Visible–Ultraviolet Spectra.—The visible and ultraviolet spectra of all the complexes were obtained with a Cary Model 14 recording spectrophotometer using aqueous solutions in 1-cm cells or, in one case, using 1-cm cells with 0.9-cm cell spacers which gave 0.1-cm path lengths.

Proton Magnetic Resonance.—All pmr spectra were obtained on a Varian Model A-60 high-resolution spectrometer, using tetramethylsilane as an internal standard in CD_3OD and C_2D_6SO, and using the methyl peaks of sodium 3-trimethylsilyl-1-propanesulfonate as a reference in D_2O. The Varian temperature control unit of the spectrometer was calibrated from the temperature dependence of the methanol resonance peaks, as recommended by the manufacturer.

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Heat of Formation and Bond Energy of Bis(cyclopentadienyl)magnesium

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The standard heat of formation of $Mg(C_5H_5)_2(c)$ at 298°K is measured to be 16.0 ± 0.8 kcal/mole from the heat of hydrolysis in 1 *N* H_2SO_4. Mass spectrometric appearance potentials are used to derive the standard heat of formation of $C_5H_5(g)$, 53 ± 12 kcal/mole. From these data and the heats of sublimation of $Mg(C_5H_5)_2$, 16.3 ± 0.3 kcal/mole, and Mg, 35.3 ± 0.3 kcal/mole, the mean magnesium–radical bond energy is found to be 54.5 ± 12 kcal/mole. Reevaluation of literature data gives mean bond energies of 53 and 77 kcal/mole for $Ni(C_5H_5)_2$ and $Fe(C_5H_5)_2$, respectively.

Introduction

Metal–cyclopentadienyl compounds exhibit a wide range of chemical behavior and a variation of bond type between ionic and π-covalent extremes. The chemical stability may be quantitatively defined by the free energy change, ΔG_r, of appropriate reactions, while the bond type may be characterized by the mean metal–radical bond energy, $\bar{B}$.

Values of free energy of formation, ΔG_f°, and bond energy, $\bar{B}$, are available only for the π-bonded compounds $Fe(C_5H_5)_2$ and $Ni(C_5H_5)_2$, for which heats of combustion[1] and vaporization[2] have been combined with both measured and calculated[3,4] entropies. In the present work ΔG_f° and $\bar{B}$ are derived for $Mg(C_5H_5)_2$ from the heat of hydrolysis in 1 *N* H_2SO_4. This method avoids difficulties with incomplete combustion and formation of energy-rich oxides and should be applicable to many cyclopentadienyl–metal compounds which hydrolyze readily. It is found that $Mg(C_5H_5)_2$ is more stable with respect to the elements than $Fe(C_5H_5)_2$ by 18 kcal/mole, even though the Mg–C_5H_5 bond is 22 kcal/mole weaker than the Fe–C_5H_5 bond.

Experimental Section

Bis(cyclopentadienyl)magnesium, $Mg(C_5H_5)_2$, was prepared, purified, and analyzed as previously described.[5] Samples were vacuum sublimed into thin Pyrex bulbs which were sealed off and weighed with vacuum corrections. The bulbs were broken under 120 g of nitrogen-flushed 1 *N* H_2SO_4 in a platinum calorimeter previously described.[6] The reaction was rapid and heat evolution complete within 1 min. The aqueous solution was analyzed for Mg for two runs by titration with EDTA which had been standardized against 99.99% Mg metal dissolved in 1 *N* H_2SO_4. The glass pieces were collected and weighed and sample weights obtained by difference. Based on these sample weights, the two analyses gave for Mg 15.6, 16.0 wt %; calcd 15.7 wt %. Separate analysis established that no magnesium remained in the organic phase.

