^*_{av}(0) = 63.42$ kJ mol^{-1}. Similarly for the singly ionized configuration ($m = n - 1$)

$$\tfrac{7}{12}\, d^m + \tfrac{5}{12}\, (d^{m-1}p) = d^{8.6}p^{0.4}$$

for which $\Delta E^*_{av}(+1) = 266.4$ kJ mol^{-1}.

Interpolation between these two extremes for a metal charge of 0.5 gives $\Delta H_{M*} = 164.9$ kJ mol^{-1}. The same procedure can be used for the other metals and the results are collected in Table 3. An alternative approach to the calculation of ΔH_{M*} assumes a constant charge (−0.12) on each CO ligand, giving charges of +0.7 (Cr), +0.6 (Fe) and +0.5 (Ni) on the metal atoms. It can be shown that this would give values of ΔH_{M*} 161.1 (Cr), 156.9 (Fe) and 163.2 (Ni) kJ mol^{-1}. We prefer the values in Table 3 as being in accord with calculations and not subject to a generalised assumption which may not be justifiable.

Conclusion

The variation in the values of $\overline{T}$ and ΔH^{M}_{CO*} is complementary. This means that the reorganization energy recovered by disruption of the M—CO bond increases with the degree of deformation (or distortion) of the CO ligand from its free state condition. As the results in Table 4 show, both ($\overline{T} + \Delta H^{M}_{CO*}$) and ΔH_{M*} are effectively constant, so that ΔH^* is also constant. This is in slight contrast to the results of Cotton [1] that ΔH^* (Cr, Fe) > ΔH^* (Ni), but this is not remarkable in view of the quality of the data available at the time. The constant value of ΔH^* shows that metal—ligand bonding is qualitatively the same in all the 3 d-transition metal carbonyls. This is in agreement, not only with the conclusions of molecular orbital calculations, but also with measurements of the C1s and O1s core electron binding energies which are constant (within experi-

TABLE 4

SUMMARY OF ENTHALPY CONTRIBUTIONS TO THE ENTHALPY OF DISRUPTION TO VALENCE STATE, ΔH^*. All values are in kJ mol^{-1}.

	$\overline{T}$	ΔH_{CO^*}	$(\overline{T} + \Delta H_{CO^*})$	ΔH_{M^*}	ΔH^*
$Ni(CO)_4$	146.9	49.2	196.1	164.9	361.0
$Co_2(CO)_8$	136.0	60.6	196.6	169.0	365.6
$Fe(CO)_5$	117.6	79.7	197.3	177.3	374.6
$Mn_2(CO)_{10}$	99.2	94.7	193.9	167.3	361.2
$Cr(CO)_6$	107.5	94.1	201.6	159.6	361.2

mental error) for these (and all other) neutral carbonyls [3]. Although the (M—CO)-π bonding contribution is dominant throughout the series [3,18,19], these and other results confirm the presence of a complementary interaction between σ- and π-bonding effects, albeit at a less significant level.

At the present time it is not possible to estimate ΔH_{M^*} for 4 *d* and 5 *d* transition metals with anything approaching the precision possible for the 3 *d* series [17]. We have sought to make an approximation in the following manner. It is assumed that the charge on the 4 *d* or 5 *d* metal is the same as that on the 3 *d* metal in the homologous and isostructural metal carbonyl, and that both the neutral and singly ionized valence electron configurations are the same. We then propose that ΔH_{M^*} for the 4 *d* and 5 *d* metal M can be represented by a change in ΔH_{M^*} for the 3 *d* homologue, M′, which is proportional to first ionization energy, I_1 of M compared to that of M′. For example, in the case of molybdenum we have

$$\Delta H_{M^*}(\mathrm{Mo}) = \Delta H_{M^*}(\mathrm{Cr}) \times I_1(\mathrm{Mo})/I_1(\mathrm{Cr})$$

There are as yet very few spectroscopic studies which provide the necessary mean stretching force constant, $\overline{K}$ for the metal carbonyls of the 4 *d* and 5 *d* transition metals with sufficient precision. Table 5 summarises the information

TABLE 5

INTRINSIC BOND ENTHALPY, ΔH^*, FOR CARBONYLS OF CHROMIUM, MOLYBDENUM, TUNGSTEN, MANGANESE, TECHNETIUM AND RHENIUM, AND RELATED QUANTITIES

