RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

August 1977

Translated from *Uspekhi Khimii*, **46** 1337 - 1367 (1977)

U.D.C. 541.11

Thermochemistry of Organic Compounds of Transition Metals

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Experimental enthalpies of formation of carbonyl, cyclopentadienyl, arene, and alkoxyl compounds of transition metals are discussed with methods for their determination. Mean dissociation energies calculated therefrom for the bonds formed by the metals in these compounds vary regularly with the nature of the ligand and the position of the metal in the Periodic System. All the thermochemical quantities cited have been recalculated on the basis of current values of the initial data. A list of 112 references is included.

CONTENTS

I.	Introduction	689
II.	Carbonyl compounds	691
III.	Cyclopentadienyl compounds	694
IV.	Arene compounds	697
V.	Alkoxy-compounds	699
VI.	Conclusion	701

I. INTRODUCTION

Organic compounds of transition metals have acquired applied importance e.g. in the industrial production of several pure metals from their carbonyls, the manufacture of metal oxide films from alkoxy-compounds of the metals, as catalysts and antiknock additives, and for other purposes. On the other hand, the great interest taken in these compounds by research workers is due to their structural features and their reactions, as well as the specific nature of the π bond formed by transition metals with organic ligands.

Although the systematic study of the properties of organic compounds of transition metals began comparatively recently—after the discovery of ferrocene in 1951—very many experimental and theoretical investigations have now been made on the molecular structure of and the nature of the chemical bonds in these compounds, on developing methods for the preparation of novel classes of such compounds, and on elucidating the mechanism of their reactions. Far less work has been done on the thermodynamic parameters of these compounds. Nevertheless, significant information is already available even on these aspects, but it has been published in diverse scientific periodicals, and has not been summarised. Yet such data are necessary for technical calculations of processes involving these compounds, and are important also for the theory of the chemical bond and of heterogeneous catalysis. In particular, the calculation of reaction enthalpies requires knowledge of the enthalpies of formation of the reactants. The same data are necessary in order to compute the energies of dissociation of chemical bonds. For these reasons the present Review will survey published information on the enthalpies of formation of organic transition-metal compounds.

The enthalpy of formation ΔH_f° of an organic compound Org (from the elements in phase states that are stable under the given conditions) is usually calculated from its enthalpy of combustion ΔH_c°:

$$\Delta H_f^\circ(\text{Org}) = \sum \nu_i \Delta H_f^\circ(i) - \Delta H_c^\circ(\text{Org}),$$

where $\Delta H_f^\circ(i)$ is the enthalpy of formation of the ith combustion product (from tables), and ν_i is its stoichiometric coefficient in the equation for the combustion of the organic compound. The enthalpy of formation of the test compound can similarly be calculated from the measured enthalpy of any other reaction involving it and known values of ΔH_f° for all the other reactants.

Many published enthalpies of formation of organic transition-metal compounds have been calculated from their experimental enthalpies of combustion. Several difficulties of technique are usually encountered during the determination of the latter in a bomb calorimeter—(*a*) complicated purification of test compounds, (*b*) their rapid oxidisability (sometimes spontaneous combustion) in air, (*c*) the explosive character of combustion in the bomb, (*d*) possibility of formation of products of incomplete combustion, (*e*) possibility of reactions between combustion products, and (*f*) complexity of analysis of combustion products—which complicate the extraction of reliable results.

With easily oxidisable crystalline organometallic compounds serious difficulties arise in preventing premature oxidation before ignition. The use of glass or polymer ampoules, which are widely employed in the study of liquids, is rarely successful because of the dispersal of crystals inside the bomb by the extremely rapid combustion. Sometimes, therefore, the weighed portion of the compressed or powdered test substance is placed in molten paraffin wax, the latter is allowed to solidify, and the two are burned together. Not only does this protect the test substance from oxidation in the preliminary stage of the experiment but it also promotes more complete combustion. A disadvantage of this method is the fairly large correction needed for the enthalpy of combustion of the paraffin wax.

Good et al.[1] determined the enthalpy of formation of decacarbonyl dimanganese by combustion in a rotating bomb. This method entailed dissolution of the combustion products in the bomb in order to establish a definite final state of the reaction system. The necessity of selecting an appropriate solvent in each specific case, the appearance of new sources of errors, and the laborious character of the series of operations prevent widespread adoption of this method.

Both thermal decomposition (into metal and carbon monoxide) and high-temperature iodination have been recommended[2] for the calorimetric investigation of carbonyls.

In the subsequent discussion of published results the method of determination will be indicated and attention will be paid to the surmounting of experimental difficulties. The observed heats of combustion from which heats of formation have been calculated are given and discussed. Values in the Review for the mean energy of dissociation $\overline{D}$ of metal–ligand bonds in compounds ML_n have been calculated as one-nth of the enthalpy of atomisation ΔH_{at}° of the compound in the gaseous state, which is given by the equation

$$\Delta H_{at}^\circ(ML_n,g) = \Delta H_f^\circ(M,g) + n\Delta H_f^\circ(L,g) - \Delta H_f^\circ(ML_n,g).$$

Methods for calculating values of $\overline{D}$ in compounds RML are described in connection with specific compounds.

In the present Review values of enthalpies of combustion or of other reactions ΔH_r° are accompanied by the accuracy indicated in the original papers. Values of enthalpies of formation and of mean bond dissociation energies have been recalculated by the Reviewers on the basis of current values for the enthalpies of formation of atoms and substances. Calculation of dissociation energies of metal–ligand bonds in cyclopentadienyl compounds is complicated by the absence of a reliably established value for the enthalpy of formation of the cyclopentadienyl radical: thus this function has been given as 45.4 ± 10,[3] ~50,[4,5] 63,[6] 53 ± 12,[7] and 47 ± 4 [8] kcal mole^{-1}; the Reviewers have adopted the arbitrary value $\Delta H_f^\circ(C_5H_5,g)$ = 50 kcal mole^{-1}. Values of the enthalpies of formation of other substances used by Reviewers in thermochemical calculations are listed in Table 1. Values in the Review are expressed in thermochemical calories (1 cal = 4.184 J) and relate to a standard pressure (always denoted by a ° sign) and the standard temperature of 298.15 K. The letters in parentheses accompanying chemical formulae (c, l, g, and s) denote respectively the crystalline, liquid, and gaseous states and a solution.

Table 1. Enthalpies of formation used in the calculations.

Substance*	ΔH_f^0, kcal mole^{-1}	Ref.	Substance*	ΔH_f^0, kcal mole^{-1}	Ref.
$Br_2(nCCl_4)$(s)	0.71±0.02	9	n-$C_5H_{11}O$(g)	−23.5±2.0	12
Cl(g)	28.993±0.006	9	t-$C_5H_{11}O$(g)	−29.0±2.0	12
$Cl_2(nCCl_4)$(s)	−4.6±0.1	9	C_2H_5OH(l)	−66.20	11
CO(g)	−26.416±0.031	9	n-C_3H_7OH(l)	−72.79	11
CO_2(g)	−94.052±0.011	9	iso-C_3H_7OH(l)	−76.04	11
CH_3(g)	34.0±1.0	9	n-C_4H_9OH(l)	−77.87	11
C_6H_6(g)	77.7±2.0	10	iso-C_4H_9OH(l)	−79.73	11
$C_6H_5CH_2$(g)	45±1	10	s-C_4H_9OH(l)	−81.90	11
$C_6H_5CH_3$(g)	11.95±0.15	11	t-C_4H_9OH(l)	−85.87	11
C_6H_4(g)	19.82±0.12	11	n-$C_5H_{11}OH$(l)	−85.55	11
C_6H_5Cl(g)	12.39±0.16	11	t-$C_5H_{11}OH$(l)	−90.71	11
1,3,5-$C_6H_3(CH_3)_3$(g)	−3.84±0.34	11	Co(g)	102.4±1.0	9
1,2,4-$C_6H_3(CH_3)_3$(g)	−3.33±0.27	11	$CoCl_2$(c)	−74.1±0.5	9
$C_6H_5C_2H_5$(g)	7.12±0.20	11	$CoBr_2$(c)	−51.55±0.50	9
o-$C_6H_4(C_2H_5)_2$(g)	−4.53±0.5	11	CoO(c)	−57.1±0.3	9
C_6H_5-iso-C_3H_7(g)	0.94±0.26	11	Co_3O_4(c)	−212±2	9
o-C_6H_4(iso-C_3H_7)$_2$(g)	−17±1	13	Cr(g)	95 0±1.0	9
cyclo-C_7H_8(g)	43.47	11	$CrCl_2$(c)	−94.5±1.0	9
CH_3O(g)	2.0±2.0	9	CrI_2(c)	−37.5±1.5	9
C_2H_5O(g)	−6.0±1.0	9	Cr_2O_3(c)	−272.6±0.4	9
n-C_3H_7O(g)	−11.2±2.0	10	Fe(g)	98.7±0.3	9
iso-C_3H_7O(g)	−12.6±2.0	10	FeI_2(c)	−27.8±2.0	9
n-C_4H_9O(g)	−17±2	10	Fe_2O_3(c)	−196.5±1.0	9
iso-C_4H_9O(g)	−18±2	10	Fe_3O_4(c)	−267.0±0.5	9
s-C_4H_9O(g)	−20±2	10	H(g)	52.098±0.006	9
t-C_4H_9O(g)	−23±2	10	HCl(g)	−21.94±0.08	9
$HCl(200H_2O)$(s)	−39.63±0.02	9	$HCl(51.3H_2O)$(s)	−39.42±0.02	9
$HCl(400H_2O)$(s)	−39.70±0.02	9	Os(g)	188.9±1.5	9
Hf(g)	148.2±1.0	9	Pr(g)	89.1±0.3	14
$HfCl_4$(g)	−210.46±0.58	9	Pr_6O_{11}(c)	−1365.6	16
$HfCl_4$(c)	−236.7±0.3	9	Pt(g)	135.3±0.5	9
HfO_2(c)	−267.1±0.5	9	Re(g)	185.4±1.5	9
$HNO_3(16H_2O)$(s)	−49.37±0.12	9	$HReO_4(20H_2O)$(s)	−191±1	9
H_2O(l)	−68.3149±0.0096	9	Rh(g)	133.0±0.5	9
I(g)	25.52±0.01	9	Ru(g)	157.0±1.5	9
I_2(g)	14.92±0.02	9	Sc(g)	91.0±0.2	14
Ir(g)	160.0±1.5	9	Sc_2O_3(c)	−456.4±0.5	17
La(g)	103.0±0.1	14	Ta(g)	187.9±1.0	9
La_2O_3(c)	−458	15	Ta_2O_5(c)	−489.3±0.4	9
Mn(g)	68.0±0.5	9	Ti(g)	113.2±1.0	9
MnI_2(c)	−63.6±1.0	9	$TiCl_4$(g)	−182.4±0.7	9
MnO(c)	−92.0±0.1	9	$TiCl_4$(l)	−192.2±0.9	9
MnO_2(c)	−124.6±0.2	9	TiO_2(c)	−225.6±0.2	9
Mn_2O_3(c)	−228.9±0.2	9	Tm(g)	59.1±0.2	14
Mn_3O_4(c)	−331.6±0.2	9	Tm_2O_3(c)	−451.4±1.4	18
$Mn(NO_3)_2(10.3H_2O)$ (s)	−148.8±0.2	9	V(g)	123.0±1.0	9
Mo(g)	156.9±0.7	9	V_2O_5(c)	−371.0±2.3	9
$MoCl_5$(g)	−105±10	9	W(g)	304.8±1.0	9
MoO_3(c)	−178.1±0.1	9	WCl_6(g)	−119.1±0.5	9
Nb(g)	172.7±1.0	9	WO_3(g)	−201.4±0.2	9
Nb_2O_5(c)	−453.6±0.4	9	Y(g)	101.5±0.2	14
Ni(g)	102.5±0.5	9	Y_2O_3(c)	−455.4±0.5	19
NiO(c)	−57.3±0.1	9	Yb(g)	36.3±0.1	14
			Yb_2O_3(c)	−433.7±0.5	20
			Zr(g)	143 4±1.5	9
			$ZrCl_4$(g)	−207.77±0.35	9
			$ZrCl_4$(c)	−234.17±0.28	9
			ZrO_2(c)	−260.0±0.2	9

*Here and subsequently: g = gaseous state; l = liquid state; c = crystalline state; and s = solution.

II. CARBONYL COMPOUNDS

1. Tetracarbonylnickel

Among determinations of the enthalpy of combustion of tetracarbonylnickel[21-23] the most soundly based[23] paid special attention to analysis of the products, including carbon and nickel monoxides. The solid products contained together with the latter a considerable quantity (9–21%) of metallic nickel. After correction for the incomplete oxidation of nickel, the enthalpy obtained for the process

$$Ni(CO)_4(l) + 2.5O_2(g) \rightarrow NiO(c) + 4CO_2(g)$$

was $\Delta H_c^\circ = -282.2 \pm 0.5$ kcal mole^{-1}, whence $\Delta H_f^\circ[Ni.(CO)_4, l] = -151.3 \pm 0.5$ kcal mole^{-1}.

