

Metal–ligand bond-energies in organometallic compounds

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Abstract - The energy contributions of metal-carbon and metal-ligand bonds in a variety of organometallic compounds are examined to seek trends as the metal or the ligand changes. In general, the bond energies $\bar{D}(M-X)$ for metals from the same group increase as the energy of atomization of the metal increases. Metal-carbon bond dissociation energies fall along the sequence $D_o(MC)$ in diatomic carbides > $\bar{D}(M-Cp)$ in cyclopentadienyls > $\bar{D}(M-arene)$ > $\bar{D}(M-alkyl)$ > $\bar{D}(M-CO)$ in metal carbonyls. For transition metals, the ligand bonding power of phosphine donors ($PEt_3 > PPh_3$) is larger than for nitrogen donors (pyridine > MeCN > NH_3), and olefine donors have similar bonding power to CO and pyridine. The irregular changes in the dissociation energies, $D_o(M_2)$, of transition dimetals on moving across the Periodic Table are considered in relation to the 'valence-state' adopted by the metal in forming metal-metal bonds.

INTRODUCTION

The enthalpies of formation of more than 400 organometallic compounds have now been determined; roughly one-half of these were obtained during the past decade, and relate to organo-compounds of the transition-metals. The most recent review (Ref.1) lists the ΔH_f^o values for 370 organometallics. Values are also now available for the dissociation-energies of ca. 300 diatomic molecules containing one or more metal atoms, including dimetals and intermetals (Ref.2), M-H, M-C, M-N (Ref.3) and M-O diatomics (Ref.4). The current data-bank is sufficient to seek possible trends in metal-ligand bond energies on passing from one metal to another, along or down the Periodic Table, but there are serious gaps and for some metals (e.g. lanthanides) very little is known.

DEFINITIONS AND SYMBOLS

The term 'bond energy' is widely used, but it needs to be defined. For a gaseous diatomic molecule, MX, the energy (ΔU_D) of the dissociation process $MX(g) \rightarrow M(g) + X(g)$ is temperature dependent. The symbol D_o is used for the dissociation energy at the absolute zero, and D for the dissociation energy at 298 K. ΔH_D^o refers to the standard enthalpy of dissociation at 298 K, i.e.

D_o = dissociation energy at 0 K

$D(MX)$ = dissociation energy at 298 K

$\Delta H_D^o(MX)$ = dissociation enthalpy at 298 K

For a polyatomic molecule MX_n (X = atom), in the gaseous form,

ΔH_a^o = enthalpy of atomization at 298 K = $\Delta H_f^o(M) + n\Delta H_f^o(X) - \Delta H_f^o(MX_n, g)$

ΔU_a^o = energy of atomization at 298 K = $\Delta H_a^o - nRT = \Delta H_a^o - 2.48 n \text{ kJ mol}^{-1}$

$\bar{D}(M-X)$ = mean bond-dissociation energy = $\Delta U_a^o/n$

For a molecule MR_n , where R is a free radical (e.g. in $Sn(CH_3)_4$, $R = \cdot CH_3 = Me$), the enthalpy of the disruption process, $MR_n(g) \rightarrow M(g) + nR(g)$ at 298 K is represented by ΔH_{dis}° , i.e.

$$\Delta H_{dis}^{\circ} = \text{enthalpy of disruption} = \Delta H_f^{\circ}(M) + n\Delta H_f^{\circ}(R) - \Delta H_f^{\circ}(MR_n, g)$$

$$\Delta U_{dis}^{\circ} = \text{energy of disruption} = \Delta H_{dis}^{\circ} - 2.48 n$$

$$\bar{D}(M-R) = \text{mean bond-dissociation energy} = \Delta U_{dis}^{\circ}/n$$

For a molecule in which the metal is bonded to different ligands, e.g. $[(Et_3P)_2PtCl_2]$, the disruption process has $\Delta U_{dis}^{\circ} = 2\bar{D}(Pt-Cl) + 2\bar{D}(Et_3P \rightarrow Pt)$ and the evaluation of the individual \bar{D} values requires acceptance of a 'transfer' value (e.g. $\bar{D}(Pt-Cl)$ from $PtCl_4$) for one of them. The partial disruption reaction, $[(Et_3P)_2PtCl_2] \rightarrow 2Et_3\bar{P} + PtCl_2(g)$ has

$$\Delta H_r^{\circ} = 2\Delta H_f^{\circ}[Et_3\bar{P}] + \Delta H_f^{\circ}[PtCl_2] - \Delta H_f^{\circ}[(Et_3P)_2PtCl_2]$$

and enables a direct measure of the mean bond-disruption energy, $\bar{D}(Et_3P - PtCl_2) = \Delta U_r^{\circ}/2$. For this same molecule, now written as

$PtP_2C_{12}H_{30}Cl_2$, the enthalpy of atomization, ΔH_a° , is given by

$$\Delta H_a^{\circ} = \Delta H_f^{\circ}(Pt) + 2\Delta H_f^{\circ}(P) + 12\Delta H_f^{\circ}(C) + 30\Delta H_f^{\circ}(H) + 2\Delta H_f^{\circ}(Cl) - \Delta H_f^{\circ}(PtP_2C_{12}H_{30}Cl_2), \text{ and}$$

$$\Delta U_a^{\circ} = \Delta H_a^{\circ} - 46 \times 2.48 \text{ kJ mol}^{-1}$$

On the basis of "bond-additivity", ΔU_a° is equated to the sum of the bond-energy contributions in the molecule, e.g.,

$$\Delta U_a^{\circ} = 2E(Pt-Cl) + 2E(Pt-P) + 6E(P-C) + 6E(C-C) + 12E(C-H, \text{ sec}) + 18E(C-H, \text{ primary})$$

and the evaluation of the individual E values is an arbitrary process, depending on the distribution rules of the scheme (Ref.5) adopted in apportioning ΔU_a° among the bonds present in the molecule.

