

THE THERMOCHEMISTRY OF THE DI- η^5 -CYCLOPENTADIENYL DERIVATIVES OF THE FIRST TRANSITION SERIES AND THEIR UNIPOSITIVE IONS *

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Summary

The heats of formation [$\Delta H_f^0(\text{MCp}_2, c, 298)$] have been determined for the di- η^5 -cyclopentadienyl derivatives of magnesium, vanadium, chromium, manganese, iron, cobalt and nickel, by static-bomb calorimetry. They are (in kJ mol^{-1}) (M =) Mg, 77.0 ± 3 ; V, 123 ± 4 ; Cr, 186 ± 3 ; Mn, 198 ± 2 ; Fe, 158 ± 4 ; Co, 205 ± 4 ; and Ni, 262 ± 3 .

The heats of formation [$\Delta H_f^0(\text{M}(\text{CO})_x\text{Cp}, c, 298)$] of tricarbonylcyclopentadienylmanganese and dicarbonylcyclopentadienylcobalt have also been determined as -478 ± 1 and $-169 \pm 10 \text{ kJ mol}^{-1}$, respectively.

By using the measured heats of formation of the metallocenes of the first transition series and other enthalpy values from the literature in Hess's law cycles, the feasibility of the process $\text{MCp}_2 \rightarrow \text{MCp}_2^+ + e$ (obtained from the photoelectron ionisation energies) has been analysed and shown to be the result of the interplay of exchange energy and ligand-field stabilisation energy terms in these low-spin complexes. The feasibility order, $\text{V} < \text{Cr} > \text{Mn} > \text{Fe} < \text{Co} > \text{Ni}$ is associated with the special stability associated with half-filled and filled shells, which, because of the large ligand-field splitting, occur at d^3 , d^6 , d^8 and d^{10} .

It is shown that bond energy additivity does not occur for the above cyclopentadienylmetal carbonyls.

Introduction

Relatively little effort has been made by inorganic chemists to rationalise thermodynamic data in the light of modern valence theory. One such study [1] examined the thermal stabilities of the trihalides of the first transition series (eq. 1, X = Cl, Br or I), where it was shown that the main feature determining the variation in the standard free-enthalpy change (ΔG_{298}^0) for reaction 1 was almost entirely the third ionisation enthalpy of the transition metal. The

* Dedicated to Professor E.G. Rochow on the occasion of his 70th birthday.

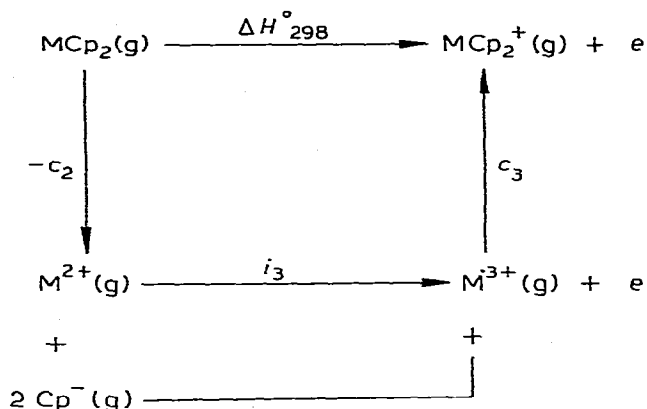


Fig. 1. Enthalpy cycle for conversion of metallocenes to their unipositive ions.

technique used was to examine a Hess's Law cycle for the decomposition, from which $\Delta G_{298}^{\circ} = l_2 - l_3 - i_3 - a_1 - 298 \Delta S_{298}^{\circ}$, where l_2 and l_3 are the lattice enthalpies of the di- and tri-halides, i_3 is the third ionisation enthalpy of the gaseous metal atom, a_1 is the standard enthalpy of formation of the halide ion and ΔS_{298}° is the standard entropy change for the decomposition. Having used thermodynamics to so restate the problem, the theory of many-electron atoms



[2] relates the overall increase of i_3 on traversing the series to the increasing nuclear charge. The discontinuity found in i_3 between Mn^{2+} and Fe^{2+} is due to the loss of exchange energy on ionisation falling to zero on going from Mn^{2+} (d^5) to Fe^{2+} (d^6). Other M^{III} to M^{II} processes have been studied [3,4] and in most of these the feasibility of the process taking place varies as ($\text{M} =$) $\text{Cr} < \text{Mn} > \text{Fe} < \text{Co}$.

This order is not always found [5]. For the reduction of the metal in hexacyano complexes the feasibility order is $\text{Cr} < \text{Mn} < \text{Fe} > \text{Co}$, due to the very large changes in ligand-field stabilisation energy that occur with the low-spin cyano complexes.

