Bond Strengths in Metal Carbonyl Clusters

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Summary A new method is outlined for assigning energies to the metal–metal and metal–ligand bonds of metal carbonyl clusters $M_x(CO)_y$, using the lengths (d) and strengths (E) of the bonds in the metals M as a basis, and assuming E(M–M) to be proportional to $[d(\text{M–M})]^{-k}$; applied to examples with M = Fe, Ru, Os, Co, Rh, or Ir, it suggests (a) that their metal–metal bonds are generally weaker, and their metal–ligand bonds generally stronger, than previous treatments indicated; and (b) that the strength of binding of the carbonyl ligands to a particular metal increases with the cluster nuclearity x.

The energies of the bonds in metal carbonyl clusters are usually discussed[1–3] in terms of energies assigned to the 2-centre electron pair metal–metal bonds they are considered to contain on the basis of the 18-electron rule; *e.g.* three such bonds in $M_3(CO)_{12}$ (M = Fe, Ru, or Os), six in $M_4(CO)_{12}$ (M = Co, Rh, or Ir), and eleven, resonating between the twelve octahedral edges, in $Rh_6(CO)_{16}$. When the lengths d(M–M) and energies E(M–M) of these bonds are compared with those of the fractional order bonds in the metals themselves, as in the Table, one finds similar length bonds differing markedly in energy, different length bonds of identical energy, and long bonds apparently stronger than short bonds. Since there is increasing evidence that metal clusters behave as metal fragments cocooned by ligands,[2,4] these discrepancies are surprising. They stem largely from the assumptions made in deriving the bond energies, *viz.* that a formally 'single' metal–metal bond will have an energy that is *independent* of its length and independent of the nuclearity of the cluster in which it occurs, and that the strength of binding of carbonyl ligands to a particular metal also does not vary with the cluster nuclearity. We believe that these assumptions (commonly acknowledged to be strictly untenable approximations, but originally made to minimise the number of variables considered) are no longer needed. We suggest that a more realistic set of bond energies for metal carbonyl clusters can be obtained by assuming that the metal–metal bonds in the clusters are like those in the metals and that, like covalent bonds in general, they have energies that decrease as their length increases.

Of the many empirical relationships that have been found to relate bond energies to bond lengths, the most generally applicable is that in equation (1), where A and k

$$E(\text{X–Y}) = A[d(\text{X–Y})]^{-k} \qquad (1)$$

are constants characteristic of the class of compound. Plots of log E(X–Y) against log d(X–Y) give good straight lines of slopes $-k$ for wide ranges of compounds: for carbon–oxygen bonds, k = *ca.* 5; for carbon–carbon bonds,[5] k = *ca.* 3·3; and for metal–oxygen bonds,[6] k lies in the range 2—7, depending on the metal. We therefore suggest that the expression $E(\text{M–M}) = A[d(\text{M–M})]^{-k}$ can be used to calculate the probable energies of cluster metal–metal bonds of known length from the known energies and lengths of the bonds in the parent metals. To do this, we need to know the value of k, which is deduced as follows.

The structures most commonly adopted by metals are face-centred cubic (f.c.c.), hexagonal close-packed (h.c.p.), and body-centred cubic (b.c.c.). In a b.c.c. crystal, each metal atom is bonded comparatively strongly to eight nearest neighbours at a distance $d_{\text{b.c.c.}}$, and rather less strongly to six next-nearest neighbours at a distance $2d_{\text{b.c.c.}}/\sqrt{3}$. In a close-packed (c.p.) structure, however, whether f.c.c. or h.c.p., each atom is bonded to twelve nearest neighbours at a distance $d_{\text{c.p.}}$ Interestingly, for metals for which both b.c.c. and c.p. structures are known, the ratio $d_{\text{c.p.}}/d_{\text{b.c.c.}}$ varies remarkably little, being 1·0177 for Ti,[7] 1·0172 for Cr,[7] 1·0171 for Fe,[7] and about 1·018 for alkali and alkaline earth metals.[8] Moreover, the b.c.c. and c.p. metal lattices differ so little in energy that their enthalpies of disruption into gaseous atoms, $\Delta H_{\text{disrupt}}$, can be taken to be identical. Equating the atomisation enthalpy to the sum of the energies of the bonds broken,