AUXILIARY DATA

The evaluation of \bar{D} or E values in organometallic compounds from their enthalpies of formation also requires ΔH_f° values for gaseous metal atoms, and for ligands or free radicals bonded to the metal. The auxiliary data for the metals, listed in Table 1, are based on the critical compilations by Glushko and Gurvich(6), Glushko and Medvedev (7), Kondratiev (8), and the N.B.S. Selected Values (9); some of the values for free radicals are included in a recent review (Ref.10). Error limits are not quoted in Table 1, but for values where the uncertainty exceeds $\pm 10 \text{ kJ mol}^{-1}$, an asterisk is attached.

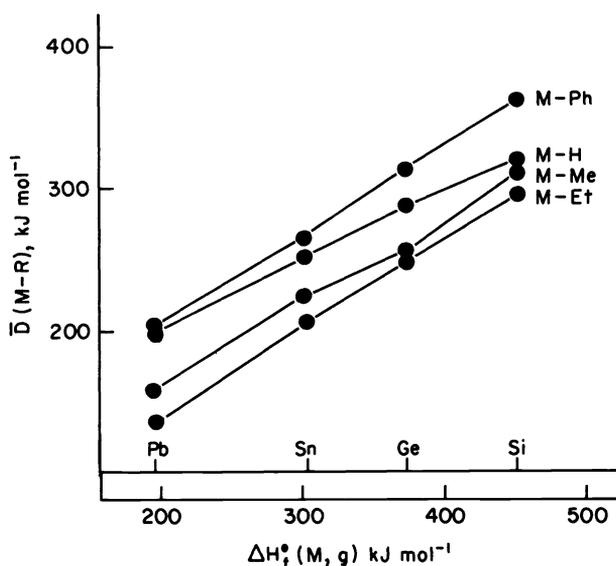
METAL HYDRIDES, ALKYL AND ARYL

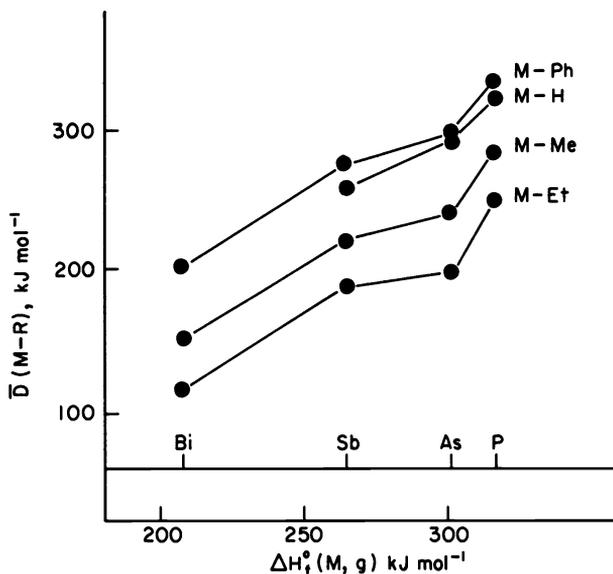
Thermochemical and bond-energy values are known for several hydrides, MH_n , alkyls and aryls, MR_n , of metals from Group I-V of the Periodic Table, but only a few such values have been determined for M-H or M-R bonds in transition metal compounds. The available data have been discussed by Pilcher (1,11), and a correlation with the enthalpies of atomization of the metals concerned was noted. Figure 1 shows this for the $\bar{D}(M-H)$, $\bar{D}(M-Me)$, $\bar{D}(M-Et)$ and $\bar{D}(M-Ph)$ values ($M = Si, Ge, Sn, Pb$), plotted against $\Delta H_f^{\circ}(g)$ for these Group IV elements. In the case of Si, Ge, and Sn (all of which adopt a stable 'diamond' lattice in the solid state), $\Delta H_f^{\circ}(g)$ of the metal is twice the M-M single-bond energy, so that the plot, in effect, implies that $\bar{D}(M-H)$ and $\bar{D}(M-R)$ increase as $\bar{D}(M-M)$ increases. It is interesting that Pb (which does not adopt a diamond structure in the solid state), fits the same correlation curve. Figure 2 shows a similar plot for the Group V elements ($M = P, As, Sb, Bi$). In the solid state, As, Sb and Bi have the same rhombohedral structure whereas P is orthorhombic, and $\Delta H_f^{\circ}(g)$ of the metal is approximately $1.5 E(M-M)$.