A more complete series of low-spin complexes are the di- η^5 -cyclopentadienyl derivatives, MCp_2^* , of the first transition series (the metallocenes); ($\text{M} =$) V, Cr, Mn, Fe, Co and Ni. Justification of these as a set of low-spin complexes is given later. The process to be studied is given by eq. 2, the formation of the metallocinium ions. The feasibility of this reaction can be obtained from the photoelectron ionisation potential of the metallocene [6,7], and can be related to values of ΔG_{298}° ($=\Delta H_{298}^{\circ} + 298 \Delta S_{298}^{\circ}$) for this process. As these complexes are isostructural, the term $298 \Delta S_{298}^{\circ}$ will be virtually constant and the feasibility order will be given by the values of ΔH_{298}° .



Analysis of ΔH_{298}° is possible by use of a Hess's Law cycle (Fig. 1), when ΔH_{298}°

* Throughout this paper $\text{Cp} = \text{C}_5\text{H}_5$.

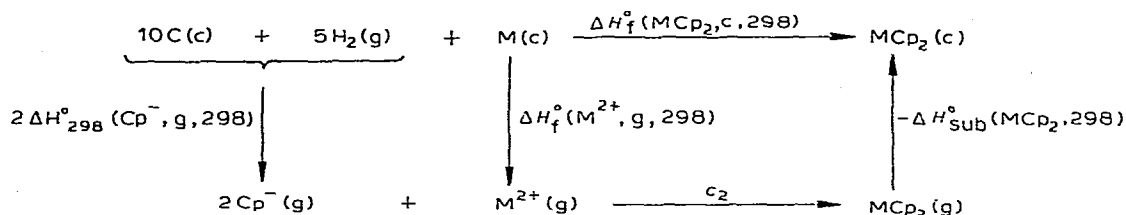


Fig. 2. Enthalpy cycle for the formation of the metallocenes.

is given by eq. 3, where c_2 and c_3 are the enthalpy changes associated with the formation of the gaseous complexes MCp_2 and MCp_2^+ from the corresponding gaseous ions. Now c_2 is related to the enthalpy of formation of the metallocene, $\Delta H_{\text{f}}^{\circ}(\text{MCp}_2, \text{c}, 298)$, by another Hess's law cycle (Fig. 2), $\Delta H_{\text{f}}^{\circ}$ being given by eq. 4, where $\Delta H_{\text{f}}^{\circ}(\text{M}^{2+}, \text{g}, 298)$ and $\Delta H_{\text{f}}^{\circ}(\text{Cp}^-, \text{g}, 298)$ are the standard enthalpies of formation of the gaseous M^{2+} and Cp^- ions, respectively, and $\Delta H_{\text{sub}}^{\circ}(\text{MCp}_2, 298)$ is the enthalpy of sublimation of the metallocene. Knowing these and the enthalpies of formation, $\Delta H_{\text{f}}^{\circ}(\text{MCp}_2, \text{c}, 298)$, of the metallocenes, c_2 can be evaluated, and then from the cycle in Fig. 1, so can c_3 . The determination of the

$$\Delta H_{298}^{\circ} = -c_2 + i_3 + c_3 \quad (3)$$

$$\Delta H_{\text{f}}^{\circ}(\text{MCp}_2, \text{c}, 298) =$$

$$\Delta H_{\text{f}}^{\circ}(\text{M}^{2+}, \text{g}, 298) + 2 \Delta H_{\text{f}}^{\circ}(\text{Cp}^-, \text{g}, 298) + c_2 - \Delta H_{\text{sub}}^{\circ}(\text{MCp}_2, 298) \quad (4)$$

quantities on the right hand side of eq. 3, and of their influence on the feasibility of the process given by eq. 2, are the major aims of this paper. Experimental measurements of the heats of formation of the metallocenes are needed to complete the cycle of Fig. 2 and eq. 4, and these have been carried out by static-bomb calorimetry. During the course of this work such values have also been reported by Rabinovich and Tel'noi [8-10]. Their values are, in general, encouragingly close to ours, and we briefly compare our results with theirs.

Whether or not bond-energy additivity occurs with these organometallic compounds is also briefly considered.

Experimental

Published methods were used to prepare the dicyclopentadienyl derivatives of vanadium [11], chromium [12], manganese [12], iron [13], cobalt [14], and nickel [14], from cyclopentadienylsodium and the appropriate metal chloride. The low-temperature amber form of manganocene was prepared; we were not able to obtain the pink isomer in high enough purity for calorimetric studies. Dicyclopentadienylmagnesium was prepared by the reaction of cyclopentadiene with magnesium turnings [15]. These metallocenes and tricarbonylcyclopentadienylmanganese (Alfa Inorganics Inc.) were purified by repeated vacuum sublimations. Dicarboxylcyclopentadienylcobalt (Alfa Inorganics Inc.) was purified by chromatography on a deactivated alumina column using light petroleum (40-60°C) as the eluent. As all of the compounds, except ferrocene and tricarbonylcyclopentadienylmanganese, are air sensitive they were prepared under dry nitrogen and handled in a glove box containing P_2O_5 and Na/K

alloy. The amount of CO₂ produced on combustion was used as an indication of the purity of the compounds.