The enthalpy of formation has been calculated also from equilibrium data on formation of the tetracarbonyl from metallic nickel and gaseous carbon monoxide[24-26], and these results have been critically examined[23,27,28]. The value -149 ± 2 kcal mole^{-1} was suggested[28] for the enthalpy of formation of tetracarbonylnickel in the liquid state. From the above results[23-28] Skinner[29] recommended the value $\Delta H_f^\circ[Ni(CO)_4, l] = -150.4 \pm 1.5$ kcal mole^{-1}. Together with the enthalpy of vaporisation $\Delta H_v^\circ[Ni(CO)_4] = 6.6 \pm 0.3$ kcal mole^{-1} this gives $\Delta H_f^\circ[Ni.(CO)_4, g] = -143.8 \pm 1.5$ kcal mole^{-1} and $\bar{D}(Ni-CO) = 35.2 \pm 0.4$ kcal mole^{-1}. Many carbonyls are partly associated in the gas phase[30]. In view of the comparative instability of these aggregates, however, disregard of association does not significantly distort the results calculated for $\bar{D}(M-CO)$.

The mean dissociation energy of the nickel–carbonyl bond has been determined also by electron bombardment[31,32]. The difference between the appearance potential of the Ni^+ ion in the process $Ni(CO)_4 + e \rightarrow Ni^+ + 4CO + 2e$ and the first ionisation potential of nickel gave values of $\bar{D}$ of 39.3 ± 1.0 and 43 ± 1 kcal mole^{-1} respectively[31,32]. These overestimates in relation to the calorimetric results were attributed[31,32] to the presence of excess energy in the mass-spectrometric breakdown products of the initial compound.

2. Pentacarbonyliron

Early results for the enthalpy of combustion[33,34] cannot be accepted because of the absence of a detailed description of the experiments[33,34]. In later work[35] each enthalpy measurement was followed by careful analysis of the gaseous combustion products for carbon dioxide and of the solid products for the presence of metallic iron and the oxides FeO, Fe_2O_3, and Fe_3O_4. Most of the iron (72 to 96%) had been oxidised to the sesquioxide. After correction for incomplete oxidation of carbon and iron the enthalpy of the reaction

$$Fe(CO)_5(l) + 3.25O_2(g) \rightarrow 0.5Fe_2O_3(c) + 5CO_2(g)$$

became $\Delta H_c^\circ = -385.9 \pm 1.7$ kcal mole^{-1}, which correspond to $\Delta H_f^\circ[Fe(CO)_5, l] = -182.6 \pm 1.8$ kcal mole^{-1}. Using the published value[36] $\Delta H_v^\circ = 9.6 \pm 0.3$ kcal mole^{-1}, we obtain $\Delta H_f^\circ[Fe(CO)_5, g] = -173.0 \pm 1.8$ kcal mole^{-1} and $\bar{D}(Fe-CO) = 28.1 \pm 0.4$ kcal mole^{-1}. Electron bombardment gives[31] for this dissociation energy the value 33 kcal mole^{-1}. It is interesting that considerably less energy is required for detachment of the first carbonyl group from the pentacarbonyl: thus mass spectrometry yields[37] $D[Fe(CO)_4-CO] \simeq 16$ kcal mole^{-1}.

3. Nonacarbonyldi-iron and Dodecacarbonyltri-iron

Skinner et al.[38] have studied the thermal decomposition of the nonacarbonyl at 553–573 K and its ionisation at 524–573 K. The results indicate that the enthalpy of the process $Fe_2(CO)_9(c) \rightarrow 2Fe(c) + 9CO(g)$ occurring at the standard temperature is 99 ± 3 kcal mole^{-1}, which corresponds to $\Delta H_f^\circ[Fe_2(CO)_9, c] = -337 \pm 3$ kcal mole^{-1}. Thermal decomposition and iodination of the dodecacarbonyl have been studied[38] over the range 494–544 K. Conversion of the results to 298.15 K gave for $Fe_3(CO)_{12}.(c) \rightarrow 3Fe(c) + 12CO(g)$ the value $\Delta H_r^\circ = 125 \pm 4$ kcal mole^{-1}, corresponding to $\Delta H_f^\circ[Fe_3(CO)_{12}, c] = -442 \pm 4$ kcal mole^{-1}.

The enthalpies of sublimation were estimated[38] as 18 ± 5 and 23 ± 5 kcal mole^{-1} for the nonacarbonyl and dodecacarbonyl respectively. From these results we obtain for $\Delta H_f^\circ(g)$ the corresponding values -319 ± 6 and -419 ± 7 kcal mole^{-1}.

4. Decacarbonyldimanganese and Decacarbonyldirhenium

Good et al.[1] determined the enthalpy of formation of the manganese carbonyl by combustion in a rotating bomb, the products being dissolved in aqueous nitric acid and hydrogen peroxide. For the reaction

$$Mn_2(CO)_{10}(c) + 4HNO_3(16H_2O, s) + 6O_2(g) \rightarrow 2Mn(NO_3)_2(10.3H_2O, s) + 10CO_2(g) + 2H_2O(l)$$

they obtained $\Delta H_c^\circ = -777.0 \pm 0.8$ kcal mole^{-1}, and hence $\Delta H_f^\circ[Mn_2(CO)_{10}, c] = -400.5 \pm 1.0$ kcal mole^{-1}. Recent measurements[2] of the enthalpy of iodination in a Calvet microcalorimeter have given for the process

$$Mn_2(CO)_{10}(c) + 2I_2(g) \rightarrow 2MnI_2(c) + 10CO(g)$$

the value $\Delta H_r^\circ = -12.6 \pm 1.5$ kcal mole^{-1}, which corresponds to $\Delta H_f^\circ[Mn_2(CO)_{10}, c] = -408.6 \pm 1.5$ kcal mole^{-1}.

Determination of the enthalpy of combustion of the rhenium carbonyl in a stationary calorimetric bomb has given[39] for the reaction

$$Re_2(CO)_{10}(c) + H_2O(l) + 8.5O_2(g) \rightarrow 2HReO_4(20H_2O, s) + 10CO_2(g)$$

the value $\Delta H_c^\circ = -857.9 \pm 0.6$ kcal mole^{-1}, whence $\Delta H_f^\circ[Re_2(CO)_{10}, c] = -396.3 \pm 2.1$ kcal mole^{-1}. Other workers[38] have measured the enthalpies of thermal decomposition and of high-temperature iodination of the same compound. For the process $Re_2(CO)_{10}(c) \rightarrow 2Re(c) + 10CO(g)$ under standard conditions they find that $\Delta H_r^\circ = 131 \pm 5$ kcal mole^{-1}, which yields -395 ± 5 kcal mole^{-1} for the heat of formation.

Table 2. Thermochemical parameters (in kcal mole^{-1}) of dimanganese and dirhenium decacarbonyls.

Carbonyl	ΔH_f^0 (c)	ΔH_s^0	ΔH_f^0 (g)	$\bar{D}$ (M–CO)
$Mn_2(CO)_{10}$	-404.6 ± 2.0	19.2 ± 0.5	-385.4 ± 2.0	23.6 ± 0.4
$Re_2(CO)_{10}$	-395.6 ± 2.0	22.3 ± 0.1	-373.3 ± 2.0	43.5 ± 0.5

Thus the use of different methods to determine enthalpy of formation has given mutually consistent results for both manganese and rhenium carbonyls. We have therefore used their average values in the thermochemical calculations (Table 2). The enthalpies of sublimation ΔH°_{s} have been discussed in detail[40]. Mass-spectrometric data have been used to calculate mean bond dissociation energies: $D[(CO)_5Mn-Mn(CO)_5] = 21 \pm 3$ [41] and $D[(CO)_5Re-Re(CO)_5] = 44.7$ [42] kcal mole^{-1}. It is noteworthy that $\bar{D}(Re-CO)$ is almost double $\bar{D}(Mn-CO)$.

5. Manganese and Rhenium Pentacarbonyls

Skinner et al.[40] have measured the enthalpies of the high-temperature iodination of several methylated and halogenated manganese and rhenium pentacarbonyls, which gives the calculated enthalpies of formation in Table 3. The enthalpies of sublimation of methylmanganese and methylrhenium pentacarbonyls have been calculated from the experimental[43,44] temperature dependence of their vapour pressure.

Table 3. Thermochemical parameters (kcal mole^{-1}) of manganese and rhenium pentacarbonyls.

Carbonyl	$-\Delta H^{0}_{f}$(c)	ΔH^{0}_{s}	$-\Delta H^{0}_{f}$(g)	$\bar{D}$ (M—CH_3)
$CH_3Mn(CO)_5$	189.8±2.2	15.0±0.5	174.8±2.3	26.7±3.2
$ClMn(CO)_5$	241.2±3	—	—	—
$BrMn(CO)_5$	231.8±2	—	—	—
$CH_3Re(CO)_5$	198.8±2.2	16.0±0.5	182.8±2.3	53.1±3.8

Values of $\bar{D}(M-CH_3)$ have been calculated by means of the formula

$$\bar{D}(M-CH_3) = \Delta H^{0}_{f}(M,g) + \Delta H^{0}_{f}(CH_3, g) + 5\Delta H^{0}_{f}(CO, g) - \Delta H^{0}_{f}[CH_3M(CO)_5, g] - 5\bar{D}(M-CO)$$

on the assumption that $\bar{D}(M-CO)$ is the same in these compounds and in the corresponding decacarbonyls $M_2(CO)_{10}$. Table 3 shows that $\bar{D}(Re-CH_3)$ is twice $\bar{D}(Mn-CH_3)$: i.e. the same ratio is found between the metal–methyl bond dissociation energies as for the metal–carbonyl bonds in the rhenium and manganese decacarbonyls.

6. Tricarbonylcyclopentadienylmanganese

Determination of the enthalpy of combustion

$$C_5H_5Mn(CO)_3(c) + 8.7O_2(g) \rightarrow MnO_2(c) + 8CO_2(g) + 2.5H_2O(l)$$

as $\Delta H^{\circ}_{c} = -918 \pm 2$ kcal mole^{-1} was recognised[45] to involve the possible formation of products of incomplete oxidation. Other workers[46] checked the completeness of combustion by determining manganese and carbon dioxides in the products; they found complete oxidation to manganese dioxide and obtained the value -922 ± 2 kcal mole^{-1}. We recommend the mean of these results[45,46]: $\Delta H^{\circ}_{c} = -920 \pm 2$ kcal mole^{-1}, from which we calculate[30] $\Delta H^{\circ}_{f}[Mn(CO)_3.C_5H_5, c] = -127.8 \pm 2$ kcal mole^{-1}. Using $\Delta H^{\circ}_{s} = 12.5 \pm 0.8$ kcal mole^{-1}, we have $\Delta H^{\circ}_{f}[Mn(CO)_3C_5H_5, g] = -115.3 \pm 2.1$ kcal mole^{-1}.

7. Chromium, Molybdenum, and Tungsten Hexacarbonyls

The results of the first investigation[47] of the thermochemical properties of the three hexacarbonyls, involving measurement of their enthalpies of combustion in a stationary calorimetric bomb, were discussed in detail by workers[48] who redetermined these enthalpies. Analysis of the solid products revealed[48] that the oxides were accompanied by a certain quantity of unoxidised metal, which entailed appropriate corrections to the enthalpies of formation. The above results[47,48] have recently been carefully checked by Skinner et al.[49–51], using not only combustion in a stationary bomb but also their calorimetric methods of thermal decomposition and high-temperature iodination.

Table 4. Enthalpies of formation (kcal mole^{-1}) of chromium, molybdenum, and tungsten hexacarbonyls.

Carbonyl	$-\Delta H^{0}_{f}$(c)	Method of determination	Ref.
$Cr(CO)_6$	249.3±0.5	combustion, $\Delta H^{0}_{c} = -451.3 \pm 0.5$	47
	257.5±0.5	combustion, $\Delta H^{0}_{c} = -443.1 \pm 0.5$	48
	234.3±1.8	iodination, $\Delta H^{0}_{r} = 23.4 \pm 1.0$	2
	234.7±0.6	combustion, $\Delta H^{0}_{c} = -465.9 \pm 0.5$	52
	238.9±4.5	combustion, $\Delta H^{0}_{c} = -461.8 \pm 4.0$	51
	233.8±0.5	decomposition, $\Delta H^{0}_{r} = 75.3 \pm 0.2$	51
$Mo(CO)_6$	235.8±0.5	combustion, $\Delta H^{0}_{c} = -506.7 \pm 0.5$	47
	235.0±0.3	combustion, $\Delta H^{0}_{c} = -507.5 \pm 0.3$	48
	229.5±1.0	decomposition, $\Delta H^{0}_{r} = 71.0 \pm 1.0$	2
	236.8±1.0	combustion, $\Delta H^{0}_{c} = -505.7 \pm 0.9$	49
	236.4±0.4	decomposition, $\Delta H^{0}_{r} = 77.9 \pm 0.4$	49
$W(CO)_6$	226.0±0.5	combustion, $\Delta H^{0}_{c} = -539.7 \pm 0.5$	47
	227.9±0.3	combustion, $\Delta H^{0}_{c} = -537.8 \pm 0.3$	48
	229.7±1.2	combustion, $\Delta H^{0}_{c} = -536.0 \pm 1.0$	50
	229.3±0.5	decomposition, $\Delta H^{0}_{r} = 70.8 \pm 0.4$	50

All published experimental values of the enthalpies of formation of chromium, molybdenum, and tungsten hexacarbonyls are listed in Table 4. The enthalpies of combustion in the third column are based on the reactions

$$Cr(CO_6)(c) + 3.75O_2(g) \rightarrow 0.5Cr_2O_3(c) + 6CO_2(g)$$
$$M(CO)_6(c) + 4.5O_2(g) \rightarrow MO_3(c) + 6CO_2(g)$$
M – Mo or W.