TABLE 1. Auxiliary data ; ΔH_f° values in kJ mol^{-1}

H	218.0	V	517.3	Rh	557.0	Ho	300.8
Li	159.3	Cr	397.1	Pd	375	Er	317.1
Be	324.0	Mn	284	Ag	284.9	Tm	232.2*
B	565.1	Fe	417.1	Cd	111.8	Yb	152.1
C	716.7	Co	426.5	In	240.4	Lu	427.6
N	472.7	Ni	429.5	Sn	301.2	Hf	622.4
O	249.2	Cu	337.6	Sb	265	Ta	782.5
F	79.4	Zn	130.5	I	106.8	W	855
Na	107.5	Ga	272.0	Cs	76.5	Re	775*
Mg	147.1	Ge	371.8	Ba	179.0	Os	790*
Al	329.7	As	301.8	La	430.0	Ir	665.3*
Si	450.0*	Br	111.9	Ce	423*	Pt	565.7
P	316.4	Rb	80.9	Pr	355.6	Au	368.8
S	277.0	Sr	160.5	Nd	327.6	Hg	61.4
Cl	121.3	Y	423.8	Sm	206.7	Tl	181
K	89.0	Zr	599.3	Eu	175.3	Pb	195.2
Ca	177.8	Nb	723.1*	Gd	397.5	Bi	208
Sc	377.7	Mo	657.6	Tb	388.7	Th	602.0
Ti	473.7	Ru	645*	Dy	290.4	U	535.6*
CH ₃	144 ± 3	Ph	332 ± 12	OiPr	-59.5 ± 8		
C ₂ H ₅	117 ± 5	C ₅ H ₅	264 ± 9	NMe ₂	123.5 ± 8		
tBuCH ₂	30 ± 6	DMP	(20 ± 20)	NEt ₂	69.4 ± 8		
PhCH ₂	204 ± 4	mhp	(25 ± 20)	OAc	-(227 ± 10)		
				acac	-(202 ± 20)		

(DMP = m-dimethoxyphenyl ; mhp = 2-oxy 6 methylpyridine)

Figure 1. $\bar{D}(M-H)$, $\bar{D}(M-R)$ v $\Delta H_f^\circ(M)$ for Group IV metals



Enthalpies of formation have been reported for compounds MR_4 of the transition-metals $M = Ti, Zr, Hf$ (Ref. 12), for $R =$ neopentyl (Me_3CCH_2), $PhCH_2$, NET_2 , $OiPr$. The derived mean bond-dissociation energies, $\bar{D}(M-R)$,

Ti-Np	185	TiBz	217	Ti- NET_2	307	Ti- $OiPr$	447
Zr-Np	221	Zr-Bz	263	Zr- NET_2	337	Zr- $OiPr$	517
Hf-Np	240			Hf- NET_2	364	Hf- $OiPr$	535

plotted against $\Delta H_f^\circ(M, g)$ of the metals, are shown in Figure 3. The dissociation-energies $D(MO)$ and $D(MN)$ of diatomic MO and MN are also plotted in Figure 3, and show a similar pattern. The metals Ti , Zr and Hf all have the same crystal form (c.p. hexagonal) at room temperature.

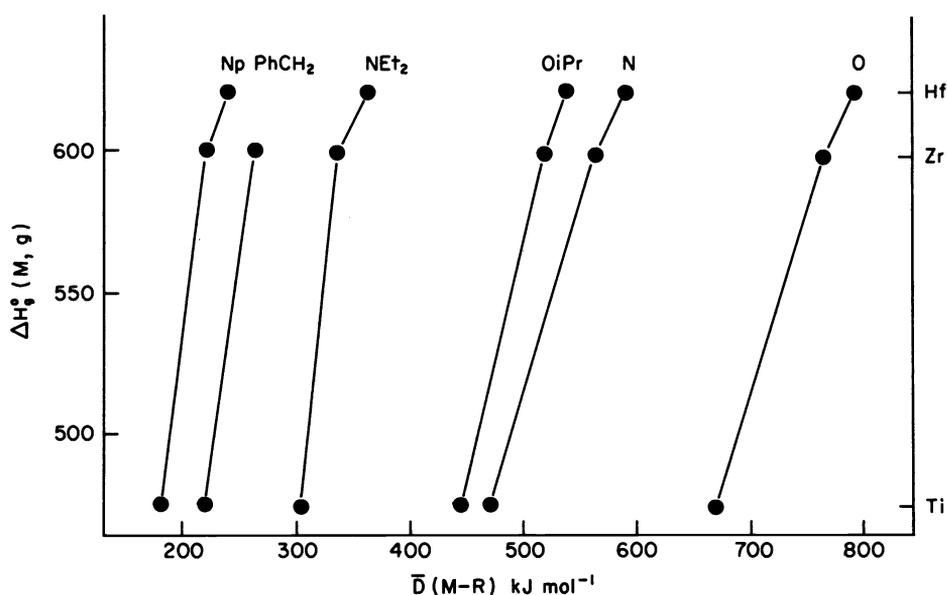


Figure 3. $\bar{D}(M-R)$ values v $\Delta H_f^\circ(M)$ for Ti , Zr , Hf .

METAL CARBONYLS

The enthalpies of formation of the mononuclear carbonyls, $M(\text{CO})_n$, of Cr, Mo, W, Fe and Ni lead directly to $\bar{D}(\text{M-CO})$ values for these metals. A pulsed laser pyrolysis technique has (Ref. 13), recently been applied to study the gas-phase thermal decomposition kinetics of mononuclear carbonyls, and provided values for the first bond dissociation energies, D_1 , e.g.,



These differ significantly from the mean \bar{D} values, viz.