Combustions were carried out under a pressure of 30 atm of oxygen (B.O.C., < 0.1% N₂) in a "Baird and Tatlock" adiabatic bomb calorimeter. Temperatures were measured using a 6° C range differential Beckman thermometer that was calibrated against a platinum resistance thermometer. The carbon dioxide in the combustion gases was analysed by absorption, after drying, on soda-lime in a U-tube train. Throughout this investigation a combustion was regarded as being incomplete, or the sample to be impure, if less than 99.7% of the estimated carbon dioxide was recovered. For no compound did this consistently occur, and we conclude that all samples were pure.

The energy equivalent of the calorimeter was determined by combustion of benzoic acid and naphthalene. It was found to be 10332.9 ± 5 J °C⁻¹. To this value was added the energy equivalent of the particular crucible used for each compound.

The air-sensitive compounds were protected before combustion by sealing them in vacuum-formed cups of polythene (I.C.I. Alkathene). Each cup was just large enough to hold 1 g of sample, and after filling was capped with a heat-sealed polythene lid. The polythene used [(CH_{2.037})_n] had an energy of combustion of -46.46 ± 0.02 kJ g⁻¹ (mean of 6 determinations).

For the combustion it is necessary to use a crucible material that does not react with the metal oxide products. The material of which the crucible, or the crucible lining, was made is shown in line 2 of Table 1. The Cr₂O₃ and Fe₂O₃

TABLE 1
SUMMARY OF TYPICAL CALORIMETRIC EXPERIMENTS

	VCP ₂	CrCP ₂	MnCP ₂	FeCP ₂
Mol. wt.	181.133	182.187	185.129	186.038
Container for combustion	SiO ₂	Cr ₂ O ₃ ^b	Mn ₃ O ₄ ^b	Fe ₂ O ₃ ^b
Mass of compound (g)	0.72796	0.71206	0.91117	0.84885
Mass of polythene (g)	0.20247	0.23971	0.19890	—
Corrected temperature rise (K)	3.340	3.393	3.759	2.606
Energy equivalent of calorimeter and contents (J K ⁻¹)	10337.9	10339.3	10338.7	10342.6
Ignition energy (J)	48.5	49.5	51.9	47.2
CO ₂ recovered (%)	100.00	99.96	99.75	99.91
Correction to standard states (kJ mol ⁻¹)	2.7	3.6	3.4	2.7
Correction to a constant pressure process (ΔnRT) (kJ mol ⁻¹)	9.1	8.0	7.7	7.8
Analysis of product (mol %)	V ₂ O ₅ 72.0 VO ₂ 28.0	Cr ₂ O ₃ 100	Mn ₃ O ₄ 78.3 MnO 21.7	Fe ₃ O ₄ 94.2 Fe ₂ O ₃ 5.8
ΔH _f ⁰ (kJ mol ⁻¹) ^a	123	184	201	163

^a Mean values in text and Table 3. ^b As lining in a silica crucible.

linings were moulded inside a silica crucible and fired at 600 and 1200°C, respectively, and the Mn₃O₄ lining was fired into discs at 1350°C and cut on a lathe to fit tightly inside silica crucibles.

Data from the calorimetric runs were treated in the usual way [16,17] to obtain heats of combustion and values of ΔH_f^0 (compound, c, 298). Allowance was made for the energy produced on fusing the platinum wire on ignition (418.4 J g⁻¹ [17]) and on combustion of the cotton fuse used to connect the sample to the ignition wire (16.240 kJ g⁻¹ [18]). One ml of distilled water was added to the bomb; this ensured that the atmosphere was saturated with water vapour, and any water produced in the combustion will then be in the liquid state.

A summary of typical calorimetric experiments is given in Table 1. Heats of formation of the oxides produced on combustion are given in Table 2. The metal oxides were identified by X-ray powder photography. In general the higher oxides were formed on the bomb walls, and the lower oxides were formed in the crucible where molten products have limited access to oxygen. The proportions of the combustion products were determined by carefully collecting them from the bomb and weighing. For one or two products this gives a unique assignment of their proportions. For the cobalt compounds, where there are three combustion products containing cobalt, the amount of one of them (Co₃O₄) was determined iodometrically.