The enthalpy of iodination of chromium hexacarbonyl relates to the process

$$Cr(CO)_6(c) + I_2(g) \rightarrow CrI_2(c) + 6CO(g).$$

The enthalpies of thermal decomposition correspond to the reactions

$$M(CO)_6(c) \rightarrow M(c) + 6CO(g)$$
M – Cr, Mo or W.

Table 4 shows good mutual agreement among values obtained for the enthalpy of formation of chromium hexacarbonyl on the basis of its iodination[2], combustion[52], and decomposition[51]. Hence we have used the average value

for our thermochemical calculations. The earlier results[47,48] for chromium hexacarbonyl must be regarded as incorrect. The most accurate values for the enthalpies of formation of molybdenum and tungsten hexacarbonyls are those of Skinner et al.[49,50], since for each substance they obtained results in good agreement by two different methods.

Table 5 gives recommended[53] enthalpies of sublimation. Values of $\bar{D}$(M–CO) in the last column have been calculated by the Reviewers from selected values of ΔH_f°.[M(CO)$_6$, g]. As for Group VII transition metals (Table 2), this bond dissociation energy increases considerably with the atomic number of the metal.

Table 5. Recommended thermochemical parameters (kcal mole^{-1}) of chromium, molybdenum, and tungsten hexacarbonyls.

Carbonyl	$-\Delta H_f^0$ (c)	ΔH_s^0	$-\Delta H_f^0$ (g)	$\bar{D}$ (M–CO)
$Cr(CO)_6$	234.3±0.4	17.1±0.1	217.2±0.4	25.6±0.1
$Mo(CO)_6$	236.6±0.2	17.6±0.2	219.0±0.3	36.2±0.1
$W(CO)_6$	229.5±0.7	18.3±0.3	211.2±0.8	42.9±0.2

Table 6. Thermochemical parameters (kcal mole^{-1}) of arenechromium tricarbonyls.

Carbonyl	$-\Delta H_f^0$ (c)	ΔH_s^0	$-\Delta H_f^0$ (g)	ΔH_r^{0*}
$(C_6H_6)Cr(CO)_3$	106±2	21.8±1	84.2±2.2	120±3
$(C_6H_5CH_3)Cr(CO)_3$	114±2	22.6±1	91.4±2.2	119±3
$[1,3,5\text{-}C_6H_3(CH_3)_3]Cr(CO)_3$	136.5±2	25.9±1	110.6±2.2	122,5±3
$[C_6(CH_3)_6]Cr(CO)_3$	166.5±3	29.5±1	137.0±3.2	132±4
$(C_6H_5Cl)Cr(CO)_3$	111±5	24.5±1	86.5±5.1	115±5
(cyclo-C_7H_8)$Cr(CO)_3$	74±3	22.5±1	51.5±3.2	111±4

*The enthalpies of decomposition of the compounds into chromium and the ligands.

8. Arenechromium Tricarbonyls

Skinner et al.[54,55] have used high-temperature calorimetry to study the thermal decomposition and the iodination of several compounds of type $Cr(CO)_3$Arene. Standard enthalpies of formation calculated from the results are given in Table 6 together with the measured[55] enthalpies of sublimation.

The last column in Table 6 indicates the enthalpies of decomposition

$$(\text{Arene})Cr(CO)_3(g) \rightarrow Cr(g) + \text{Arene}(g) + 3CO(g).$$

It was assumed[55] that the energy of dissociation of the chromium–carbonyl bond is the same in all these chromium compounds, 25.6 kcal mole^{-1} as in chromium hexacarbonyl. To this approximation they found that the ligands formed the sequence

$$\text{cyclo-}C_7H_8 \simeq C_6H_5Cl < C_6H_6 \simeq C_6H_5CH_3 \simeq \simeq C_6H_3(CH_3)_3 < C(CH_3)_6$$

according to the mean energy of dissociation of the bonds formed with chromium. However, the hypothesis that $\bar{D}$(Cr–CO) has the same value in these carbonyl derivatives requires experimental confirmation.

9. Mesitylenemolybdenum Tricarbonyl

The Reviewers have measured the enthalpy of combustion by the method of Ref. 46. Determinations of molybdenum trioxide and carbon dioxide established the absence of products of incomplete combustion. They found for the reaction

$$[C_6H_3(CH_3)_3]Mo(CO)_3(c) + 15O_2(g) \rightarrow MoO_3(c) + 12CO_2(g) + 6H_2O(l)$$

the value $\Delta H_c^\circ = -1598 \pm 1$ kcal mole^{-1}, which corresponds to $\Delta H_f^\circ[Mo(CO)_3C_6H_3(CH_3)_3, c] = -119 \pm 1$ kcal mole^{-1}.

10. Carbonyl Compounds of Cobalt

Calorimetric determinations[56,57] have yielded for the enthalpies ΔH_r° of the reactions

$$Co_2(CO)_8(c) + 2Br_2(n\text{-}CCl_4, s) \rightarrow 2CoBr_2(c) + 8CO(g);$$
$$Co_3(CCl)(CO)_9(c) + 4.5Cl_2(n\text{-}CCl_4, s) \rightarrow 3CoCl_2(c) + 9CO(g) + CCl_4(l);$$
$$Co_3(CBr)(CO)_9(c) + 4.5Br_2(n\text{-}CCl_4, s) \rightarrow 3CoBr_2(c) + 9CO(g) + CBr_4(n\text{-}CCl_4, s).$$

the respective values -19.5 ± 0.5, -107.5 ± 1.6, and -191.4 ± 1.0 kcal mole^{-1}. Skinner et al.[38], using thermal decomposition and high-temperature iodination, found that the enthalpies of the processes

$$Co_2(CO)_8(c) \rightarrow 2Co(c) + 8CO(g)$$
$$Co_4(CO)_{12}(c) \rightarrow 4CO(c) + 12CO(g)$$

occurring under standard conditions were respectively 87 ± 1 and 124 ± 4 kcal mole^{-1}.

Table 7. Thermochemical parameters (kcal mole^{-1}) of cobalt carbonyls.

Carbonyl	$-\Delta H_f^0$ (c)	ΔH_s^0	$-\Delta H_f^0$ (g)
$Co_2(CO)_8$	297.1±1.0	15.6±0.8	281.5±1.3
$Co_4(CO)_{12}$	441±4	(23±5)	418±7
$Co_3(CCl)(CO)_9$	280.5±2.2	23.8±0.4	256.7±2.2
$Co_3(CBr)(CO)_9$	280.3±2.4	28.1±0.6	252.2±2.5

The enthalpies of formation of cobalt carbonyls calculated from the above data[38,56,57] are given in Table 7. The value found in Refs. 56 and 57 for the enthalpy of formation of octacarbonyldicobalt agrees with the calculated[38] value (-296.3 ± 1.2 and -298 ± 2 kcal mole^{-1}). The average of these results is therefore given in Table 7. The enthalpy of sublimation of the dodecacarbonyl has been estimated[38]. Those of the remaining compounds have been calculated[57] from the temperature dependence of their vapour pressure studied by Knudsen's effusion method over the range 288–318 K.

From the mass-spectrometric value of $D[(CO)_4Co–Co(CO)_4] = 14.5 \pm 2.0$ kcal mole^{-1} and $\Delta H_f^\circ[Co_2(CO)_8, g] = -281.5 \pm 1.3$ kcal mole^{-1}, we calculate that $\bar{D}$(Co–CO) = 32.6 ± 0.4 kcal mole^{-1}.

11. Carbonyl Compounds of Ruthenium, Rhodium, Osmium, and Iridium

Skinner et al.[38,58] have used thermal decomposition and high-temperature iodination to determine the enthalpies of formation of polynuclear carbonyls of these platinum

metals. Table 8 lists the results together with the estimated enthalpies of sublimation.

The molecule of a polynuclear carbonyl in general contains three types of chemical bonds—terminal and bridging metal–carbonyl bonds and metal–metal bonds—whose energies of rupture are denoted [38] by the respective symbols $\overline{T}$, $\overline{B}$, and $\overline{M}$. Table 8A gives the enthalpies of the dissociation processes

$$M_m(CO)_n(g) \rightarrow m\,M(g) + n\,CO(g)$$

with the types and numbers of bonds undergoing rupture.

Table 8. Thermochemical parameters (kcal mole^{-1}) of ruthenium, rhodium, osmium, and iridium carbonyls.

Carbonyl	$-\Delta H_f^0$ (c)	ΔH_s^0	$-\Delta H_f^0$ (g)
$Ru_3(CO)_{12}$	459±5	(24±5)	435±7
$Rh_4(CO)_{12}$	435±3	(24±5)	411±6
$Rh_6(CO)_{16}$	578±4	(28±5)	550±6
$Os_3(CO)_{12}$	418±5	(25±5)	393±7
$Ir_4(CO)_{12}$	435±4	(25±5)	410±7

Table 8A.

Carbonyl	Enthalpy of dissociation, kcal mole^{-1}	No. of bonds broken on dissociation
$Fe_2(CO)_9$	281±6	$6\overline{T}+6\overline{B}+\overline{M}$
$Fe_3(CO)_{12}$	401±7	$10\overline{T}+4\overline{B}+3\overline{M}$
$Co_2(CO)_8$	275±2	$6\overline{T}+4\overline{B}+\overline{M}$
$Co_4(CO)_{12}$	511±7	$9\overline{T}+6\overline{B}+6\overline{M}$
$Ru_3(CO)_{12}$	589±7	$12\overline{T}+3\overline{M}$
$Rh_4(CO)_{12}$	626±6	$9\overline{T}+6\overline{B}+6\overline{M}$
$Rh_6(CO)_{16}$	925±7	$12\overline{T}+8\overline{B}+11\overline{M}$
$Os_3(CO)_{12}$	643±7	$12\overline{T}+3\overline{M}$
$Ir_4(CO)_{12}$	733±7	$12\overline{T}+6\overline{M}$

Table 8B.

Carbonyl	$\overline{T}$, kcal mole^{-1}	$\overline{M}$, kcal mole
$Ru_3(CO)_{12}$	42	29
$Rh_4(CO)_{12}$	40	27
$Rh_6(CO)_{16}$	40	27
$Os_3(CO)_{12}$	46	31
$Ir_4(CO)_{12}$	46	31

The energies of rupture of these bonds were calculated [38,58] on the assumption that $\overline{T}$, $\overline{B}$, and $\overline{M}$ each have the same value in $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$, when we obtain for $\overline{B}$ and $\overline{M}$ the values 15.5 and 19.3 kcal mole^{-1} respectively. The further assumption that corresponding bond dissociation energies are equal in $Co_2(CO)_8$ and $Co_4(CO)_{12}$ gives corresponding values of 15.0 and 22.0 kcal mole^{-1}. Hence for the iron and cobalt carbonyls we have $\overline{M} \simeq 0.68\overline{T}$ and $\overline{B} \simeq 0.5\overline{T}$. On the assumption of the same energy distribution among bonds also in polynuclear carbonyls of ruthenium, rhodium, osmium, and iridium, the values in Table 8B were calculated [38] for $\overline{T}$ and $\overline{M}$ in these compounds. This calculation is tentative in character, because of the use of estimates of enthalpies of sublimation, and also the hypothesis of constant ratios between $\overline{T}$, $\overline{B}$, and $\overline{M}$ in carbonyls differing significantly in composition and structure.

III. CYCLOPENTADIENYL COMPOUNDS

1. Dicyclopentadienyls of 3*d* elements

Cotton and Wilkinson [4] calculated the enthalpy of formation of crystalline ferrocene from its enthalpy of combustion measured in a stationary calorimetric bomb. Chemical analysis showed that the solid product was a mixture of Fe_2O_3 and Fe_3O_4, which was allowed for in the calculations. (The quantity of iron oxidised to the sesquioxide did not exceed 18%.) They obtained the value ΔH_f°. $[(C_5H_5)_2Fe, c] = 33.8 \pm 1.3$ kcal mole^{-1}. These workers also measured the enthalpy of combustion of dicyclopentadienylnickel [59], found by chemical analysis that the solid products comprised a mixture of unoxidised nickel and the monoxide, and established that the quantity of nickel oxidised did not exceed 50%. They calculated that $\Delta H_f^\circ[(C_5H_5)_2Ni, c] = 63.0 \pm 0.6$ kcal mole^{-1}.

More recent measurements have been made [60–62] of the enthalpies of combustion both these compounds and of the dicyclopentadienyl derivatives of vanadium, chromium, manganese, and cobalt. These yielded the values [61,62] 40.3 ± 0.4 and 68.2 ± 0.4 kcal mole^{-1} for the enthalpies of formation of crystalline ferrocene and dicylcopentadienylnickel respectively. In view of the experimental difficulties in the thermochemical study of this class of compound, the agreement between the results [4,59,61,62] for the two derivatives must be regarded as satisfactory. Average values are therefore given for them in Table 9.