	Cr(CO) ₆	Mo(CO) ₆	W(CO) ₆	Fe(CO) ₅	Ni(CO) ₄
\bar{D}	105	149	176	116	144
D_1	152	167	190	171	102

and in an irregular fashion. Variations of this order of magnitude are not uncommon ; in the case of the dialkyls of Zn, Cd and Hg (Ref. 14), $D_1 \gg \bar{D} \gg D_2$, and in CH_4 , D_1 exceeds D_4 by nearly 100 kJ mol^{-1} . Such differences are to be expected in molecules MR_n where the 'valence-state' of M differs from the ground-state of the atom, since the excitation energy required to achieve it is recovered during stepwise dissociation, but not uniformly at each step. The valence-states of Cr, Fe and Ni in the carbonyls $\text{Cr}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$ and $\text{Ni}(\text{CO})_4$ are considered to derive from zero-valent d^6 , d^8 and d^{10} configurations of these atoms ; the excitation energies required with Cr and Fe are quite high (Ref. 15), whereas the v_0, d^{10} valence-state of Ni lies only 176 kJ mol^{-1} above the ground-state, 3F . This is consistent with $D_1 > \bar{D}$ in $\text{Cr}(\text{CO})_6$ and $\text{Fe}(\text{CO})_5$ by a substantial amount. The excitation energy to reach v_0, d^6 in Mo is almost certainly less than with Cr (the state $^1I, d^6$ in Mo lies 473 kJ mol^{-1} above ground-level, whereas the corresponding state in Cr has not been observed, and probably lies above the ionization limit). The finding that $(D_1 - \bar{D})$ in $\text{Mo}(\text{CO})_6$ is less than in $\text{Cr}(\text{CO})_6$ may reflect this. States of configuration d^6 have not been identified in the atomic spectrum of W. The reverse situation ($D_1 > \bar{D}$) in $\text{Ni}(\text{CO})_4$ suggests a change in valence-state from v_0, d^{10} , in $\text{Ni}(\text{CO})_4$ to $v_2, d^8 s^2$, in $\text{Ni}(\text{CO})_3$, with a simultaneous drop in excitation energy from 176 to 88 kJ mol^{-1} (Ref. 15). This would require that the $\text{Ni}(\text{CO})_3$ radical has a triplet ground-state.

The thermochemical data on polynuclear carbonyls (e.g. $\text{Mn}_2(\text{CO})_{10}$, $\text{Ru}_3(\text{CO})_{12}$, $\text{Ir}_4(\text{CO})_{12}$) do not provide $\bar{D}(\text{M-CO})$ values directly, but have been used by Connor et al (16), on the basis of a subdivision of metal-carbonyl bonds into 'terminal' (M-CO) and 'bridging' (M-CO-M) types, to obtain bond-energy contributions in these molecules. Figure 4 shows a plot of 'terminal' bond energy values against $\Delta H_f^\circ(\text{g})$ for the metals ; the value for Os-CO may be too low, since the thermal decomposition studies on $\text{Os}_3(\text{CO})_{12}$ were not conclusive, and should be re-examined.

METAL ARENES AND CYCLOPENTADIENYLS

Enthalpies of formation have been determined (Ref. 17, 18) for a number of bis-arenes of Cr, and for bis-benzene Mo and bis-toluene W. The derived mean bond dissociation energies, $\bar{D}(\text{Cr-arene})$, depend on the arene, and range from ca. 164 kJ mol^{-1} in $[\text{Cr}(\text{C}_6\text{H}_6)_2]$ to 144 kJ mol^{-1} in bis-naphthalene Cr. The \bar{D} values along the series $[\text{Cr}(\text{C}_6\text{H}_6)_2] \rightarrow [\text{Mo}(\text{C}_6\text{H}_6)_2] \rightarrow [\text{W}(\text{C}_6\text{H}_5\text{CH}_3)_2]$ increase with increasing ΔH_f° of the metal (Fig.4)

The enthalpies of formation of tris-cyclopentadienyls of Sc, Y, La, Pr, Tm and Yb, and of bis-cyclopentadienyls of transition metals from the first row, have been obtained from measurements of their energies of combustion (Ref. 19, 20). The derived $\bar{D}(\text{M-Cp})$ values are included in Table 2, in which available bond dissociation energy values for metal-carbon bonds of different types are collected together for comparison. The gaps in this table outnumber the data items, some of which are subject to considerable uncertainty (bracketted values). Nevertheless, a clear pattern is discernable, which indicates that the strongest metal-carbon bonds occur in the metal carbide diatomic molecules, followed by $\text{M-Cp} > \text{M-arene} > \text{M-CH}_3 > \text{M-CO}$. This pattern matches expectation in that the 'bond-orders' of the metal-carbon bonds diminish in passing from MC to MCH_3 ; the bond-order rises again at M-CO, and it is the large reorganization energy of the CO ligand on dissociation which effectively

lowers $\bar{D}(M-CO)$.