CoCp ₂	NiCp ₂	MgCp ₂	Mn(CO) ₃ Cp	Co(CO) ₂ Cp
189.124	188.901	154.503	204.065	180.05
Co	Ni	SiO ₂	Mn ₃ O ₄ ^b	Co
0.80568	0.84284	0.66810	1.00070	0.31740
0.20063	0.21150	0.19595	—	0.22368
3.268	3.407	3.410	1.828	1.607
10335.7	10336.0	10339.4	10338.6	10334.9
50.4	50.3	49.9	50.4	47.1
99.88	99.96	99.98	99.93	100.04
3.6	3.8	3.5	3.1	1.7
7.0	6.5	7.4	1.0	4.4
Co ₃ O ₄ 5.3	NiO 22.6	MgO 100	Mn ₃ O ₄ 95.7	Co ₃ O ₄ 22.1
CoO 59.3	Ni 77.4		MnO 4.3	CoO 56.0
Co 35.4				Co 21.9
211	263	75	-480	-172

TABLE 2
HEATS OF FORMATION OF OXIDES USED IN CALCULATIONS

ΔH_f^0 (kJ mol ⁻¹) ^a		ΔH_f^0 (kJ mol ⁻¹) ^a	
CO ₂ (g)	-393.51 ^b	Fe ₂ O ₃	-824.2
CO(g)	-110.53 ^b	Fe ₃ O ₄	-1118
H ₂ O(l)	-285.830 ^b	CoO	-237.9
VO ₂	-713.58	Co ₃ O ₄	-891.2
V ₂ O ₅	-1551	NiO	-239.7
Cr ₂ O ₃	-1140	MgO	-601.5 ^b
Mn ₃ O ₄	-1388		
MnO	-385.2		

^a From ref. 38 except where marked otherwise. ^b CODATA recommended values, J. Chem. Thermodynamics, 10 (1978) 903.

Results and discussion

Heats of formation

The enthalpies of formation of ferrocene and nickelocene were measured some time ago [19,20] and those of all the metallocenes measured here have recently been reported by one other group [8–10]. Considering the experimental problems involved in making thermochemical measurements on organo-metallic compounds [21], particularly the need to quantitatively determine in each experiment which oxides of the metals are formed on combustion, the agreement is good (Table 3). Differences in technique between ourselves and other workers are worthy of comment.

(a) Tel'noi and Rabinovich [8,9] did not weigh the metallocene, but assumed 100% combustion and calculated its weight from the weight of CO₂ produced. We weighed both metallocene and CO₂, and for each combustion could check that it was complete.

(b) The combustion of paraffin wax, used by Tel'noi and Rabinovich to protect the metallocenes from aerial oxidation, accounted for some 85% of the observed temperature rise. We used polythene capsules which contributed only some 25% to the temperature rise.

(c) We successfully lined crucibles with the oxides that were produced in the combustion and hence eliminated any possible reaction between the reaction products and the crucible. That this may be serious is shown by the early value of ΔH_f^0 for ferrocene which is considerably lower than the two recent determinations. Alumina crucibles were used [22] and the reaction of the iron oxides produced with the crucible may account for the low value obtained. We observed considerable reaction of the iron oxides with silica crucibles.

(d) The metal oxides produced on combustion in this work and that of others [8,9,19,20] agree, except for vanadocene [8], where up to $\frac{1}{3}$ of our product was VO₂.

As a check on the use of static-bomb calorimetry for determining the heats of formation of metallocenes we have also measured the heat of combustion of di- η^5 -cyclopentadienylmagnesium. A value of ΔH_f^0 (MgCp₂, c, 298) of 67.0 ± 3.3 kJ mol⁻¹ has been obtained by Hull et al. using solution calorimetry [23]. By

TABLE 3
THERMODYNAMIC QUANTITIES OF DI- η^5 -CYCLOPENTADIENYL DERIVATIVES OF THE FIRST TRANSITION SERIES
All thermochemical quantities are in kJ mol^{-1}

M	ΔH_f^0 (MCP ₂ , e, 298)	ΔH_{sub}^0 (MCP ₂ , 298)	ΔH_{298}^0	ΔH_f^0 (M ²⁺ , g, 298)	t_3^m	c_2	c_3
	This work ^a	Previous					
V	123 ± 4(6)	138 ^b	72.8 ^f	640 ^k	2828	-2552	-4740
Cr	186 ± 3(6)	179 ^c	72.8 ^f	538 ^j	2987	-2556	-5006
Mn	198 ± 2(6)	201 ^c	72.4 ^g	590 ^k	3251	-2415	-5076
Fe	158 ± 4(6)	169 ^c 141 ^d	73.5 ^h	656 ^j	2958	-2675	-4977
Co	205 ± 4(6)	236 ^c	72.8 ^f	523 ^k	3230	-2725	-5432
Ni	252 ± 3(5)	285 ^c 263 ^e	72.4 ⁱ	609 ^j	3397	-2753	-5541

^a Mean ± S.D. of mean; number of determinations in parentheses. ^b Ref. 8, ^c Ref. 9, ^d Ref. 19, ^e Ref. 20, ^f See text, ^g Ref. 12, ^h Mean of ref. 30 and ref. 31, ⁱ Ref. 30, ^j Calculated from the vertical ionisation energies of Rabalais et al. [6] and Evans et al. [7], corrected to adiabatic values using the Frank-Condon factors given by Rabalais et al. [6], plus 6.2 kJ mol^{-1} (as given by eq. 5). ^k Calculated from the vertical ionisation energies of Evans et al. [7], corrected to adiabatic values using an estimated Frank-Condon factor of 20 kJ mol^{-1} , plus 6.2 kJ mol^{-1} (as given by eq. 5). For manganese the band of lowest energy is very weak; this band has been used here. ^l Ref. 1, ^m Ref. 32.

static-bomb calorimetry we find $\Delta H_f^0 = 77.0 \pm 3 \text{ kJ mol}^{-1}$ (mean of 6 determinations). These values agree within the limits of experimental error, and indicate that the calorimetric technique used here is capable of giving satisfactory results for organometallic compounds.