Table 9. Thermochemical parameters (kcal mole^{-1}) of dicyclopentadienyls of 3*d* metals.

Compound	$-\Delta H_c^0$ (c)	ΔH_f^0 (c)	ΔH_s^0	$-\Delta H_f^0$ (g)	$\overline{D}$ (M–C_5H_5)
$(C_5H_5)_2V$	1502±2	34±2	14±1	48±2	88±1
$(C_5H_5)_2Cr$	1461.0±0.5	42.6±0.5	16.7±0.4	59.3±0.6	67.8±0.6
$(C_5H_5)_2Mn$	1440.7±0.5	48.1±0.5	18.1±0.4	66.2±0.6	50.9±0.4
$(C_5H_5)_2Fe$	1408.1±1.0	37.0±1.0	17.5±0.2	54.5±1.0	72.6±0.6
$(C_5H_5)_2Co$	1395.5±0.5	56.3±0.6	16.8±0 5	73.1±0.8	64.6±0.6
$(C_5H_5)_2Ni$	1405.0±1.0	65.6±1.0	17.3±0.3	82.9±1.0	59.8±0.6

Table 9A.

Compound	Combustion products	Compound	Combustion products
$(C_5H_5)_2V$	VO_2(10%)+V_2O_5	$(C_5H_5)_2Fe$	Fe_2O_3 (7–14%)+Fe_3O_4
$(C_5H_5)_2Cr$	Cr_2O_3 (100%)	$(C_5H_5)_2Co$	Co (7–25%)+CoO (54–71%)+Co_3O_4 (12–25%)
$(C_5H_5)_2Mn$	MnO (10–24%)+Mn_3O_4	$(C_5H_5)_2Ni$	Ni (16–50%)+NiO

Table 9B.

Bond	V–C_5H_5	Cr–C_5H_5	Mn–C_5H_5	Fe–C_5H_5	Co–C_5H_5	Ni–C_5H_5
$\overline{D}$, kcal mole^{-1}	90; 91	90; 69	72	75; 72	78	69; 69

In order to prevent premature oxidation and to achieve complete combustion the test substances were placed [60-62] under vacuum conditions in a known mass of molten paraffin wax, which was allowed to solidify, after which the experiments were made on the composite specimens. Because of its stability, ferrocene was ignited in several experiments in polyethylene ampoules. The mass of the organometallic compound taken for an experiment was established by determining the quantity of carbon dioxide among the combustion products. The solid products were subjected to quantitative X-ray examination and chemical analysis, which gave the compositions listed in Table 9A.

The enthalpies of combustion in Table 9 were based on the processes

$$\left.\begin{array}{l}(C_5H_5)_2V(c) + 55/4O_2(g) \rightarrow 1/2V_2O_5(c)\\ (C_5H_5)_2Cr(c) + 53/4O_2(g) \rightarrow 1/2Cr_2O_3(c)\\ (C_5H_5)_2Mn(c) + 79/6O_2(g) \rightarrow 1/3Mn_3O_4(c)\\ (C_5H_5)_2Fe(c) + 79/6O_2(g) \rightarrow 1/3Fe_3O_4(c)\\ (C_5H_5)_2Co(c) + 13O_2(g) \rightarrow CoO(c)\\ (C_5H_5)_2Ni(c) + 13O_2(g) \rightarrow NiO(c)\end{array}\right\} + 10CO_2(g) + 5H_2O(l)\ .$$

Enthalpies of sublimation were calculated from the temperature dependence [60-65] of vapour pressure. The mean $M-C_5H_5$ bond dissociation energies in Table 9 (where M = V, Cr, Mn, Fe, Co, Ni) were found by means of the equation

$$\bar{D}(M-C_5H_5) = 1/2\,\{\Delta H_f^0(M, g) + 2\Delta H_f^0(C_5H_5, g) - \Delta H_f^0[(C_5H_5)_2M, g]\}\ .$$

Mass-spectrometric study of these compounds yielded the values in Table 9B. [66,67]

Thus values of $\bar{D}(M-C_5H_5)$ obtained mass-spectrometrically in all cases exceed the corresponding thermochemical values. This is attributed to excess energy in the mass-spectrometric breakdown products of the initial compounds, which is difficult to allow for.

2. Cyclopentadienyl Compounds of Titanium, Zirconium, and Hafnium

The Reviewers [60,68-70] have measured the enthalpies of combustion of cyclopentadienyltitanium trichloride and of a series of compounds of general formula $(C_5H_5)_2MR_2$, where M = Ti, Zr, Hf and R = Cl, CH_3, C_6H_5, $C_6H_5CH_2$, C_6H_5OCO. A stationary calorimetric bomb made of a special chromium–nickel steel was used for experiments on the combustion of chlorinated compounds, in order to avoid reaction of the combustion products with the material of the bomb. Conversion into hydrogen chloride of all the chlorine present in a chlorinated compound, which was necessary to obtain a quite definite thermochemical equation, was accomplished by introducing an appropriate quantity of hydrazine hydrochloride into the bomb, in aqueous solution on the glass cloth covering its internal surface. The mass of substance taken for combustion was determined from the quantity of carbon dioxide formed. X-Ray diffraction revealed the crystalline dioxides of the metals among the products. Chemical analysis of the solid products indicated the absence of unoxidised or incompletely oxidised metals.

Table 10. Thermochemical parameters (kcal mole^{-1}) of cyclopentadienyl compounds of titanium, zirconium, and hafnium.

Compound	$-\Delta H_c^0$ (c)	ΔH_f^0 (c)	ΔH_s^0	ΔH_f^0 (g)	$\bar{D}$ (M–C_5H_5)	$\bar{D}$ (M–R)
$(C_5H_5)TiCl_3$	737.8±1.6	−145.5±1.6	(25±2)	−120.5±3	62±3	—
$(C_5H_5)_2TiCl_2$	1427.2±1.8	−91.6±1.8	28.4±0.5	−63.2±1.8	64.3±1.0	—
$(C_5H_5)_2Ti(CH_3)_2$	1914±2*	13±2	(19±1)	32±2	—	60±2
$(C_5H_5)_2Ti(CH_2C_6H_5)_2$	3349.3±1.2	46.8±1.2	(20±2)	66.8±2	—	54±2
$(C_5H_5)_2Ti(OCOC_6H_5)_2$	2935±3	−231±3	—	—	—	—
$(C_5H_5)_2ZrCl_2$	1427.5±0.7	−128.6±0.7	25.1±0.5	−103.5±0.9	85.7±1.0	—
$(C_5H_5)_2Zr(CH_3)_2$	1927.6±0.5	−10.6±0.5	19.4±0.5	8.8±0.7	—	65.6±1.1
$(C_5H_5)_2Zr(C_6H_5)_2$	3081.2±2.6	65.9±2.6	(22±1)	87.9±3	—	69.8±2.0
$(C_5H_5)_2HfCl_2$	1432.0±0.6	−128.1±0.6	25.5±0.5	−102.8±0.8	85.8±0.6	—

*Value corrected by the authors [68].

Values of ΔH_c° in Table 10 for alkylated or arylated compounds relate to their oxidation to the crystalline metal dioxide, gaseous carbon dioxide, and liquid water. Combustion of the chlorinated compounds is represented by the equations

$$(C_5H_5)TiCl_3(c) + 6.5O_2(g) \rightarrow TiO_2(c) + 5CO_2(g) + H_2O(l) + 3HCl(400H_2O, s)$$
$$(C_5H_5)_2MCl_2(c) + 13O_2(g) \rightarrow MO_2(c) + 10CO_2(g) + 4H_2O + 2HCl(200H_2O, s)$$
M–Ti, Zr or Hf.

Values of the enthalpy of sublimation in parentheses (Table 10) have been estimated from values of this function for compounds of similar composition and structure. Values of ΔH_s° in the remaining cases have been calculated from the temperature dependence of vapour pressure measured by the Knudsen effusion method. We regard as incorrect the values of −1366 ± 5 and −1398 ± 5 kcal mole^{-1} obtained [71] for the enthalpies of combustion of dicyclopentadienyl-titanium and -zirconium dichlorides, because of inaccurate determination [71] of the composition of the products.

The bond dissociation energies in the last two columns in Table 10 have been calculated by means of the equations

$$\bar{D}(M-C_5H_5) = 1/2\,\{\Delta H_f^0(M, g) + 2\Delta H_f^0(C_5H_5, g) + 2\Delta H_f^0(Cl, g) - \Delta H_f^0[(C_5H_5)_2MCl_2, g] - 2\bar{D}(M-Cl)\};$$
$$\bar{D}(M-R) = 1/2\,\{\Delta H_f^0(M, g) + 2\Delta H_f^0(C_5H_5, g) + 2\Delta H_f^0(R, g) - \Delta H_f^0[(C_5H_5)_2MR_2, g] - 2\bar{D}(M-C_5H_5)\}.$$

The values of $\bar{D}(M-C_5H_5)$ have been obtained on the assumption that metal–chlorine bond dissociation energies are approximately the same in the dicyclopentadienylmetal dichlorides as in the corresponding tetrachlorides. Thus within the limits of experimental error the Ti–Cl bonds have the same length in $(C_5H_5)_2TiCl_2$ as in $TiCl_4$ (2.24 ± 0.01 [72] and 2.21 ± 0.03 Å [73]); and this applies also to the Zr–Cl bonds in $(C_5H_5)_2ZrCl_2$ and $ZrCl_4$ (2.31 ± 0.01 [74] and 2.33 ± 0.05 Å [73]). The bond dissociation energies in the tetrachlorides have been calculated from the data in Table 1 as respectively 102.9 ± 0.3, 116.8 ± 0.4, and 118.6 ± 0.3 kcal mole^{-1} for $\bar{D}(Ti-Cl)$, $\bar{D}(Zr-Cl)$, and $\bar{D}(Hf-Cl)$. It is significant that such calculation gives closely similar bond dissociation energies $\bar{D}(Ti-C_5H_5)$ in $C_5H_5TiCl_3$ and $(C_5H_5)_2TiCl_2$ (Table 10). This is consistent with structural measurements indicating that all the carbon atoms in these compounds are equidistant from the

titanium atom [75]. Since the error in the value adopted $\Delta H_f^\circ(C_5H_5, g) = 50$ kcal mole^{-1} is unknown (Section I), it is not included in the error in the determination of $\overline{D}(M-C_5H_5)$ given in Table 10.

Study of the thermochemistry of a compound having the empirical formula $(C_5H_5)_2Ti$ was based [60] on the assumption of a monomeric ferrocene-like structure. However, it has been established [76] that this compound has a more complicated structure. Therefore the Reviewers' earlier value [60,77] of $\overline{D}(Ti-C_5H_5) = 108$ kcal mole^{-1} is not the mean dissociation energy of the titanium–cyclopentadienyl bond, but represents the total enthalpy of several processes.

In the calculation of $\overline{D}(M-R)$ it has been assumed that the metal–cyclopentadienyl bond dissociation energy is the same in corresponding compounds $(C_5H_5)_2MCl_2$ and $(C_5H_5)_2MR_2$. It must be noted that the unreliability of the value of $\Delta H_f^\circ(C_5H_5, g)$ does not affect the accuracy of the calculated $\overline{D}(M-R)$ values.

The above results show clearly that $\overline{D}(Zr-C_5H_5)$ and $\overline{D}(Hf-C_5H_5)$ are closely similar and exceed $\overline{D}(Ti-C_5H_5)$ by 21 kcal mole^{-1}. Like the above relations among values of $\overline{D}(M-CO)$ for transition metals (Table 2–5) this corresponds to the rule [78] that the dissociation energy of the bonds formed with a given ligand (atom) increases with the atomic mass of the transition metal down a particular subgroup.

The mean dissociation energy of the zirconium–phenyl bond exceeds that of the zirconium–methyl bond by 4.2 kcal mole^{-1}. It is interesting that a difference of the same order is always found for non-transition metals [79]. The enthalpy of combustion $\Delta H_c^\circ = -2995 \pm 3$ kcal mole^{-1} measured [68] for $(C_5H_5)_2Ti(C_6H_5)_2(c)$ led to an abnormally high dissociation energy calculated for the titanium–phenyl bond. For this reason the value given [68] for the enthalpy of combustion must be regarded as tentative.

3. Cyclopentadienyl Compounds of Molybdenum and Tungsten

The Reviewers have used a calorimeter with a stationary bomb to measure [69,80] the enthalpies of combustion of compounds $(C_5H_5)_2MX_2$, where M = Mo, W and X = H, Cl, I. For the combustion of chlorinated compounds reaction between the walls of the bomb and the products of combustion was prevented by the insertion of a tightly fitting tantalum pot, whose inner surface was covered with glass cloth impregnated with 10 ml of water containing 0.05 mass % of hydrogen peroxide (to ensure completely conversion of chlorine into hydrogen chloride). In all experiments the mass of hydrochloric acid found among the combustion products coincided, within the limits of experimental error, with that calculated from the mass of the initial compound. The quantity of substance taken for combustion was determined from the amount of carbon dioxide among the products. X-Ray determinatin indicated that the solid products were the crystalline trioxides of the metals. No unoxidised or incompletely oxidised metal was detected. The enthalpies of combustion [69,80] listed in Table 11 are based on the reactions

$$(C_5H_5)_2MH_2(c) + 14.5O_2(g) \rightarrow MO_3(c) + 10CO_2(g) + 6H_2O(l)$$
$$(C_5H_5)_2MCl_2(c) + 13.5O_2(g) \rightarrow MO_3(c) + 10CO_2(g) + 4H_2O(l) + 2HCl\,(200H_2O, s)$$
$$(C_5H_5)_2MI_2(c) + 14O_2(g) \rightarrow MO_3(c) + 10CO_2(g) + 5H_2O(l) + I_2(c).$$

The enthalpies of sublimation of the "hydrides" were calculated from the temperature dependence of vapour pressure measured [80] by the Knudsen effusion method. Those for the remaining compounds were estimated on the basis of their monomeric character is the gas phase.