	Ref.	Cr	Mo	W	Mn	Tc	Re
$\overline{\nu}$ (cm^{-1})	12	2017.7	2018.8	2011.0			
$\overline{\omega}$ (cm^{-1})	12	2052.0	2048.9	2041.0			
$\overline{\nu}/\overline{\omega}$		0.9833	0.9853	0.9853			
$\overline{\nu}$ (cm^{-1})	4—10	2018.2	2020.4		2017.8	2025.1	2022.0
K (10^2 Nm^{-1})	4—10	16.472	16.502	16.34 [12]	16.462	16.577	16.527
$\overline{T}$ (kJ mol^{-1})	3	107.5	151.7	178.2	99.2	170 ^{a}	187
$\Delta H^{M}_{CO^*}$ (kJ mol^{-1})		94.1	92.4	101.8	94.7	88.0	90.9
ΔH_{M^*} (kJ mol^{-1})		159.6	167.5	188.3	167.3	163.7	177.2
ΔH^* (kJ mol^{-1})		361.2	411.6	468.3	361.2	422	455.1
I_1(M) (eV)	20	6.765	7.099	7.98	7.434	7.276	7.375

^{a} Estimated from ΔH_f^0[Tc, g] [3].

which is available, together with the other quantities, $\overline{T}$, $\Delta H^{\mathrm{M}}_{\mathrm{CO}*}$, $\Delta H_{\mathrm{M}*}$ and ΔH^* obtained in the manner already described. In the light of our earlier discussion there would appear to be no reason to expect that the value of ΔH^* will be very different from ca. 415 kJ mol^{-1} (4 *d* metals) and ca. 460 kJ mol^{-1} (5 *d* metals) for other members of these transition series which form homoleptic carbonyls. Insofar as the contribution of $\Delta H_{\mathrm{M}*}$ to the value of ΔH^* is of major importance, a more precise definition of this quantity in relation to 4 *d* and 5 *d* metals than the one which we have proposed would be desirable. The second most important influence on the value of ΔH^* is seen to be the value of $\overline{T}$, which is much more precisely defined than $\Delta H_{\mathrm{M}*}$. The close relationship between $\overline{T}$ and the heat of sublimation of the metal, ΔH_f^0[M, g] has been discussed elsewhere [3], and leads to the expectation that $\overline{T}$ will not vary widely for the 4 *d* and 5 *d* metals.

References

1 F.A. Cotton, A.K. Fischer and G. Wilkinson, J. Amer. Chem. Soc., 81 (1959) 800.
2 A.F. Schreiner and T.L. Brown, J. Amer. Chem. Soc., 90 (1968) 3366.
3 J.A. Connor, J. Organometal. Chem., 94 (1975) 195; J.A. Connor, Topics Current Chem., in press.
4 G. Bor, Inorg. Chim. Acta, 1 (1967) 81.
5 G. Bor, J. Organometal. Chem., 10 (1967) 343.
6 G. Bor, J. Organometal. Chem., 94 (1975) 181.
7 G. Bor, Inorg. Chim. Acta, 3 (1969) 191.
8 G. Bor, Chem. Commun., (1969) 696.
9 G. Bor and G. Sbrignadello, J. Chem. Soc. Dalton, (1974) 440.
10 G. Bor, Inorg. Chim. Acta, 3 (1969) 69; G. Bor, G. Sbrignadello and G. Battiston, to be published.
11 G. Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules, 2nd ed., Van Nostrand, Toronto, 1950.
12 L.H. Jones, J. Chem. Phys., 47 (1967) 1196; L.H. Jones, R.S. McDowell and M. Goldblatt, J. Chem. Phys., 58 (1973) 3757; L.H. Jones, R.S. McDowell, M. Goldblatt and B.I. Swanson, J. Chem. Phys., 57 (1972) 2050; L.H. Jones, R.S. McDowell and M. Goldblatt, Inorg. Chem., 8 (1969) 2349.
13 I.H. Hillier and V.R. Saunders, Mol. Phys., 22 (1971) 1025.
14 J.A. Connor, L.M.R. Derrick, M.B. Hall, I.H. Hillier, M.F. Guest, B.R. Higginson and D.R. Lloyd, Mol. Phys., 28 (1974) 1193.
15 I.H. Hillier, M.F. Guest, B.R. Higginson and D.R. Lloyd, Mol. Phys., 27 (1974) 215.
16 D.A. Brown, W.J. Chambers, N.J. Fitzpatrick and R.M. Rawlinson, J. Chem. Soc. Dalton, (1971) 720.
17 H. Basch, A. Viste and H.B. Gray, J. Chem. Phys., 44 (1966) 10.
18 E.J. Baerends and P. Ros, Mol. Phys., 30 (1975) 1735.
19 J.A. Connor, M.B. Hall, I.H. Hillier, W.N.E. Meredith, M. Barber and Q. Herd, J. Chem. Soc. Faraday II 69 (1973) 1677.
20 J.L. Franklin, J.G. Dillard, H.M. Rosenstock, J.T. Herron, K. Draxl and F.H. Field, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand., 26, 1969.