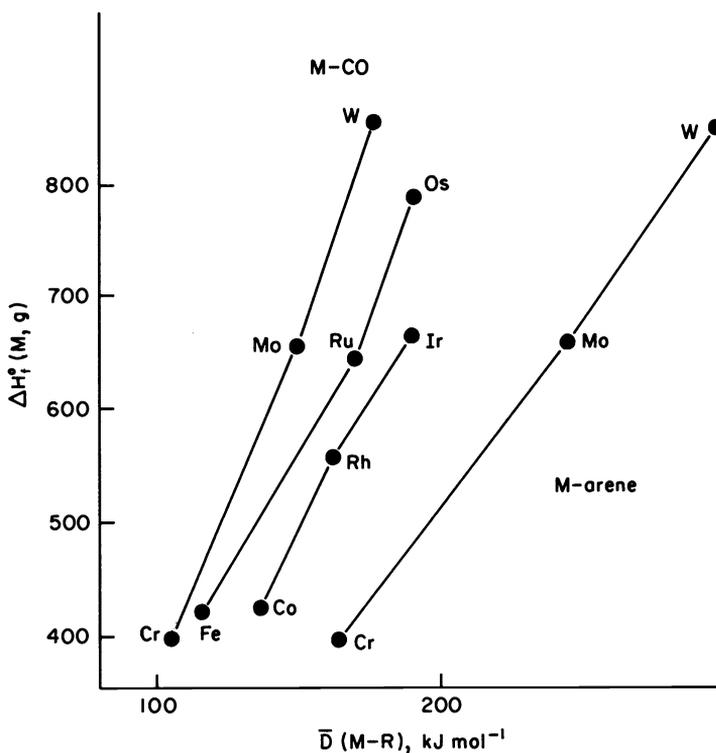


Figure 4. $\bar{D}(M-CO)$ values plotted against $\Delta H_f^0(M, g)$

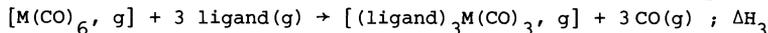
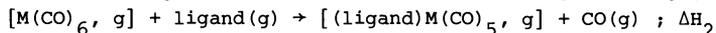
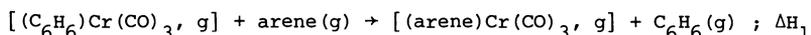
TABLE 2. Metal-carbon bond energies, \bar{D} .

Metal	$D_o(MC)$	$\bar{D}(M-Cp)$	$\bar{D}(M-C_6H_6)$	$\bar{D}(M-CH_3)$	$\bar{D}(M-CO)$
Sc	< 440	360	-	-	-
Y	~ 417	381	-	-	-
La	453	355	-	-	-
Ti	< 432	(318)	-	(255 - 280)	-
Zr	< 556	(411)	-	(274 - 325)	-
Hf	< 536	(412)	-	(340)	-
V	419	419	286	-	(156)
Nb	564	-	-	-	-
Ta	-	-	-	256	-
Cr	-	340	164	-	105
Mo	478	(403)	245	(152)	149
W	-	(447)	298	155(203)	176
Mn	-	263	-	(153)	(93)
Tc	561	-	-	-	-
Re	-	-	-	(218)	(179)
Fe	-	350	-	-	116
Ru	645	-	-	-	(170)
Os	645	-	-	-	(189)
Co	-	323	-	-	(133)
Rh	580	-	-	-	(160)
Ir	622	-	-	-	(189)
Ni	-	298	-	-	144
Pd	430	-	-	-	-
Pt	606	(366)	-	260(213)	-

LIGAND REPLACEMENT ENTHALPIES

Enthalpies of formation are known for a variety of ligand-substituted metal carbonyls, from which ligand-replacement heats are readily derived. Examples include the replacement of benzene in $[(C_6H_6)Cr(CO)_3]$ by a different arene (Ref. 21) and the replacement of CO in mononuclear carbonyls by a different ligand, such as pyridine or acetonitrile (Ref. 13, 22).

The displacement enthalpies, ΔH_1 , ΔH_2 , ΔH_3 for



are negative if the replacement ligand is more strongly bonded than the displaced ligand, and are positive when the reverse is the case. Values of ΔH_1 , ΔH_2 and ΔH_3 are given in Table 3.

TABLE 3. Ligand replacement enthalpies (kJ mol^{-1})

Arene	ΔH_1	Ligand	ΔH_2	ΔH_3
C_6Me_6	-26	Ph_3P (in $W(CO)_6$)	-123	-
Mesitylene	-12	Piperidine (in $W(CO)_6$)	+5	-
$PhNMe_2$	-3	Pyridine (in $W(CO)_6$)	+27	+15
Toluene	+4	CH_3CN (in $W(CO)_6$)	-	+26
$PhOCH_3$	+14	Pyridine (in $Mo(CO)_6$)	-	+18
$PhCl$	+19	CH_3CN (in $Mo(CO)_6$)	-	+39
Naphthalene	+26	Piperidine (in $Cr(CO)_6$)	+8	-
$PhCOCH_3$	+44	Pyridine (in $Cr(CO)_6$)	+28	-
$PhCOOCH_3$	+64	Ethylene (in $Fe(CO)_5$)	+22	-

The weakness of methylbenzoate and acetophenone (relative to benzene) is consistent with electron withdrawal from the ring by the $\cdot COCH_3$ and $\cdot COOCH_3$ substituent groups ; the relative strength of methyl-substituted benzenes, and of dimethylaniline is likewise indicative of electron donation to the ring by alkyl and $\cdot NMe_2$ substituents. The ΔH_2 , ΔH_3 values show that phosphine donors are stronger than nitrogen donors, and that CO donor is at least as strong as pyridine, and stronger than methyl cyanide and ethylene. Recent studies on complexes $[L_2PtCl_2]$ and $[L_2PdCl_2]$ have also shown the phosphine donors as appreciably stronger than nitrogen donors (Ref. 23), the $\bar{D}(L-PtCl_2)$ values diminishing along the series $L = PiPr_3 > P(C_6H_{11})_3 > PEt_3 > PPh_3 > \text{olefin (in cyclo-octa 1,5 diene)} > \text{pyridine} > \text{methylamine} > NH_3$; the $\bar{D}(L-PdCl_2)$ values for $L = PPh_3, \text{olefin and MeCN}$ are of similar magnitude to one another.