$$\Delta H_{\text{disrupt}} = 4A[d_{\text{b.c.c.}}]^{-k} + 3A[2d_{\text{b.c.c.}}/\sqrt{3}]^{-k} = 6A[d_{\text{c.p.}}]^{-k} \qquad (2)$$

we can write equation (2), since four bonds of length $d_{\text{b.c.c.}}$ and three of length $2d/\sqrt{3}$ are severed per atom for the b.c.c. structure, and six of length $d_{\text{c.p.}}$ for the c.p. structure. Taking $d_{\text{c.p.}}$ to be 1·017 $d_{\text{b.c.c.}}$ we obtain k = *ca.* 4·6. [A corollary of this is that we can obtain E(M–M) of the eight nearest neighbour bonds of a b.c.c. structure by dividing $\Delta H_{\text{disrupt}}$ by 5·55, *not* 4 as in the conventional treatment, and the energies of the six bonds to the next-nearest neighbours by dividing $\Delta H_{\text{disrupt}}$ by 10·76].

Using the known length and strength of the bonds in the metals themselves as the basis, we have calculated the new cluster metal–metal bond energy terms in the Table from their lengths, using the relationship $E(\text{M–M}) \propto d(\text{M–M})^{-4.6}$. These in turn have been used to calculate mean disruptive energies, $\bar{D}$(M–CO), for the removal of the carbonyl groups from these clusters, using published values of the disruption enthalpies, $\Delta H_{\text{disrupt}}$, for the process $M_x(CO)_y(g) \rightarrow xM(g) + yCO(g)$ [$y\bar{D}(\text{M–CO}) = \Delta H_{\text{disrupt}} - \Sigma E(\text{M–M})$].

The results are listed in the Table, together with the results from earlier treatments[1,3] for comparison. The final columns of the Table show the percentage of $\Delta H_{\text{disrupt}}$ attributed to the metal–metal bonding, *i.e.* $100\,\Sigma E(\text{M–M})/[\Sigma E(\text{M–M}) + y\bar{D}(\text{M–CO})]$.

The following features emerge.

(a) The metal–metal bonds in these clusters are generally weaker than suggested by treatments based on the electron-pair bond, and the metal–ligand bonds are rather stronger. These conclusions are consistent with those drawn from a recent reassessment of the data for $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$.[9]

(b) The metal–metal bonding accounts for only *ca.* 6% of the

TABLE. Bond lengths and bond energies of metals and metal carbonyls

	$\Delta H_{\mathrm{disrupt}}$ /kJ mol^{-1}	d(M–M)[a] /pm	E(M–M)/kJ mol^{-1}		D(M–CO)/kJ mol^{-1}		%[b]	
			(ref. 1)	(this work)[c]	(ref. 1)	(this work)[d]	(ref. 1)	(this work)
Fe	417(4)[e]	248[f,g]	104	75[f]	—	—	—	—
$Fe(CO)_5$	585(8)[h]	—	—	—	117	117	0	0
$Fe_2(CO)_9$	1173(25)[h]	252[i]	82	70	121	123	7	6
$Fe_3(CO)_{12}$	1676(29)[h]	256[j]	82	65	121	126	14	10
		268	82	52				
Ru	651(8)[h]	265[g]	109	109	—	—	—	—
$Ru_3(CO)_{12}$	2414(29)[h]	285[k]	117	78	172	182	15	10
Os	790(8)[h]	268[g]	132	132	—	—	—	—
$Os_3(CO)_{12}$	2690(29)[l]	288[m]	130	94	190	201	15	11
Co	428(2)[e]	251[g]	71	71	—	—	—	—
$Co_2(CO)_8$	1160(12)[h]	252[n]	83	70	136	136	7	6
$Co_4(CO)_{12}$	2121(29)[l,o]	249[p,q]	83	74	136	140	24	21
Rh	557(4)[r]	269[g]	93	93	—	—	—	—
$Rh_4(CO)_{12}$	2648(29)[h]	273[p,q]	114	86	166	178	26	20
$Rh_6(CO)_{16}$	3874(29)[s]	278[t]	105	80	166	182	32	25
Ir	665(8)[r]	271[g]	111	111	—	—	—	—
$Ir_4(CO)_{12}$	3051(29)[h]	268[q]	130	117	190	196	26	23