Table 11. Thermochemical parameters (kcal mole^{-1}) of cyclopentadienyl compounds of molybdenum and tungsten.

Compound	$-\Delta H_c^0$(c)	ΔH_f^0(c)	ΔH_s^0	ΔH_f^0(g)
$(C_5H_5)_2MoH_2$	1575.1±0.6	46.6±0.6	22.1±0.5	68.7±0.8
$(C_5H_5)_2MoCl_2$	1448.2±0.6	−22.9±0.6	(24±1)	1.1±1.2
$(C_5H_5)_2MoI_2$	1467.4±0.5	7.2±0.5	(24±1)	31.2±1.1
$(C_5H_5)_2WH_2$	1611.7±0.6	59.9±0.6	23.0±0.5	82.9±0.8
$(C_5H_5)_2WCl_2$	1477.4±0.6	−17.0±0.6	(25±1)	8.0±1.2
$(C_5H_5)_2WI_2$	1511.5±0.7	28.0±0.7	(25±1)	53.0±1.2

The calculation of $\overline{D}(M-C_5H_5)$ and $\overline{D}(M-X)$ for these compounds was similar to the above calculation of bond dissociation energies for titanium, zirconium, and hafnium compounds $(C_5H_5)_2MR_2$. It was assumed that here $\overline{D}(Mo-Cl)$ and $\overline{D}(W-Cl)$ are approximately equal to those in the hexachlorides (72.6 ± 1.7 and 83.0 ± 0.2 kcal mole^{-1}) calculated from the data in Table 1. This postulate should correspond to approximate equality of metal–chlorine internuclear distances between the molybdenum and tungsten test compounds and their respective hexachlorides. Unfortunately, the structural data required for comparison are lacking. However, the molybdenum–chlorine bond length is known to be 2.47 Å [81] in $(C_5H_5)_2$. $MoCl_2$, but 2.27 ± 0.02 Å [73] in molybdenum pentachloride. Since a decrease in the energy of rupture of a bond corresponds to an increase in its length, and $\overline{D}(Mo-Cl)$ is 9.1 kcal mole^{-1} smaller in molybdenum hexachloride than in the pentachloride (calculated from standard data [9]), the bond is probably longer in the hexachloride, and the postulated approximate equality of $\overline{D}(Mo-Cl)$ in $(C_5H_5)_2MoCl_2$ and $MoCl_6$ is likely to be correct. The calculated results in Table 12 show that both $\overline{D}(M-C_5H_5)$ and $\overline{D}(M-X)$ are larger for tungsten than for molybdenum.

4. Cyclopentadienyl Compounds of Platinum

A massive microcalorimeter has been used [82] to measure the enthalpies of combustion of crystalline cyclopentadienyltrimethylplatinum and dicyclopentadienyldimethylplatinum as respectively −1270.8 ± 0.5 and −1706.3 ± 1.7 kcal mole^{-1}, the products being gaseous carbon dioxide, liquid water, and crystalline platinum. These values were used to calculate the corresponding heats of formation $\Delta H_f^\circ(c)$ are 40.3 ± 0.5 and 31.2 ± 1.7 kcal mole^{-1}.

The enthalpy of sublimation of the trimethyl derivative was calculated from the temperature dependence of the vapour pressure studied by the Knudsen effusion method, which gave $\Delta H_S^\circ = 18.6 \pm 0.5$ kcal mole^{-1} for the range 290–305 K. The enthalpy of sublimation of the dicyclopentadienyl compound was taken to be 20 ± 1 kcal mole^{-1}. We then have for the heats of formation in the gaseous state $\Delta H_f^\circ(g)$ the respective values 58.9 ± 0.7 and 51.2 ± 1.9 kcal mole^{-1}.

On the assumption that bond dissociation energies are constant in these compounds, comparison of the heats of formation in the gaseous state yields $\overline{D}(Pt-C_5H_5) = 75 \pm 3$ and $\overline{D}(Pt-CH_3) = 51 \pm 1$ kcal mole^{-1}.

Table 12. Mean dissociation energies (kcal mole^{-1}) in cyclopentadienyl compounds of molybdenum and tungsten.

Compound	$\overline{D}$(M–C_5H_5)	$\overline{D}$(M–H)	$\overline{D}$(M–I)
$(C_5H_5)_2MoCl_2$	84.3±1.8	—	—
$(C_5H_5)_2MoI_2$	84.3±1.8	—	54.1±2.0
$(C_5H_5)_2MoH_2$	84.3±1.8	61.9±1.9	—
$(C_5H_5)_2WCl_2$	94.4±0.8	—	—
$(C_5H_5)_2WI_2$	94.4±0.8	—	57.0±1.1
$(C_5H_5)_2WH_2$	94.4±0.8	68.6±1.0	—

5. Tricyclopentadienyl Derivatives of Rare-earth Metals

Enthalpies of combustion have been measured[83] for the tricyclopentadienyl compounds of scandium, yttrium, lanthanum, praseodymium, thulium, and ytterbium. X-ray diffraction has established formation of the crystalline oxide Pr_6O_{11} but the crystalline sesquioxides of the other five rare-earth metals. Neither unoxidised metals nor oxides of other compositions were detected among the products of combustion. Table 13 lists the standard enthalpies of combustion to gaseous carbon dioxide, liquid water, and the metal oxide. It includes the standard enthalpies of formation in crystalline and gaseous states together with the mean M–C_5H_5 bond dissociation energies.

Table 13. Thermochemical parameters (kcal mole^{-1}) of tricyclopentadienyls of rare-earth metals.

Compound	$-\Delta H_c^0$ (c)	ΔH_f^0 (c)	ΔH_s^0	ΔH_f^0 (g)	$\overline{D}$(M–C_5H_5)
$(C_5H_5)_3Se$	2148±1	−3.2±1	26.2±1	23.0±1.5	72.7±0.5
$(C_5H_5)_3Y$	2140±1	−10.8±1	26.7±1	15.9±1.5	78.5±0.5
$(C_5H_5)_3La$ *	2146±1	−6.4±1	27.4±1	21.0±1.5	77.3±0.5
$(C_5H_5)_3Pr$	2144±2	−6.7±2	30.0±1	23.3±2.0	71.9±1.0
$(C_5H_5)_3Tm$	2137±1	−11.8±1	26.6±1	14.8±1.5	64.8±0.5
$(C_5H_5)_3Yb$	2147±1	7.0±1	26.0±1	33.0±1.5	51.1±0.5

*We have used the value $\Delta H_f^\circ(La_2O_3, c) = -458$ kcal mole^{-1} taken from tables[15] in calculating $\Delta H_f^\circ[(C_5H_5)_3La, c]$. In Ref. 84 the enthalpy of formation of lanthanum sesquioxide was given as −428.6 kcal mole^{-1}, which is significantly lower than the values for scandium and yttrium sesquioxides (−456.4 and −455.4 kcal mole^{-1}). This casts doubt on the accuracy of the latter results[84], since the enthalpies of formation of the same type of oxides of other transition metals increase with the atomic number of the metal (Table 1).

Heats of formation of the gaseous cyclopentadienyls have been calculated from enthalpies of sublimation found from the temperature dependence of vapour pressure[85,86] over the range 473–673 K. We assumed that the enthalpies of sublimation of these compounds at 298.15 K exceed by 3 ± 1 kcal mole^{-1} the experimental values for the above temperature range. Mass-spectrometric results were used[87] to calculate the enthalpy of the process

$$(C_5H_5)_3Yb(g) \rightarrow (C_5H_5)_2Yb(g) + C_5H_5(g),$$

as 58 ± 5 kcal mole^{-1}. Together with data in Table 13 this yields $\Delta H_f^\circ[(C_5H_5)_2Yb, g] = 41 \pm 5$ and $\overline{D}(Yb-C_5H_5) = 48 \pm 3$ kcal mole^{-1}. Hence the energies of dissociation of the ytterbium–cyclopentadienyl bond in tri- and di-cyclopentadienylytterbium are closely similar, which indicates a low energy of transition of ytterbium from the bivalent to the tervalent state.

IV. ARENE COMPOUNDS

1. Dibenzenevanadium

The enthalpy of combustion of dibenzenevanadium

$$(C_6H_6)_2V(c) + 16.25O_2(g) \rightarrow 0.5V_2O_5(c) + 12CO_2(g) + 6H_2O(l)$$

was determined[88] as $\Delta H_c^\circ = -1732.7 \pm 1.8$ kcal mole^{-1}, which corresponds to $\Delta H_f^\circ[(C_6H_6)_2V, c] = 8.7 \pm 2.4$ kcal mole^{-1}. Premature oxidation was prevented by placing the compound in glass ampoules. However, the combustion products were not analysed[88], so that the above value for the enthalpy of combustion cannot be accepted as reliable, in view of the tendency of vanadium to exist in various states of oxidation (VO, V_2O_3, VO_2, and V_2O_5).

For the enthalpy of sublimation Fischer et al.[88,89] give the value 8.9 kcal mole^{-1}. However, this has been shown[90] to be incorrect, for $\Delta H_s^\circ \simeq 18$ kcal mole^{-1}. From this we find that $\Delta H_f^\circ[(C_6H_6)_2V, g] = 26.7 \pm 2.6$ kcal mole^{-1}, whence we obtain also $\overline{D}(V-C_6H_6) = 77.0 \pm 1.4$ kcal mole^{-1}.

2. Dibenzenechromium

The enthalpy of combustion in a stationary calorimetric bomb was given[91] as $\Delta H_c^\circ = -1696 \pm 8$ kcal mole^{-1}. The dibenzenechromium was placed in molten thymol to eliminate premature oxidation. More accurate determination was regarded[91] as impossible because of the large heat of combustion, the need to use auxiliary materials, and the difficulties in calculating several corrections. However, this is unconvincing, since the work[91] involved defects of method. The quantity of heat produced by the combustion of thymol amounted to 50–70% of the total quantity evolved in the bomb during the experiment. The heat of combustion, which was required to calculate the appropriate correction, was found with an error of ~0.2%. It can easily be reckoned that this will lead to an error of 3–6 kcal mole^{-1} in $\Delta H_c^\circ[(C_6H_6)_2Cr, c]$.

Furthermore, determination of carbon dioxide and analysis of the solid products showed[91] that a high degree of combustion was not achieved: the quantity of the former was considerably smaller than expected, and the solid products contained elementary chromium. Since neither free nor combined carbon was detected in the solid phase, it was concluded[91] that the gaseous products included carbon monoxide, whose quantity was calculated.

Appropriate corrections for incomplete oxidation of carbon and chromium (respectively 5–49 and 3–21 kcal mole^{-1}) were made in processing the experimental results. However, such a procedure for determining the quantity of carbon monoxide among the combustion products is not exact, since carbon-containing products of thermal decomposition of the initial compound may be formed in the absence of a high degree of combustion.

A subsequent determination[92] of the enthalpy of combustion of dibenzenechromium gave $\Delta H_c^\circ = -1725.4 \pm 2.0$ kcal mole^{-1}. It is impossible to assess the reliability of this value because of the absence of any detailed description of the experiment[92].

Because of the sharp divergence between these results[91,92] the Reviewers redetermined the enthalpy of combustion of dibenzenechromium[93]. The compound was purified by repeated vacuum sublimation, and placed in polyethylene ampoules in the bomb. The mass taken for combustion was established by determining carbon dioxide in the products. Analysis of the solid products showed that neither unoxidised chromium nor unoxidised carbon was present, and a qualitative test for carbon monoxide in the gaseous products (which were passed through aqueous palladium dichloride) gave a negative result. The values obtained were $\Delta H_c^\circ = -1710 \pm 2$ and $\Delta H_f^\circ[(C_6H_6)_2Cr, c] = 35 \pm 2$ kcal mole^{-1}. Other workers[54] studied the high-temperature iodination of dibenzenechromium and obtained for the heat of formation 34 ± 2 kcal mole^{-1}, which agrees with the Reviewers' value[93] within the limits of experimental error.