TRANSITION METAL MOLECULE-IONS

Beauchamp and co-workers (24,25) have reported ion-beam studies of reactions of the type $M^+ + R_2 \rightarrow MR + R$, for the transition-metal ions $M^+ = Cr^+, Mn^+, Fe^+, Co^+, Ni^+$ with $R_2 = H_2, C_6H_6, C_2H_4$ and O_2 , leading to values for the dissociation energies $D(M^+-H), D(M^+-CH_3), D(M^+-CH_2)$ and $D(M^+-O)$. These relate to the ground-states of the ions, $Cr^+ d^5, Mn^+ d^5s, Fe^+ d^6s, Co^+ d^8$ and $Ni^+ d^9$. Beauchamp has argued that the configurations d^n are less able to form strong σ -bonds than the configurations $d^{n-1}s$, reflected by the relatively low $D(M^+-H), D(M^+-CH_3)$ and $D(M^+-CH_2)$ values for $M^+ = Cr^+, Co^+$ and Ni^+ . In Table 4, the experimental D_0 values are given along side D_0^* values, measured with respect to the lowest-lying state, $d^{n-1}s$, of the ions from Cr^+, Co^+ and Ni^+ . Comparison of $D_0^*(M-X)$ with $D_0(M-1)-X$ of iso-electronic neutral molecules shows these to be of similar magnitude, in the few cases where comparison is possible.

METAL-METAL BONDS

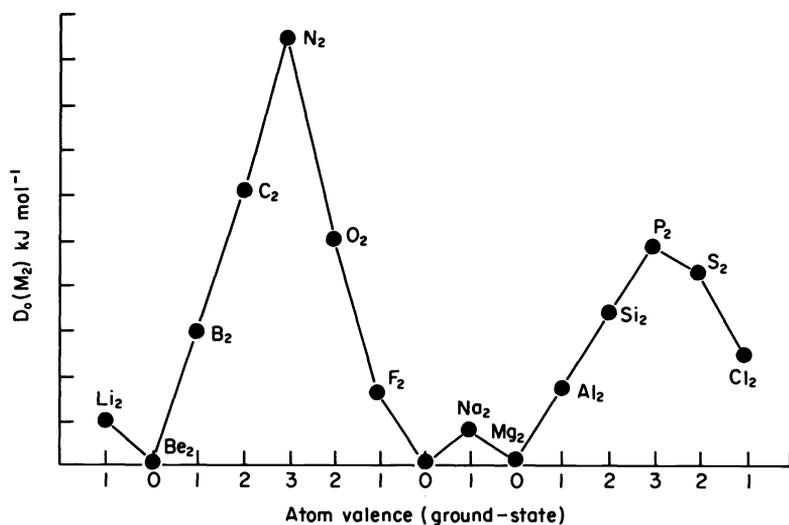
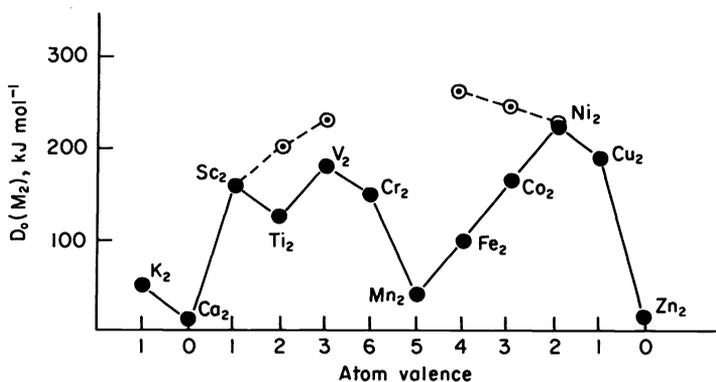
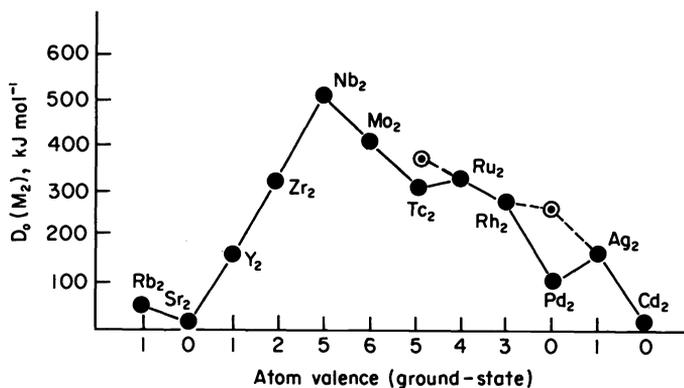
The dissociation-energies, $D_0(M_2)$, of some 50 homonuclear dimetals have been reported (Refs. 2,3). The values for diatoms of the 1st and 2nd row elements, plotted against atomic number (Fig. 5), rise and fall as the valences of the atoms change in passing from Li to Cl. The plot (Fig. 6) of $D_0(M_2)$ for the 1st row transition metals (from K to Zn) shows no such regularity. The higher valence atoms (Cr, Mn, Fe, Co) have $D_0(M_2)$ values which are less