[a] E.s.d. $\leqslant$ 1 pm. [b] % = 100 ΣE(M–M)/$\Delta H_{\mathrm{disrupt}}$. [c] Mean e.s.d. *ca.* 2 kJ mol^{-1}. [d] Mean e.s.d. *ca.* 3 kJ mol^{-1}. [e] J. Chao, JANAF Thermochemical Tables, 1965, 1968, Dow Chemical Company, Midland, Michigan, U.S. Dept. of Commerce, Nat. Bureau of Standards, Institute for Applied Technology. [f] The values of d and E quoted for iron relate to the b.c.c. structure; E(M–M) = $\Delta H_{\mathrm{disrupt}}/5{\cdot}55$. [g] 'Tables of Interatomic Distances, Supplementary Volume', ed. L. E. Sutton, Chem. Soc. Spec. Publ. No. 18, 1965. [h] Ref. 1. [i] F. A. Cotton and J. M. Troup, *J.C.S. Dalton*, 1974, 800. [j] F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, 1974, **96**, 4155. [k] M. R. Churchill, F. J. Hollander, and J. P. Hutchinson, *Inorg. Chem.*, 1977, **16**, 2655. [l] J. A. Connor, H. A. Skinner, and Y. Virmani, *Faraday Symp. Chem. Soc.*, 1973, **8**, 18. [m] M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 1977, **16**, 878. [n] G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Cryst.*, 1964, **17**, 732. [o] D. L. S. Brown, J. A. Connor, H. A. Skinner, C. P. Demain, M. L. Leung, J. A. Martinho-Simoes, and M. T. Zafarani, *J. Organometallic Chem.*, 1977, **142**, 321. [p] F. A. Cotton, F. H. Carre, and B. A. Frenz, *Inorg. Chem.*, 1976, **15**, 380. [q] C. H. Wei, G. R. Wilkes, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1967, **89**, 4792. [r] G. Pilcher, in M.T.P. Internat. Rev. Sci., Series 2, Phys. Chem., 1975, vol. 10, p. 45. [s] D. L. S. Brown, J. A. Connor, and H. A. Skinner *J.C.S. Faraday I*, 1975, **71**, 699. [t] E. R. Corey, L. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, 1963, **85**, 1202.

heat of disruption in dinuclear clusters, 10% in trinuclear clusters, 20% in tetranuclear clusters, and 25% in hexanuclear clusters.

(c) There is a slight but apparently significant increase in the strength of the metal–ligand bonds with increasing nuclearity of the clusters, *i.e.* as the number of carbonyl groups per metal atom decreases.

It should be stressed that these conclusions are not a consequence of the particular bond length–bond energy relationship used. Similar results are obtained if one uses other values of k (*e.g.*, by allowing k to range from 3 to 6) or other bond length–bond energy relationships that allow a realistic decrease in energy with increasing length. Moreover, because it associates bond energy with length, irrespective of bond order, the approach we have used is applicable to any system for which bond lengths are known, whether or not localized 2-centre bond descriptions are appropriate. Its use to predict the enthalpies of formation of clusters of known structure but uninvestigated thermochemistry, and to explore the relative affinity of carbon monoxide for terminal or bridging sites in metal clusters, and its application to metal–hydrocarbon π-complexes and to compounds with metal–metal multiple bonds, will be discussed elsewhere.

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