Taking the average of these results[54,93] and using the heat of sublimation[94] $\Delta H_s^\circ = 19.6 \pm 0.5$ kcal mole^{-1}, we have $\Delta H_f^\circ[(C_6H_6)_2Cr, c] = 35.4 \pm 1.0$ and $\Delta H_f^\circ[(C_6H_6)_2Cr, g] = 54.1 \pm 1.1$ kcal mole^{-1}, and find from the latter that $\bar{D}(Cr-C_6H_6) = 40.2 \pm 0.7$ kcal mole^{-1}. This result agrees well with the mass-spectrometric values[95,96] of 40.5 and 39 kcal mole^{-1}, but is lower than the mass-spectrometric value[97] of 46 kcal mole^{-1}. It is interesting that considerably less energy is required to detach the first benzene ring than to detach the second: thus[96] $D_1(C_6H_6-CrC_6H_6) = 23$ and $D_2(Cr-C_6H_6) = 55$ kcal mole^{-1}.

3. Compounds of Chromium with Alkylated Benzenes

A stationary calorimetric bomb was used[92] to measure the enthalpies of combustion of compounds formed by chromium with methylated benzenes, and the Reviewers have studied[98] ethyl and isopropyl derivatives of dibenzenechromium by the same method. The enthalpies obtained for combustion of these compounds to crystalline chromium(III) oxide, gaseous carbon dioxide, and liquid water, together with the calculated standard enthalpies of formation and the mean chromium–ligand bond dissociation energies, are given in Table 14. Analytical data were absent[92] for solid and gaseous combustion products from compounds (I) and (II). In view of the closely similar results obtained for them (as was to be expected for compounds having the same composition and similar structures), however, the values given for the enthalpies of combustion are probably feasible: the formation of products of the incomplete combustion of (I) and (II) of the same nature and mass is improbable because of the non-standard conduct of the experiments. The solid combustion products from compounds (III)–(VI) were subjected[98] to X-ray examination and chemical analysis, when products of the incomplete oxidation of chromium were not detected.

Table 14 contains for compound (VI) the chromium–isopropylbenzene bond dissociation energy, calculated by means of the equation

$$\bar{D}(Cr-C_6H_5C_3H_7) = \Delta H_f^\circ(Cr, g) + \Delta H_f^\circ[C_6H_4(C_3H_7)_2, g] + \\ + \Delta H_f^\circ(C_6H_5C_3H_7, g) - \Delta H_f^\circ[(VI), g] - \bar{D}[Cr-C_6H_4(C_3H_7)_2]$$

on the assumption that $\bar{D}[Cr-C_6H_4(C_3H_7)_2]$ has the same value in (V) and (VI).

The enthalpies of sublimation of (I) and (II) were calculated[92] from the measured temperature dependence of vapour pressure as respectively 15.4 and 8.0 kcal mole^{-1}. The marked difference between these values casts doubt on their accuracy. In order to calculate $\Delta H_f^\circ(g)$ the Reviewers have assumed that the enthalpies of sublimation of these compounds differ little from the value for dibenzenechromium and are ~20 kcal mole^{-1}. The enthalpies of vaporisation of compounds (III)–(VI) have been taken from the literature[90,94,99–101].

Table 14 shows that the chromium–ligand bond dissociation energy in compounds (I)–(VI) is the same within the limits of experimental error. Mass spectrometry gave[97] for $\bar{D}[Cr-C_6H_3(CH_3)_3]$ in compound (I) the value 61 kcal mole^{-1}, which is considerably larger than the corresponding thermochemical value. The discrepancies often met between published thermochemical and mass-spectrometric results are due mainly to the absence of a reliably established mechanism of the breakdown of an organometallic compound on electron bombardment and also to the presence of excess energy in the breakdown products.

4. Diarenechromium Halides

Enthalpies of combustion have been measured and standard enthalpies of formation calculated[93] for dibenzenechromium chloride and bromide, and ditoluene, di-*m*-xylene, dimesitylene-, and dibiphenyl-chromium iodides

Table 14. Thermochemical parameters (kcal mole^{-1}) of compounds of chromium with alkylated benzenes.

No.	Compound	$-\Delta H_c^0$	ΔH_f^0	ΔH_s^0	ΔH_v^0	ΔH_f^0 (g)	$\bar{D}$ (Cr – Ligand)
(I)	$[1,3,5\text{-}C_6H_3(CH_3)_3]_2Cr(c)$	2638.0±3.0	−11.0±3.0	20±1	—	9.0±3.1	39.1±1,6
(II)	$[1,2,4\text{-}C_6H_3(CH_3)_3]_2Cr(c)$	2640.0±1.9	−9.0±1.9	20±1	—	11.0±2.2	38.7±1,3
(III)	$(C_6H_5C_2H_5)_2Cr(l)$	2340.1±0.8	15.9±0.8	—	18±2	33.9±2.2	37.7±1,3
(IV)	$[o\text{-}C_6H_4(C_2H_5)_2]_2Cr(l)$	2962.5±1.7	−11.3±1.7	—	18±2	6,7±2.6	39.6±1.5
(V)	$[o\text{-}C_6H_4(iso\text{-}C_3H_7)_2]_2Cr(l)$	3576.6±1.8	−46.7±1.8	—	24±2	−22.7±2.6	41.8±1.5
(VI)	$[o\text{-}C_6H_4(iso\text{-}C_3H_7)_2]Cr(C_6H_5\ iso\text{-}C_3H_7)(l)$	3106.5±1.6	−29.7±1.6	—	24±2	−5.7±2.5	42.8±2.2

(Table 15). A tightly fitting tantalum pot prevented interaction between the walls of the bomb and the halides. In the determination of the enthalpy of combustion of dibenzenechromium chloride complete conversion of chlorine into hydrogen chloride was ensured by covering the inside surface of the bomb also with glass cloth impregnated with aqueous hydrazine dihydrochloride. Absence of unoxidised or incompletely oxidised chromium and carbon was shown in every experiment by analysis of the combustion products. Furthermore, hydrogen bromide was absent from the products of the combustion of dibenzenechromium bromide, and hydrogen chloride from those of the chloride.

Skinner et al.[54] obtained for the thermal decomposition

$$(C_6H_6)_2CrI(c) \rightarrow Cr(c) + 2C_6H_6(g) + 0.5I_2(g)$$

the enthalpy $\Delta H_r^\circ = 35 \pm 1$ kcal mole^{-1}, which corresponds to $\Delta H_f^\circ[(C_6H_6)_2CrI, c] = 12 \pm 1$ kcal mole^{-1}. In determining the enthalpy of combustion the Reviewers[102] paid especial attention to purifying the compound, and obtained for the process

$$(C_6H_6)_2CrI(c) + 15.75O_2(g) \rightarrow 0.5Cr_2O_3(c) + 12CO_2(g) + 6H_2O(l) + 0.5I_2(c)$$

the value† $\Delta H_c^\circ = -1684.8 \pm 0.5$ kcal mole^{-1}, corresponding to $\Delta H_f^\circ[(C_6H_6)_2CrI, c] = 10.0 \pm 0.5$ kcal mole^{-1}, close to Skinner's result[54].

Table 15. Thermochemical parameters (kcal mole^{-1}) of diarenechromium halides.

Compound	$-\Delta H_c^0$ (c)	Combustion products	ΔH_f^0 (c)
$(C_6H_6)_2CrCl$	1670±3	Cr_2O_3 (c), CO_2 (g), H_2O (l), HCl (400 H_2O, s)	−10±3
$(C_6H_6)_2CrBr$	1674±2	Cr_2O_3 (c), CO_2 (g), H_2O (l), Br_2 (l)	−1±2
$(C_6H_5CH_3)_2CrI$	1983±1	Cr_2O_3 (c), CO_2 (g), H_2O (l), I_2 (c)	−17±1
$(m\text{-}C_6H_4(CH_3)_2)_2CrI$	2297±2	Cr_2O_3 (c), CO_2 (g), H_2O (l), I_2 (c)	−27±2
$(1,3,5\text{-}C_6H_3(CH_3)_3)_2CrI$	2604±2	Cr_2O_3 (c), CO_2 (g), H_2O (l), I_2 (c)	−45±2
$(C_6H_5C_6H_5)_2CrI$	3113±2	Cr_2O_3 (c), CO_2 (g), H_2O (l), I_2 (c)	36±2

Table 16. Thermochemical parameters (kcal mole^{-1}) of tetra-alkoxytitanium compounds $(RO)_4Ti$.

R	ΔH_r^0	$-\Delta H_f^0$ [$(RO)_4Ti$ (l)]	ΔH_o^0	$-\Delta H_f^0$ [$(RO)_4Ti$, (g)]	$\bar{D}$ (RO—Ti)
C_2H_5	—	349.0±1.4	(24±2)	325.0±2.5	102.8±1.0
n-C_3H_7	0.602±0.00	376±4.2	(18±2)	358±4	107±2
iso-C_3H_7	10.57±0.09	379±1.6	(17±2)	362±3	106±2
n-C_4H_9	−1.98±0.02	398±1.6	(22±2)	376±3	105±2
iso-C_4H_9	0.305±0.002	403±1.5	(22±2)	381±2	105±2
s-C_4H_9	6.88±0.05	404±1.5	(22±2)	382±2	104±2
t-C_4H_9	15.8±0.12	411±1.5	15.8±0.8	395±2	104±2
n-C_5H_{11}	−2.29±0 03	429±2.2	(25±2)	404±2	106±2
t-C_5H_{11}	11.27±0.08	458±2	18.5±0.9	439±2	109±2

5. Dibenzenemolybdenum

The enthalpy of combustion was found[88] to be ΔH_c°. $[(C_6H_6)_2Mo, c] = -1789.8 \pm 2.2$ kcal mole^{-1}, but no analysis of the combustion products was reported[88]. The assumed equation

$$(C_6H_6)_2Mo(c) + 16.5O_2(g) \rightarrow MoO_3(c) + 12CO_2(g) + 6H_2O(l),$$

yielded $\Delta H_f^\circ[(C_6H_6)_2Mo, c] = 73.2 \pm 2.2$ kcal mole^{-1}. Using[88,101] $\Delta H_S^\circ = 22 \pm 1$ kcal mole^{-1}, we find that $\Delta H_f^\circ[(C_6H_6)_2Mo, g] = 95.2 \pm 2.4$ kcal mole^{-1}. Mass spectrometry gives[104] $\bar{D}(Mo-C_6H_6) = 59$ kcal mole^{-1}.

V. ALKOXY-COMPOUNDS

1. Alkoxy-compounds of Titanium

Determinations[105] of the enthalpies of the processes

$$TiCl_4(l) + 4C_2H_5OH(l) \rightarrow (C_2H_5O)_4Ti(l) + 4HCl(g)$$
$$TiCl_4(l) + 4C_2H_5OH(l) \rightarrow (C_2H_5O)_4Ti(l) + 4HCl(51.3H_2O, s)$$

gave respectively 19.5 ± 0.4 and −49.1 ± 0.6 kcal mole^{-1}, from which calculation gave for the enthalpy of formation of liquid tetraethoxytitanium the values −349.7 ± 1.8 and −348.4 ± 2.0 kcal mole^{-1} in good agreement.

The enthalpy of formation of solid tetraethoxytitanium was calculated[106] from the enthalpy of combustion determined in a stationary calorimetric bomb: for the process

$$(C_2H_5O)_4Ti(c) + 12O_2(g) \rightarrow TiO_2(c) + 8CO_2(g) + 10H_2O(l)$$

the value $\Delta H_c^\circ = -1308.6 \pm 1.2$ was obtained, whence it was found that $\Delta H_f^\circ[(C_2H_5O)_4Ti, c] = -352.6 \pm 1.2$ kcal mole^{-1}. The enthalpy of fusion of this compound was estimated[106] as 3–6 kcal mole^{-1}. Good agreement is evident between these results[105,106].

Averaging the results[105] gave $\Delta H_f^\circ[(C_2H_5O_4)_4Ti, l] = -349.0 \pm 1.4$ kcal mole^{-1}, which was used to find[107] enthalpies of formation of several other alkoxytitanium compounds. For this purpose calorimetric determinations were made[107] of the enthalpies of the reactions

$$(C_2H_5O)_4Ti(l) + 4ROH(l) \rightarrow (RO)_4Ti(l) + 4C_2H_5OH(l),$$

where R = n-C_3H_7, iso-C_3H_7, n-C_4H_9, iso-C_4H_9, s-C_4H_9, t-C_4H_9, n-C_5H_{11}, and t-C_5H_{11}. The results of these measurements (ΔH_r°) and those of the corresponding calculations are given in Table 16.

The heats of formation of tetra-n-butoxy- and tetra-t-pentyloxy-titanium were checked[107] by studying the thermochemistry of the processes

$$[(C_2H_5)_2N]_4Ti(l) + 4n\text{-}C_4H_9OH(l) \rightarrow n\text{-}C_4H_9O)_4Ti(l) + 4(C_2H_5)_2NH(l),$$

$$[(C_2H_5)_2N]_4Ti(l) + 4t\text{-}C_5H_{11}OH(l) \rightarrow (t\text{-}C_5H_{11}O)_4Ti(l) + 4(C_2H_5)_2NH(l),$$

for which ΔH_r° was respectively −69.4 ± 0.6 and −55.4 ± 0.4 kcal mole^{-1}. From the value found[107] for the heat of formation of tetrakisdiethylaminetitanium $\Delta H_f^\circ(l) = -116.8$ kcal mole^{-1} and the known values for the alcohols and diethylamine it was calculated[107] that $\Delta H_f^\circ[(n\text{-}C_4H_9O)_4Ti, l] = -399$ and $\Delta H_f^\circ[(t\text{-}C_5H_{11}O)_4Ti, l] = -457$ kcal mole^{-1}, in good agreement with the values in Table 16.