TABLE 4. Dissociation energies in molecule-ions

Compound	$D_0(M^+-X)$	$D_0^*(M^+-X)$	Comparison
Cr^+	146 ± 17	289^*	
Cr^+CH_3	155 ± 29	298^*	
$Cr^+=CH_2$	272 ± 29	415^*	VC 419
Mn^+H	222 ± 12	222	CrH (275 ± 50)
Mn^+CH_3	297 ± 29	297	
$Mn^+=CH_2$	393 ± 25	393	
Fe^+H	243 ± 21	243	MnH (241)
Fe^+CH_3	285 ± 17	285	
$Fe^+=CH_2$	402 ± 21	402	
Co^+H	218 ± 17	256^*	
Co^+CH_3	255 ± 12	293^*	
$Co^+=CH_2$	356 ± 29	393^*	
Ni^+H	180 ± 8	280^*	CoH (309)
Ni^+CH_3	201 ± 21	301^*	
$Ni^+=CH_2$	360 ± 25	460^*	
Cu^+H	(<60)	<(320)	NiH 297
Zn^+H	241	241	CuH 264
Zn^+CH_3	280	280	
Cd^+H	203	203	AgH 220
Cd^+CH_3	226	226	
Hg^+H	289	289	AuH 311
Hg^+CH_3	293	293	

than $D_0(Cu_2)$, deriving from monovalent Cu, $d^{10}s$. The very weak bonding in Group II dimetals is essentially van der Waals in character, consistent with the zero-valent ground-states ($^1S, s^2$) of the atoms, and the large promotion energies needed to achieve a divalent state (e.g. $^3P, sp$). The weak binding in Mn_2 is less easily explained; the ground-state, $^6S, d^5s^2$, of the Mn atom, is capable in principle of forming a quintuple Mn-Mn bond, and the weakness of the bond formed suggests that d-electrons can only form weak bonds with one another. The evidence from other transition dimetals (e.g. $Nb_2, D_0 = (503 \pm 10) \text{ kJ mol}^{-1}$, deriving from ground-state Nb, $^6D, d^4s$) contradicts this; an alternative suggestion (Ref. 25) is that the configuration $d^n s^2$ has less linear bonding-power than $d^{n+1}s$. In the case of Mn_2 , the excitation energy needed to reach $^6D, d^6s$ (208 kJ mol^{-1}) is probably prohibitive. On the other hand the excitation energies $d^n s^2 \rightarrow d^{n+1}s$ for Fe, Co and Ni are not large, and the dimetals of these could well originate from excited $d^{n+1}s$ configurations. The binding-energies, $D_0^*(M_2)$ for Ni_2, Co_2 and Fe_2 , measured with respect to the lowest-lying configurations, $d^{n+1}s$, are plotted by the broken line in Figure 6, and change with valence in the expected manner.

The broken curve in Figure 6, would however, imply D_0^* for $Cr_2 > 300 \text{ kJ mol}^{-1}$, which is twice as large as the experimental value. The spectroscopic evidence (Ref. 26) clearly indicates a very short bond-length ($r_e = 1.68 \text{ \AA}$), consistent with sextuple bonding, and the ground-state configuration, $^1\Sigma_g^+$ is in accord with this. Curiously, it is the very shortness of the bond in Cr_2 which could account for the seemingly low value of D_0 - in that the σ -component of the sextuple bond is under considerable strain, compressed from its normal length by as much 0.7 \AA , and no longer very effective energetically as a binding agent. A factor of relevance to this suggestion is that the bond-energy contribution of the quadruple-bond, Cr-Cr, in a number of organic complexes of dichromium appears to be at least as large as $D_0(Cr_2)$, although the Cr-Cr bond-lengths in these are longer than in the dimetal. In these complexes

Figure 5. $D_0(M_2)$ values from Li_2 to Cl_2 .Figure 6. $D_0(M_2)$ values from K_2 to Zn_2 .Figure 7. $D_0(M_2)$ values from Rb_2 to Cd_2 .

(dichromium tetraacetate, $Cr_2(mhp)_4$, $Cr_2(DMP)_4$, Ref. 27) the ligand - Cr bonds are directed at right-angles to the Cr - Cr bond, and the quadruple bond need not involve a σ -component. The broken curve through Sc_2 , Ti_2 and V_2 is tentative; the ground-state of Sc_2 , from spectroscopic studies by Knight (28), is identified as the quintet $^5\Sigma$, and originates from excited Sc. The ground-state of V_2 is reported to be $^3\Sigma_g^-$ (Ref. 29), and the bond-length (1.77 Å) implies a high bond-order corresponding to a quintuple bond.

Figure 7 plots the $D_0(M_2)$ values for the second-row transition metals from Rb to Cd, showing the changing valence of the ground-states of the metal atoms. The low D_0 values for Sr_2 and Cd_2 reflect predominantly van der Waals interactions in these diatoms, deriving from the zero-valent ground-state atoms, but the D_0 in Pd_2 implies chemical bonding, and it seems clear that the low-lying d^9s , divalent state of Pd (3D_3 , d^9s , lies only 78.5 kJ mol $^{-1}$ above

the zero-valent ground-state, $^1S, d^{10}$, of the Pd atom) is the parent from which the dimetal derives. The D_0 values for Ru_2 , Ti_2 and Zr_2 are estimates only.

The broken curve refers to D_0^* values, relating to d^{n+1} s valence-states of the atoms. Bond-lengths and ground-state multiplicities are not yet determined for the second-row transition dimetals.