The feasibility of the process $M^{II} \rightarrow M^{III}$ for low-spin complexes

(i) Introduction

Both crystal-field and molecular-orbital theory predict that the 3d-orbitals in the metallocenes will be split into e_{2g} (d_{xy} and $d_{x^2-y^2}$), ε_{1g} (d_{z^2}) and e_{1g} (d_{xz} and d_{yz}) levels of increasing energy, with the separation of the e_{2g} and ε_{1g} levels being small compared with that between them and the e_{1g} level. The ratio of these energy differences is about 1 : 3.6 [24] *. Thus, although the orbitals are different, the pattern of splitting is similar to that for an octahedral complex. We shall call the lower set of orbitals (e_{2g} and ε_{1g}) θ and the upper set (e_{1g}) ϵ . Of the 6 metallocenes, MCp_2 (M =) V, Cr, Mn, Fe, Co and Ni, five are low spin as is evident from the magnetic moments [25], i.e., the θ orbitals are filled first. The exception is manganocene, which under certain conditions (e.g., in solution or in a MgCp_2 host) is undoubtedly high-spin, but under other conditions (e.g., in a FeCp_2 host) seems to be low-spin, and may sometimes exist as an equilibrium mixture of the two forms (e.g., in the vapour?) [24,26,27]. From the information available, it seems likely that the energy difference between the two forms is very small, and we shall assume that it is $0 \pm 10 \text{ kJ mol}^{-1}$. All of the metallocinium ions, MCp_2^+ , that have been studied magnetically are low-spin, and the only one that has not (MnCp_2^+) is most likely to be low-spin, by analogy with the iso-electronic neutral compound, CrCp_2 , and from the fact that spin pairing occurs more readily in the ions (comparing FeCp_2^+ with MnCp_2). Thus the metallocenes and their ions provide a series of compounds comparable to low-spin octahedral complexes such as the hexacyanides.

(ii) The enthalpy of ionisation of the metallocenes (ΔH_{298}^0)

This is the quantity that measures the feasibility of the ionisation (eq. 2). It is related to the ionisation potential [6,7], I , of the metallocene by eq. 5 [28]. Values of ΔH_{298}^0 are given in Table 3.

$$\Delta H_{298}^0 = I + \frac{5}{2}(298R) = I + 6.2 \text{ kJ mol}^{-1} \quad (5)$$

Before these values can be discussed in terms of the interplay of the quantities (i_3 , c_2 and c_3) given in the cycle (Fig. 1 and eq. 3), it is first necessary to calculate their values.

(a) The enthalpy of formation of the gaseous metallocene from its ions (c_2).

This is obtained from the cycle (Fig. 2 and eq. 4), and requires the standard enthalpies of formation of the metallocene, $\Delta H_f^0(\text{MCp}_2, c, 298)$, of the gaseous M^{2+} ion, $\Delta H_f^0(M^{2+}, g, 298)$, and of the cyclopentadienyl anion, $\Delta H_f^0(\text{Cp}^-, g, 298)$. Values for the first two are given in Table 3. The enthalpy of formation of the cyclopentadienyl anion has been measured as $79 \pm 8 \text{ kJ mol}^{-1}$ [29]. An error in this value would be unimportant here, since it makes a uniform contribution to c_2 and we are only interested in the variations of c_2 .

* Ratio calculated from energy levels given in ref. 24 assuming $D_t = 0.55D_g$ for all metallocenes.

The standard heats of sublimation of the metallocenes $\Delta H_{\text{sub}}^{\circ}(\text{MCp}_2, 298)$ are also required. These have been determined for ferrocene [30,31], nickelocene [30], and manganocene [12], and the mean of these values has been used for the remaining metallocenes, since they are iso-structural and have very similar melting points (Table 3). By using eq. 4 values of c_2 , given in Table 3, are obtained.

(b) *The third ionisation enthalpies of the metals (i_3).* Values for these, given in Table 3, are already known [32].

(c) *The enthalpy of formation of the gaseous metallocinium ion from its ions (c_3).* This can be calculated by means of eq. 3. Values so obtained are given in Table 3.