Enthalpies of vaporisation (Table 16) were estimated[107] from the experimental values for tetra-t-butoxy- and tetra-t-pentyloxy-titanium, with allowance for depolymerisation of the compounds on evaporation. Table 16 shows that values of $\bar{D}$(RO—Ti) are little affected by the nature of the radical, and the mean must be taken as 105 ± 2 kcal mole^{-1}.

† In an earlier determination[103] we had obtained the low value $\Delta H_c^\circ = -1664$ kcal mole^{-1}, probably owing to inadequate purification of the specimen of dibenzenechromium iodide.

Shaulov et al.[108] used combustion in a stationary calorimetric bomb, and obtained for the enthalpies of formation of tetraisopropoxytitanium and tetra-n-butoxytitanium the respective values -372.3 ± 1.2 and -392.7 ± 4.2 kcal mole^{-1}, which differed by a few kilocalories per mole from those in Ref. 107 (Table 16).

Lappert et al.[109] determined the enthalpy of the process

$$TiCl_4(l) + 4iso\text{-}C_3H_7OH(l) \rightarrow (iso\text{-}C_3H_7O)_4Ti(l) + 5HCl(g)$$

and obtained $\Delta H_r^\circ = 19.3 \pm 1.2$ kcal mole^{-1}, which corresponds to $\Delta H_f^\circ[(iso\text{-}C_3H_7O)_4Ti, l] = -389 \pm 2$ kcal mole^{-1}. This value exceeds by 10 and 17 kcal mole^{-1} respectively those obtained by the above workers[107,108]. The reasons for the discrepancy in these results[107-109] are obscure. Nevertheless, the detailed discussion[107] of the experimental conditions and the necessary corrections lead to acceptance of the results in Ref. 107 as the most soundly based.

2. Alkoxy-compounds of Vanadium and Chromium

Bradley and Hillyer[110] determined the enthalpies of the reactions of vanadium tetrachloride and of tetra-t-butoxyvanadium with aqueous hydrochloric acid, and found the enthalpy of the overall process

$$VCl_4(l) + 4t\text{-}C_4H_9OH(l) \rightarrow (t\text{-}C_4H_9O)_4V(l) + 4HCl(51.3H_2O, s)$$

to be -22.7 ± 0.9 kcal mole^{-1}. Table 17 gives the enthalpy of formation of tetrabutoxyvanadium calculated from this result together with that of tetra-t-butoxychromium calculated[110] from its enthalpy of hydrolysis in aqueous sulphuric acid, allowing for the possibility of disproportionation of quadrivalent chromium to the tervalent and sexivalent states.

Table 17. Thermochemical parameters (kcal mole^{-1}) of alkoxy-derivatives of vanadium and chromium.

Compound	$-\Delta H_f^0$ (l)	ΔH_v^0	$-\Delta H_f^0$ (g)	$\bar{D}$(t-C$_4$H$_9$O-M)
(t-C$_4$H$_9$O)$_4$V	344±1	(15.8±1)	328.2±1.4	90±2
(t-C$_4$H$_9$O)$_4$Cr	321±1	(15.8±1)	305.2±1.4	77±2

The enthalpies of vaporisation of these complexes were equated[110] to the experimental value for tetra-t-butoxytitanium (Table 16).

3. Alkoxy-compounds of Zirconium and Hafnium

Lappert et al.[109] found that the enthalpy ΔH_r° of the process

$$MCl_4(l) + 4iso\text{-}C_3H_7OH(l) \rightarrow (iso\text{-}C_3H_7O)_4M(c) + 4HCl(g)$$

was respectively 21.4 ± 1.8 and 10.4 ± 1.8 kcal mole^{-1} when M = Zr and Hf. Enthalpies of formation of the alkoxy-compounds of zirconium and hafnium calculated from the results are given in Table 18. Enthalpies of sublimation were estimated[109] from the enthalpy of vaporisation of tetraisopropoxytitanium (Table 16) and their assumed value of 3 kcal mole^{-1} for the enthalpy of fusion.

Comparison of the values in Table 18 with that in Table 16 for $\bar{D}$(RO–Ti) indicates that

$$\bar{D}(iso\text{-}C_3H_7\text{–}Ti) < \bar{D}(iso\text{-}C_3H_7O\text{–}Zr) < \bar{D}(iso\text{-}C_3H_7O\text{–}Hf)$$

i.e. $\bar{D}$(RO–M) increases with increase in the atomic number of the metal as Group IV of the Periodic System is descended.

Table 18. Thermochemical parameters (kcal mole^{-1}) of alkoyx-derivatives of zirconium and hafnium.

Compound	$-\Delta H_f^0$ (c)	ΔH_s^0	$-\Delta H_f^0$(g)	$\bar{D}$(iso-C$_3$H$_7$O-M)
(iso-C$_3$H$_7$O)$_4$Zr	429±1.8	(20±5)	409±5	126±2
(iso-C$_3$H$_7$O)$_4$Hf	443±1.8	(20±5)	423±5	130±2

4. Alkoxy-compounds of Niobium and Tantalum

The Reviewers[111] have determined the enthalpies of combustion of the penta-alkoxy-compounds $(RO)_5M$, in which M = Nb, Ta and R = CH_3, C_2H_5, n-C_3H_7. X-Ray phase analysis showed that the solid combustion products were niobium and tantalum pentoxides respectively. No products of incomplete oxidation of the metals were detected. Combustion of the test compounds was represented by the equation

$$(C_nH_{2n+1}O)_5M(l, c) + 7.5O_2(g) \rightarrow 0.5M_2O_5(c) + 5nCO_2(g) + (5n + 2.5)H_2O(l).$$

The values obtained for the enthalpies of combustion and the standard enthalpies of formation calculated from them are given in Table 19 together with the mean RO–M bond dissociation energies. Enthalpies of vaporisation were calculated from the temperature dependence of vapour pressure measured by the Knudsen effusion method. The enthalpies of fusion of crystalline niobium and tantalum methoxides were estimated as 3 ± 1 kcal mole^{-1}.

Table 19. Thermochemical parameters (kcal mole^{-1}) of alkoxy-compounds of niobium and tantalum.

Compound	$-\Delta H_c^0$	$-\Delta H_f^0$	ΔH_s^0	ΔH_v^0	$-\Delta H_f^0$(g)	$\bar{D}$ (RO–M)
(CH$_3$O)$_5$Nb(c)	871.5±0.4	337.9±0.6	19.2±2.5	—	318.7±2.6	100.3±2.0
(C$_2$H$_5$O)$_5$Nb(l)	1642.6±0.4	378.6±0.6	—	18.9±2.0	359.7±2.1	99.8±1.0
(n-C$_3$H$_7$O)$_5$Nb(l)	2426.4±0.8	406.7±1 0	—	24.4±1.6	382,3±1.8	99.8±2.0
(CH$_3$O)$_5$Ta(c)	878.3±0.4	349.0±0.6	21.1±3.2	—	327.9±3.3	105.2±2.0
(C$_2$H$_5$O)$_5$Ta(l)	1647.3±0.5	391.8±0.7	—	18.9±2.0	273.9±2.1	105.5±1.0
(n-C$_3$H$_7$O)$_5$Ta(l)	2430.2±0.8	420.7±1.0	—	26.6±2.1	394.1±2.3	105.2±2.0

Comparison of the RO–M bond dissociation energies in Table 19 with the RO–V value in Table 17 indicates that

$$\bar{D}(RO\text{–}V) < \bar{D}(RO\text{–}Nb) < \bar{D}(RO\text{–}Ta).$$

Thus, as in other cases, the RO–M bond dissociation energy increases with atomic number of the metal.

VI. CONCLUSION

The most reliable values for the enthalpies of formation ΔH_f° of organic compounds of transition metals and the mean bond dissociation energies $\bar{D}$ calculated from them are assembled in Tables 20–23. The experimental results collected in them and illustrated by Figs. 1–4 reveal corresponding rules for the mean energy of dissociation of the chemical bonds formed by transition metals in their organic compounds.

Table 20. Thermochemical parameters (kcal mole^{-1}) of carbonyl compounds of transition metals.

Carbonyl	$-\Delta H_f^0$*	$-\Delta H_f^0$(g)	$\bar{D}$(M-CO)
$Ni(CO)_4$(l)	150.4±1.5	143.8±1.5	35.2±0.4
$Fe(CO)_5$(c)	182.6±1.8	173.0±1.8	28.1±0.4
$Fe_2(CO)_9$(c)	337±3	319±6	—
$Fe_3(CO)_{12}$(c)	442±4	419±7	—
$Mn_2(CO)_{10}$(c)	404.6±2.0	385.4±2.0	23.6±0.4
$CH_3Mn(CO)_5$(c)	189.8±2.2	174.8±2.3	—
$ClMn(CO)_5$(c)	241.2±3	—	—
$BrMn(CO)_5$(c)	231.8±2	—	—
$C_2H_5Mn(CO)_3$(c)	127.8±2	115.3±2.1	—
$Cr(CO)_6$(c)	234.3±0.4	217.2±0.4	25.6±0.1
$(C_6H_6)Cr(CO)_3$(c)	106±2	84.2±2.2	—
$(C_6H_5CH_3)Cr(CO)_3$(c)	114±2	91.4±2.2	—
$[1,3,5\text{-}C_6H_3(CH_3)_3]Cr(CO)_3$(c)	136.5±2	110.6±2.2	—
$[C_6(CH_3)_6]Cr(CO)_3$(c)	166.5±3	137.0±3.2	—
$(C_6H_5Cl)Cr(CO)_3$(c)	111±5	86.5±5.1	—
$(cyclo\text{-}C_7H_8)Cr(CO)_3$(c)	74±3	51.5±3.2	—
$Mo(CO)_6$(c)	236.6±0.2	219.0±0.3	36.2±0.1
$[1,3,5\text{-}C_6H_3(CH_3)_3]Mo(CO)_3$(c)	119±1	—	—
$W(CO)_6$(c)	229.5±0.7	211.2±0.8	42.9±0.2
$Co_2(CO)_8$(c)	297.1±1.0	281.5±1.3	32.6±0.4
$Co_4(CO)_{12}$(c)	441±4	418±7	—
$Co_3(CCl)(CO)_9$(c)	280.5±2.2	256.7±2.2	—
$Co_3(CBr)(CO)_9$(c)	280.3±2.4	252.2±2.5	—
$Re_2(CO)_{10}$(c)	395.6±2.0	373.3±2.0	43.5±0.5
$CH_3Re(CO)_5$(c)	198.8±2.2	182.8±2.3	—
$Ru_3(CO)_{12}$(c)	459±5	435±7	(42)
$Rh_4(CO)_{12}$(c)	435±3	411±6	(40)
$Rh_6(CO)_{16}$(c)	578±4	550±6	(40)
$Os_3(CO)_{12}$(c)	418±5	393±7	(46)
$Ir_4(CO)_{12}$(c)	435±4	410±7	(46)

*This column gives either ΔH_f°(c) or ΔH_f°(l), the appropriate symbol—(c) or (l)—being placed immediately after the formula of the compound.

1. For a given ligand the mean dissociation energy of its bond with a transition metal increases with the atomic number of the metal in a given group of the Periodic System. This energy is considerably smaller for transition metals of the first series than for those of the second series, whereas metals of the second and third series usually have closely similar values. The interest of this rule established by the Reviewers [61,70,77,78,80,111] is enhanced by the fact that non-transition elements exhibit the opposite relationship: the mean energy of dissociation of the bonds formed by an element with a given radical diminishes with increase in the atomic number of the element down a group in the Periodic System [79].

2. For a given transition metal M we find in all cases that

$$\bar{D}(M-OR) > \bar{D}(M-C_5H_5) > \bar{D}(M-C_6H_6) > \bar{D}(M-CO).$$

3. Any effect of alkyl substituents in the benzene ring in diarenechromium compounds on the mean chromium–ligand bond dissociation energy lies within the experimental error of its determination [77,98].

Table 21. Thermochemical parameters (kcal mole^{-1}) of cyclopentadienyl compounds of transition metals.