The available knowledge of dissociation energies, bond-lengths and ground-state multiplicities is insufficient to reach firm conclusions on the factors that influence metal-metal binding energy, but the variations with transition metals (and lanthanides) are irregular, and do not change with the ground-state valence of the metal atom in a regular manner. The role of "valence-state" is frequently ignored by thermochemists in evaluating "bond energies" (we do not usually relate the energies of carbon bonds in organic compounds to a tetravalent carbon atom!), and transition metal bonds seem to expose a real need to do so.

REFERENCES

- G. Pilcher and H.A. Skinner, Chap.2 in The Chemistry of the Metal-Carbon Bond, (F.R. Hartley and S. Patai, Eds.), J. Wiley (1982).
- K.A. Gingerich, Faraday Symposium of the Chem.Soc., No.14, Diatomic Metals and Metallic Clusters, 109-125 (1980).
- K.P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure, IV : Constants of Diatomic Molecules, Van Nostrand Reinhold, New York (1979).
- J.B. Pedley and E.M. Marshall, Thermochemical Data for Gaseous Monoxides, in the Industrial Use of Thermochemical Data, (T.I. Barry, Ed.), The Royal Soc. of Chemistry, p.83, London (1980).
- J.D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Chap.7, Academic Press, London (1970).
- Thermodynamic Properties of Individual Substances, (V.P. Glushko, L.V. Gurvich et al, Eds.), Vols.I-IV, Akad.Nauk., Moscow (1978-82).
- Thermal Constants of Substances, (V.P. Glushko, V.A. Medvedev, G.A. Bergman, L.V. Gurvich et al., Eds), Vols.I-X, Acad.Sci.USSR, VINITI, Moscow (1965-82).
- L.V. Gurvich, G.V. Karachevtsev, V.N. Kondratiev, Yu. A. Lebedev, V.A. Medvedev, V.K. Potapov and Yu. S. Hodiev, Energies of Dissociation of Chemical Bonds, Akad.Nauk.USSR, Moscow (1974).
- NBS Tables of Chemical Thermodynamic Properties, J.Phys.Chem.Ref.Data, Vol.11, Supplement No.2 (1982).
- M.N. Jones and H.A. Skinner, Ann.Rep.Chem.Soc., C, Chap.2, 'Thermochemistry', (1982).
- G. Pilcher, in Thermochemistry and its Application to Chemical and Biochemical Systems, NATO ASI Series, C 119, p.353-382, D. Reidel Publishing Co., Dordrecht, (1984).
- M.F. Lappert, D.S. Patel and J.B. Pedley, J.C.S. Chem.Comm., 830, (1975).
- K.E. Lewis, D.M. Golden and G.P. Smith, J.Am.Chem.Soc., (in Press).
- H.A. Skinner, Trans.Faraday Soc., 45, 20 (1949).
- H.A. Skinner and F.H. Sumner, J.Inorg.Nucl.Chem., 4, 245 (1957).
- J.A. Connor, H.A. Skinner and Y. Virmani, Faraday Symposia of the Chem.Soc., No.8, p.18 (1973).
- J.A. Connor, J.A. Martinho-Simoes, H.A. Skinner and M.T. Zafarani-Moattar, J.Organomet.Chem., 179, 331 (1979).
- J.A. Connor, N.I. El-Saied, J.A. Martinho-Simoes and H.A. Skinner, J.Organomet.Chem., 212, 405 (1981).
- C.G. Devyatikh, I.B. Rabinovitch, V.I. Tel'noi, G.K. Boisov and L.F. Zyazina, Dokl.Akad.Nauk., SSSR, 217, 673 (1974).
- V.I. Tel'noi, K.V. Kirynov, V.I. Ermolaev and I.B. Rabinovitch, Dokl.Akad.Nauk. SSSR, 209, 197 (1973).
- G. Al-Takhin, J.A. Connor, H.A. Skinner and M.T. Zafarani-Moattar, J.Organomet.Chem., 260, 189 (1984).
- G. Al-Takhin, J.A. Connor, G. Pilcher and H.A. Skinner, J.Organomet.Chem., 265, 263 (1984).
- G. Al-Takhin, H.A. Skinner and A.A. Zaki, J.C.S. Dalton Trans., 2323 (1983) and 371 (1984).
- P.B. Armentrout and J.L. Beaumont, Chem.Phys., 50, 37 (1980) ; J.Amer.Chem.Soc., 103, 784 and 6628 (1981) ; J.Chem.Phys., 74, 2819 (1981).
- P.B. Armentrout, L.F. Halle and J.L. Beaumont, J.Amer.Chem.Soc., 103, 962, 6501 and 6624 (1981) ; J.Chem.Phys., 76, 2449 (1982).
- D.L. Michalopoulos, E. Geusic, S.G. Hansen, D.E. Powers and R.E. Smalley, J.Phys.Chem., 86, 3914 (1982).
- K.J. Cavell, C.D. Garner, J.A. Martinho-Simoes, G. Pilcher, H. Al-Samman, H.A. Skinner, G. Al-Takhin, I.B. Walton and M.T. Zafarani-Moattar, J.C.S. Faraday Trans., 77, 2927 (1981).
- L.B. Knight, Jr., R.J. Van Zee, W. Weltner, Jr., Chem.Phys.Lett., 94, 296 (1983).
- P.R.R. Langridge-Smith, M.D. Morse, G.P. Hansen, R.E. Smalley and A.J. Merer, J.Chem.Phys., 80, 593 (1984).