The enthalpy of ionisation of the metallocenes (ΔH_{298}°), together with $-c_2$, c_3 and i_3 are plotted in Fig. 3. It can be seen that the order of feasibility of ionisation (measured by ΔH_{298}°) of MCp_2 is (M =) $\text{V} < \text{Cr} > \text{Mn} > \text{Fe} < \text{Co} > \text{Ni}$. This is to be contrasted with the order for the similar process of high-spin complexes, (reverse of eq. 1) where the order for MX_2 is (M =) $\text{V} \approx \text{Cr} > \text{Mn} < \text{Fe} > \text{Co} > \text{Ni}$. Also the general increase in ΔG_{298}° found for the oxidation of the metal dihalides [1], is not present in the ionization of the metallocenes. Clearly the feasibility order here is not determined, as for the halides, by the variations in i_3 , but by a more subtle interplay of the three contributing terms c_2 , c_3 and i_3 .

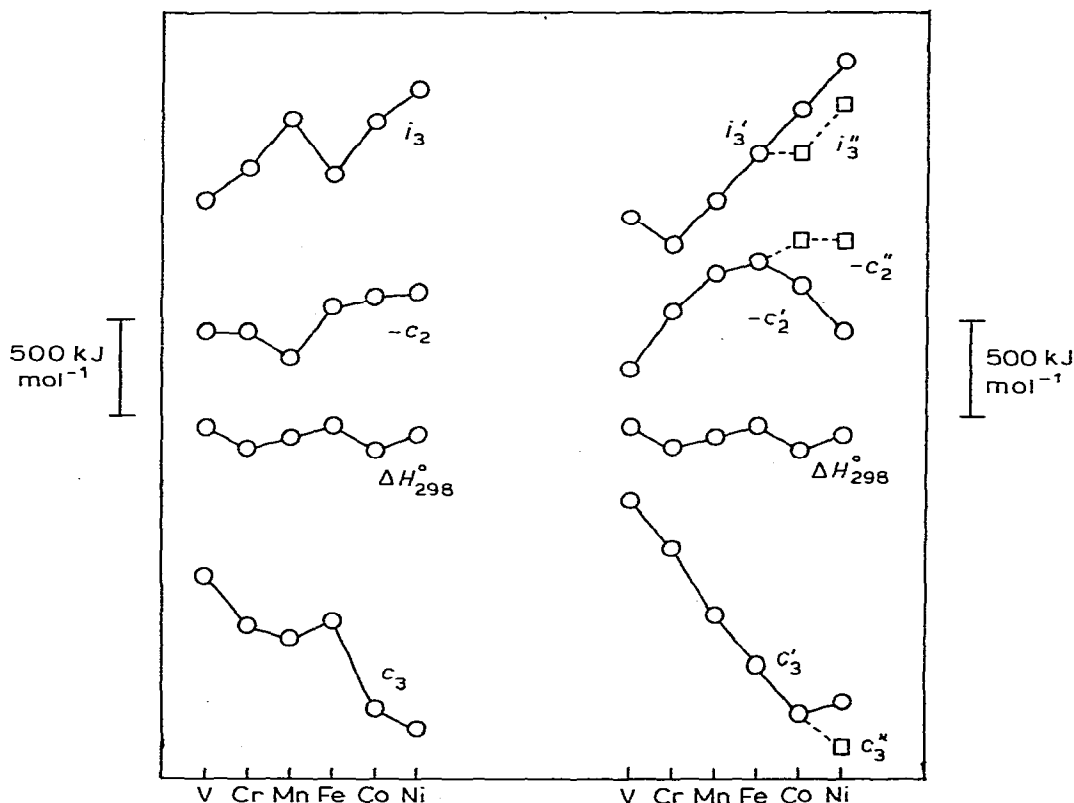


Fig. 3. Variation of enthalpy terms in eq. 3, for the metallocenes of the first transition series.

TABLE 4
 ENTHALPY TERMS FOR HESS'S LAW CYCLE FOR DI- η^5 -CYCLOPENTADIENYL DERIVATIVES OF THE FIRST TRANSITION SERIES
 All thermochemical quantities are in kJ mol⁻¹

M	d ⁿ	Pairing energy (ϵ^p_n)	ΔP on ionisation ($d^{n-1} - d^n$)	c'_2 ($c_2 - P_{n-1}$)	c'_3 ($c_3 - P_{n-1}$)	i'_3 ($i_3 + \Delta P$)	c''_2	c''_3	i''_3	ΔH_{sub}^0 (M, 298) ^b	$\bar{D}(\text{M-Cp})$ ^c
V	d ³	0	0	-2552	-4740	2828				514	369
Cr	d ⁴	297	-297	-2853	-5005	2690				397	279
Mn	d ⁵	628	-331	-3043	-5373	2920				281	212
Fe	d ⁶	427	201	-3102	-5605	3159				416	302
Co	d ⁷	259	167	-2984	-5859	3397	-3214		3167	425	283
Ni	d ⁸	0	259	-2753	-5800	3656	-3213	-6030	3426	430	258