Compound	ΔH_f^0 (c)	ΔH_f^0(g)	$\bar{D}$(M-C5H5)
$(C_5H_5)_2V$(c)	34±2	48±2	88±1
$(C_5H_5)_2Cr$(c)	42.6±0.5	59.3±0.6	67.8±0.6
$(C_5H_5)_2Mn$(c)	48.1±0.5	66.2±0.6	50.9±0.4
$(C_5H_5)_2Fe$(c)	37.0±1.0	54.5±1.0	72.6±0.5
$(C_5H_5)_2Co$(c)	56.3±0.6	73.1±0.8	64.6±0.6
$(C_5H_5)_2Ni$(c)	65.6±1.0	82.9±1.0	59.8±0.8
$(C_5H_5)TiCl_3$(c)	−145.5±1.6	−120.5±3.0	62±3
$(C_5H_5)_2TiCl_2$(c)	−91.6±1.8	−63.2±1.8	64.3±1.0
$(C_5H_5)_2Ti(CH_3)_2$(c)	13±2	32±2	—
$(C_5H_5)_2Ti(CH_2C_6H_5)$(c)	46.8±1.2	66.8±2.0	—
$(C_5H_5)_2Ti(OCOC_6H_5)_2$(c)	−231±3	—	—
$(C_5H_5)_2ZrCl_2$(c)	−128.6±0.7	−103.5±0.9	85.7±1.0
$(C_5H_5)_2Zr(CH_3)_2$(c)	−10.6±0.5	8.8±0.7	—
$(C_5H_5)_2Zr(C_6H_5)_2$(c)	65.9±2.6	87.9±3.0	—
$(C_5H_5)_2HfCl_2$(c)	−128.1±0.6	−102.6±0.8	85.8±0.6
$(C_5H_5)_2MoH_2$(c)	46.6±0.6	68.7±0.8	—
$(C_5H_5)_2MoCl_2$(c)	−22.9±0.6	1.1±1.2	84.3±1.8
$(C_5H_5)_2MoI_2$(c)	7.2±0.5	31.2±1.1	—
$(C_5H_5)_2WH_2$(c)	59.9±0.6	82.9±0.8	—
$(C_5H_5)_2WCl_2$(c)	−17.0±0.6	8.0±1.2	94.4±0.8
$(C_5H_5)_2WI_2$(c)	28.0±0.7	53.0±1.2	—
$(C_5H_5)Pt(CH_3)_3$(c)	40.3±0.5	58.9±0.7	75±3
$(C_5H_5)_2Pt(CH_3)_2$(c)	31.2±1.7	51.2±1.9	75±3
$(C_5H_5)_3Sc$(c)	−3.2±1	23.0±1.5	72.7±0.5
$(C_5H_5)_3Y$(c)	−10.8±1	15.9±1.5	78.5±0.5
$(C_5H_5)_3La$(c)	−6.4±1	21.0±1.5	77.3±0.5
$(C_5H_5)_3Pr$(c)	−6.7±2	23.3±2.0	71.9±1.0
$(C_5H_5)_3Tm$(c)	−11.8±1	14.8±1.5	64.8±0.5
$(C_5H_5)_3Yb$(c)	7.0±1	33.0±1.5	51.1±0.5

Table 22. Thermochemical parameters (kcal mole^{-1}) of arene compounds of transition metals.

Compound	ΔH_f^0*	ΔH_f^0(g)	$\bar{D}$(M-Ligand)
$(C_6H_6)_2V$(c)	8.7±2.4	26.7±2.6	77.0±1.4
$(C_6H_6)_2Cr$(c)	34.5±1.0	54.1±1.1	40.2±0.7
$[1,3,5\text{-}C_6H_3(CH_3)_3]_2Cr$(c)	−11.0±3.0	9.0±3.1	39.1±1.6
$[1,2,4\text{-}C_6H_3(CH_3)_3]_2Cr$(c)	−9.0±1.9	11.0±2.2	38.7±1.3
$(C_6H_5C_2H_5)_2Cr$(l)	15.9±0.8	33.9±2.2	37.7±1.3
$[o\text{-}C_6H_4(C_2H_5)_2]_2Cr$(l)	−11.3±1.7	6.7±2.6	39.6±1.5
$[o\text{-}C_6H_4(iso\text{-}C_3H_7)_2]_2Cr$(l)	−46.7±1.8	−22.7±2.6	41.8±1.5
$[o\text{-}C_6H_4(iso\text{-}C_3H_7)_2]Cr(C_6H_5\text{-}iso\text{-}C_3H_7)$(l)	−29.7±1.6	−5.7±2.5	42.8±2.2
$(C_6H_6)_2CrCl$(c)	−10±3	—	—
$(C_6H_6)_2CrBr$(c)	−1±2	—	—
$(C_6H_6)_2CrI$(c)	11±1	—	—
$(C_6H_6)_2CrI$(c)	−17±1	—	—
$(C_6H_5CH_3)_2CrI$(c)	−27±2	—	—
$[m\text{-}C_6H_4(CH_3)_2]_2CrI$(c)	−45±2	—	—
$[1,3,5\text{-}C_6H_3(CH_3)_3]_2CrI$(c)	36±2	—	—
$(C_6H_5C_6H_5)_2CrI$(c)	73.2±2.2	95.2±2.4	50.7±1.2
$(C_6H_6)_2Mo$(c)			

*See footnote to Table 20.

Table 23. Thermochemical parameters (kcal mole^{-1}) of alkoxy-compounds of transition metals.

Compound	$-\Delta H_f^0$*	$-\Delta H_f^0$ (g)	$\bar{D}$(RO-M)
$(C_2H_5O)_4Ti$(l)	349.0±1.4	325.0±2.5	102.8±1.0
$(n\text{-}C_3H_7O)_4Ti$(l)	376±4.2	358±4	107±2
$(iso\text{-}C_3H_7O)_4Ti$(l)	379±1.6	362±3	106±2
$(n\text{-}C_4H_9O)_4Ti$(l)	398±1.6	376±3	105±2
$(iso\text{-}C_4H_9O)_4Ti$(l)	403±1.5	381±2	105±2
$(s\text{-}C_4H_9O)_4Ti$(l)	404±1.5	382±2	104±2
$(t\text{-}C_4H_9O)_4Ti$(l)	411±1.5	395±2	104±2
$(n\text{-}C_5H_{11}O)_4Ti$(l)	429±2.2	404±2	106±2
$(t\text{-}C_5H_{11}O)_4Ti$(l)	458±2	439±2	109±2
$(t\text{-}C_4H_9O)_4V$(l)	344±1	328.2±1.4	90±2
$(t\text{-}C_4H_9O)_4Cr$(l)	331±1	305.2±1.4	77±2
$(iso\text{-}C_3H_7O)_4Zr$(c)	429±1.8	409±5	126±2
$(iso\text{-}C_3H_7O)_4Hf$(c)	443±1.8	423±5	130±2
$(CH_3O)_5Nb$(c)	337.9±0.6	318.7±2.6	100.3±2.0
$(C_2H_5O)_5Nb$(c)	378.6±0.6	359.7±2.1	99.8±1.0
$(n\text{-}C_3H_7O)_5Nb$(l)	406.7±1.0	382.3±1.8	99.8±2.0
$(CH_3O)_5Ta$(c)	349.0±0.6	327.9±3.3	105.2±2.0
$(C_2H_5O)_5Ta$(l)	391.8±0.7	273.9±2.1	105.5±1.0
$(n\text{-}C_3H_7O)Ta$(l)	420.7±1.0	394.1±2.3	105.2±2.0

*See footnote to Table 20.

4. In the series—vanadium, chromium, manganese, and iron—the mean methyl–cyclopentadienyl bond dissociation energy depends on the atomic number of the element qualitatively in the same way as does the enthalpy of atomisation of the metal (Fig. 5). This evidently means that the specific electronic structure of atoms of 3*d* elements has a qualitatively similar influence on π-bond formation in sandwich compounds and on that of a metallic bond in the elements. Despite the closely similar enthalpies of atomisation of iron, cobalt, and nickel (Table 1), however, the energy of dissociation of the Fe–C_5H_5 bond exceeds by 8 kcal mole^{-1} the value of $\bar{D}$(Co–C_5H_5), which in turn is 5 kcal mole^{-1} larger than $\bar{D}$(Ni–C_5H_5). A correlation between $\bar{D}$(M–C_5H_5) and the enthalpy of atomisation of the metal is observed also in a series of tricyclopentadienyl compounds of rare-earth metals—lanthanum, praseodymium, thulium, and ytterbium (Tables 1 and 13).

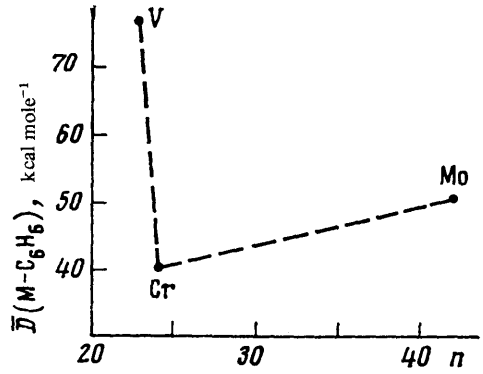


Figure 3. Variation of mean M–C_6H_6 bond dissociation energy with atomic number of metal.

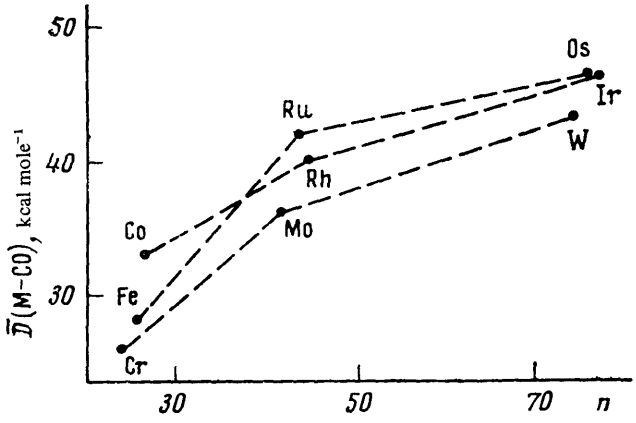


Figure 1. Variation of mean M–CO bond dissociation energy with atomic number of metal.

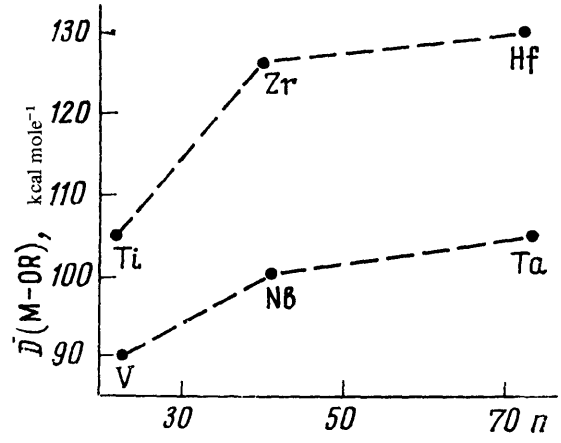


Figure 4. Variation of mean M–OR bond dissociation energy with atomic number of metal.

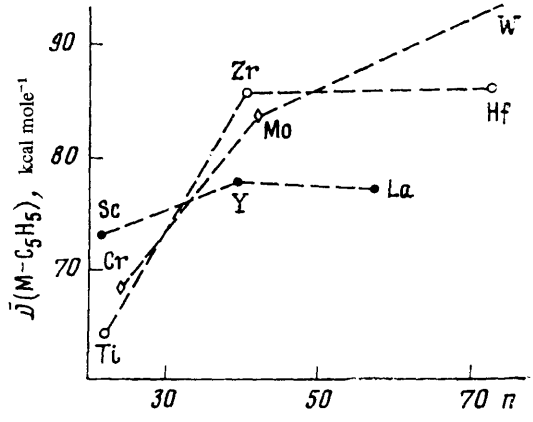


Figure 2. Variation of mean M–C_5H_5 bond dissociation energy with atomic number of metal.

Armstrong and his coauthors[112] have recently used the CNDO–MO method to describe the electronic properties of unsubstituted metallocenes of transition metals of the 3*d* series. They have calculated the charges on the metal atoms and the degree of completion of their orbitals; they have also computed the metal–carbon bond orders, which they assume[112] to be a quantitative measure of the interaction between metal and ring. According to the negative charges on the metal atoms in these compounds in the ground state the metals form the sequence

Fe>Cr>Co>Ni>V>Mn;

and according to the bond orders the sequence

Fe>Cr>Mn>V>Co>Ni,

whereas the experimental values of $\bar{D}$(M–C_5H_5) yield

V>Fe>Cr>Co>Ni>Mn.

Hence it is only for the series

$(C_5H_5)_2Fe$, $(C_5H_5)_2Cr$, $(C_5H_5)_2Co$, $(C_5H_5)_2Ni$

that a qualitative correspondence exists between the trend of variation in the experimental mean M–C_5H_5 bond dissociation energy and the bond order calculated from the

electronic structure of the metallocene. No analogous calculations have yet been made for other series of organic compounds of transition metals[112]. It must be supposed that further extension of experimental thermochemical investigations of these compounds, together with the development of quantum-mechanical calculations of the electronic characteristics of their molecules, will provide a deeper insight into the laws governing the energy parameters of organic compounds of metals.

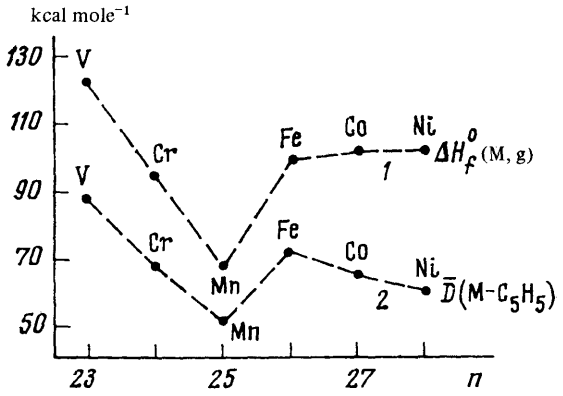


Figure 5. Influence of atomic number of metal in the 3*d* series of the Periodic System on: 1) enthalpy of atomisation of metal; 2) mean M–C_5H_5 bond dissociation energy.

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