^a For CoCp₂, Co²⁺(g) (d^7) is increased in energy by 230 kJ mol⁻¹; hence c'_2 is increased by 230 and i'_3 decreased by 230. For NiCp₂, Ni²⁺(g) (d^8) is increased in energy by 460 kJ mol⁻¹, and Ni³⁺(g) (d^7) is increased by 230 kJ mol⁻¹; hence c'_2 is increased by 460, c'_3 is increased by 230, and i'_3 is decreased by 230 (see text).
^b Ref. 38, $cD = [\Delta H_{\text{sub}}^0(\text{M}, 298) + 2 \Delta H_f^0(\text{Cp}^+, \text{g}, 298) - \Delta H_f^0(\text{MCp}_2, \text{c}, 298) - \Delta H_{\text{sub}}^0(\text{MCp}_2, \text{g}, 298)]/2$. $\Delta H_f^0(\text{Cp}^+, \text{g}, 298)$ has been taken as 210 kJ mol⁻¹ [37].

The enthalpy cycle being used for these low-spin compounds (Fig. 1) has the metal ions $[M^{2+}(g)$ and $M^{3+}(g)]$ in a high-spin state. It is helpful to consider another cycle where the gaseous metal ions remain in the same spin state as in the metallocenes, by adjusting c_2 , c_3 , and i_3 by the energy required to pair electrons. Pairing energies can be calculated from the theory of many-electron atoms, using Racah parameters. The parameters B and C have been calculated as 10.4 and 46.9 kJ mol⁻¹, respectively, by fitting the observed ionisation energies of the high spin M^{2+} ions [1] to the theoretical expressions given by Griffith [2]. These are thus average values for M^{2+} and M^{3+} ions and for all M . The enthalpy changes c_2 and c_3 and the ionization enthalpies when so adjusted are given in Table 4 (as c'_2 , c'_3 and i'_3), and are plotted in Fig. 3.

The origin of the variations in the feasibility of reaction 2 (ΔH_{298}^0) is now more obvious. The decrease from vanadium ($d^3 \rightarrow d^2$) to chromium ($d^4 \rightarrow d^3$) stems from the fall in i'_3 . This is because the exchange-energy loss is zero for $d^4 \rightarrow d^3$ when the 4 d -electrons are in the θ orbitals. The decrease from iron ($d^6 \rightarrow d^5$) to cobalt ($d^7 \rightarrow d^6$) stems from a sharp drop in $-c'_2$, which may be associated with the fact that CoCp_2 (d^7) has an electron in the ϵ level, which depresses the orbital contribution to the ligand-field stabilisation energy. The fall in $-c'_2$ continues after cobalt, as the ϵ level is filled further, but it is then compensated for by the analogous rise in $+c'_3$, as the ϵ level starts being filled in the ion. The orbital contribution to the ligand-field stabilisation energies of the molecule and the ion tend to cancel each other, but their maxima (at d^6) are displaced by one element, and produce a discontinuity at this point.

We can show that this break at d^6 is due to the orbital part of the ligand-field stabilisation energy, by making the gaseous metal ions in the energy cycle (Fig. 1) have the same d -orbital splitting as the corresponding metallocene or metallocinium ion by raising the energy of the ϵ orbital by Δ , the θ - ϵ splitting in the complex; i.e., by raising the energy of d^7 ions by Δ and d^8 ions by 2Δ . Using 230 kJ mol⁻¹ for Δ *, adjusted values of c'_2 , c'_3 and i'_3 are given in Table 4 (as c''_2 , c''_3 and i''_3), and are plotted on Fig. 3 as dotted lines. The decrease in ΔH_{298}^0 on going from iron [$\text{FeCp}_2(d^6) \rightarrow \text{FeCp}_2^+(d^5)$] to cobalt [$\text{CoCp}_2(d^7) \rightarrow \text{CoCp}_2^+(d^6)$] has now been located in i''_3 , and the fluctuations in ΔH_{298}^0 for the whole series is now mirrored by similar fluctuations in i'_3 (V-Fe) and i''_3 (Co and Ni). We have by this treatment been able to identify the various "subtle effects of electron repulsion" [7] that contribute towards the ionisation energies of the metallocenes.

These results well illustrate that stability associated with half-filled and fully-filled electron shells (or sub-shells) arises for two different reasons. The stability of the half-filled shell arises because of the reversion of the exchange-energy loss on ionisation to zero for the ion with one electron more than the half-filled shell (or sub-shell), whilst the stability of the fully-filled shell arises simply because the next available level is of higher energy. The order of feasibility for the $M^{II} \rightarrow M^{III}$ process given by i'_3 and i''_3 , ($M =$) V < Cr > Mn > Fe < Co > Ni is similar to that found for the hexacyanides [5], and is likely to be general for

* The value of Δ used here has been obtained by using the values of D_s and D_t calculated by Warren [24, p. 70] from the data of Prins and Van Voorst [33]. $\Delta = (5D_s + 20D_t)/3$.

low-spin complexes. It differs from that found for high-spin complexes in that the positions of special stability associated with half-filled and filled shells or sub-shells, appear at d^5 and d^{10} for high-spin complexes, but at d^3 , d^6 , d^8 and d^{10} for low-spin complexes, as the ligand-field interactions change from being weaker than the spin interactions in the first case to stronger in the second.

Metal—ligand bond energies

Mean M—Cp bond energies (Table 4) for the dicyclopentadienyl compounds have been discussed elsewhere [10,34]. The dominant term in determining the bond energy is the enthalpy of sublimation of the metal $\Delta H_{\text{sub}}^{\circ}(\text{M}, 298)$ (Table 4) and this parallels \bar{D} , except for cobaltocene and nickelocene. For these two compounds the values of \bar{D} are lower than this comparison would suggest, presumably because one and two electrons respectively are in the high energy e_{1g} orbitals of the metal. The mean bond energies appear to have no simple relationship with the bond order sequence [35] or the average metal—ring distance [34].

We have measured the enthalpies of formation of two compounds containing cyclopentadienyl and carbonyl ligands. One of these, that of tricarbonylcyclopentadienylmanganese has been measured before [36], the value obtained, $\Delta H_{\text{f}}^{\circ}[\text{Mn}(\text{CO})_3\text{Cp}, \text{c}, 298] = -535 \pm 8 \text{ kJ mol}^{-1}$, is considerably different from our value of $-478 \pm 1 \text{ kJ mol}^{-1}$ (mean of 6 determinations). In this earlier work it is reported, solely on the basis of solubility in hot concentrated sulphuric acid, that the metal oxide formed on combustion was manganese dioxide. We find that the oxidation products are a mixture of trimanganese tetraoxide and manganese monoxide. The X-ray powder photograph was confirmed by weighing the products, and in no case was the weight of oxide sufficient to indicate formation of the dioxide. These oxides, Mn_3O_4 and MnO , are also soluble in hot concentrated sulphuric acid, and this would indicate that Evstigneeva's identification of the products was erroneous.

The enthalpy of formation of dicarbonylcyclopentadienylcobalt was found to be $-169 \pm 10 \text{ kJ mol}^{-1}$ (mean of 3 determinations), and together with the manganese compound this can be used to test the additivity of bond energies for these cyclopentadienyl carbonyl complexes. $\bar{D}(\text{Mn—CO})$ and $\bar{D}(\text{Co—CO})$ can be calculated for $\text{Mn}(\text{CO})_3\text{Cp}$ and $\text{Co}(\text{CO})_2\text{Cp}$ [$\bar{D}(\text{M—Cp}) + x\bar{D}(\text{M—CO}) = \Delta H_{\text{sub}}^{\circ}(\text{M}, 298) + \Delta H_{\text{f}}^{\circ}(\text{Cp}^*, \text{g}, 298) + x\Delta H_{\text{f}}^{\circ}(\text{CO}, \text{g}, 298) - \Delta H_{\text{f}}^{\circ}(\text{M}(\text{CO})_x\text{Cp}, \text{g}, 298)$]. $\Delta H_{\text{sub}}^{\circ}(\text{M}, 298)$ and $\Delta H_{\text{f}}^{\circ}(\text{CO}, \text{g}, 298)$ are given in Tables 4 and 2, and $\Delta H_{\text{f}}^{\circ}(\text{Cp}^*, \text{g}, 298)$ is $209 \pm 3 \text{ kJ mol}^{-1}$ [37]. Using values of $\bar{D}(\text{M—Cp})$ given in Table 4, $\bar{D}(\text{Mn—CO})$ and $\bar{D}(\text{Co—CO})$ are calculated to be 142 and 150 kJ mol^{-1} , respectively.

These two bond energies have been calculated for the pure carbonyls, decacarbonyldimanganese and octacarbonyldicobalt. Using the enthalpies of formation of these two compounds, together with those of the gaseous metal atoms (Table 4), the enthalpy of formation of carbon monoxide, and the enthalpies of dissociation of the Mn—Mn and Co—Co bonds, $\bar{D}(\text{Mn—CO})$ and $\bar{D}(\text{Co—CO})$ have been calculated [10,34] as 99 and 136 kJ mol^{-1} , respectively. These values are lower than those obtained from the cyclopentadienylmetal carbonyls, indicating that in these compounds bond energy additivity does not occur. However, it must be remembered that the metal atom in MnCp_2 or CoCp_2 does not have the same number of electrons as it has in $\text{Mn}(\text{CO})_3\text{Cp}$ or $\text{Co}(\text{CO})_2\text{Cp}$, and a break-

down in the additivity principle here need not mean that the principle does not hold for compounds in which the valency state of the metal is fixed.

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