Two electrical calibrations, agreeing within ±0.2%, were performed after each reaction. Operation of the calorimeter was satisfactorily checked by measuring the heat of solution of Mg metal in 1 *N* HCl.[6] A thin layer of freshly distilled liquid cyclopentadiene was placed on the surface of the sulfuric acid to ensure that cyclopentadiene formed by hydrolysis of $Mg(C_5H_5)_2$ was in the liquid state and to ensure saturation of the acid with cyclopentadiene. The calorimeter was closely, but not completely, sealed to avoid excessive evaporation. A small correction amounting to $0.16v$ cal was added to the observed heat evolution to allow for evaporation of C_5H_6 and H_2O into the evacuated volume v of the sample bulbs on breaking. The correction was calculated from the known vapor pressures and heat of vaporization of C_5H_6[5] and H_2O[7] at the calorimeter temperature. The volume v was the measured external bulb volume (2–3 cm^3), corrected for glass and sample volumes. Blank runs with empty bulbs confirmed the magnitude of this calculated correction.

The heat absorbed by vaporization of C_5H_6 and H_2O into the free space of the calorimeter (15 cm^3) due to a temperature rise ΔT was calculated to be $0.10\Delta T$ cal. This amounted to $<0.1\%$ of total heat for both reaction and calibration and hence cancelled out within experimental error.

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An experiment run in a glass vessel, so that the organic residue could be separated by vacuum distillation, showed at least 95 mole % monomeric C_5H_6 to be formed. Since the heat of formation of liquid monomer, 25.04 kcal/mole,[8] is close to those of solid dimer and trimer, 28.0 and 30.2 kcal/mole, respectively,[9] no correction for polymerization appeared warranted. A further check was made by breaking bulbs containing only liquid C_5H_6 in the calorimeter. Negligible heat effects were observed, confirming the retention of the C_5H_6 in the liquid state and the absence of appreciable reaction with the aqueous H_2SO_4.

To find the heat of mixing of $[MgSO_4 \cdot 200H_2O]$ with 1.01 *N* H_2SO_4, samples of the appropriate weight of $MgSO_4$ solution, made from AnalaR $MgSO_4 \cdot 7H_2O$ and checked by analysis with EDTA, were weighed into glass bulbs which were broken under 120 g of 1.01 *N* H_2SO_4.

Results

Enthalpy of Formation.—$\Delta H_f°_{298}$ for $Mg(C_5H_5)_2$ was evaluated from the enthalpy changes of the following reactions

$$Mg(C_5H_5)_2(c) + [66H_2SO_4 \cdot 7200H_2O] \longrightarrow [MgSO_4 \cdot 65H_2SO_4 \cdot 7200H_2O] + 2C_5H_6(l) \quad (1)$$

$$[MgSO_4 \cdot 200H_2O] + [65H_2SO_4 \cdot 7000H_2O] \longrightarrow [MgSO_4 \cdot 65H_2SO_4 \cdot 7200H_2O] \quad (2)$$

$$200H_2O(l) + [65H_2SO_4 \cdot 7000H_2O] \longrightarrow [65H_2SO_4 \cdot 7200H_2O] \quad (3)$$

$$Mg(c) + S(rh) + 2O_2(g) + 200H_2O(l) \longrightarrow [MgSO_4 \cdot 200H_2O] \quad (4)$$

$$H_2(g) + S(rh) + 2O_2(g) + [65H_2SO_4 \cdot 7200H_2O] \longrightarrow [66H_2SO_4 \cdot 7200H_2O] \quad (5)$$

Reaction 1 represents the hydrolysis of $Mg(C_5H_5)_2$ in 1 *N* H_2SO_4 at the average of the reactant ratios shown in Table I. The average enthalpy change, $\Delta H_{298}(1)$, corrected for vaporization as described earlier, is -78.0 ± 0.6 kcal. Reaction 2 represents the heat of mixing of $[MgSO_4 \cdot 200H_2O)]$ with the appropriate amount of 1.01 *N* H_2SO_4 to give the same final magnesium concentration as reaction 1. Two experiments gave enthalpy changes, $\Delta H_{298}(2)$, of 2.36, 2.36 (av 2.36 ± 0.05) kcal. Reaction 3 represents the dilution of aqueous H_2SO_4, for which the enthalpy change is tabulated[7] to be -2.6 cal/mole of H_2O, so that $\Delta H_{298}(3)$ is -0.52 kcal. Reaction 4 represents the standard heat of formation of $MgSO_4$ in aqueous solution of mole ratio 1:200 H_2O, for which the tabulated[7] enthalpy change is -326.23 kcal/mole. Finally reaction 5 represents the partial molar heat of formation of H_2SO_4 in 1 *N* H_2SO_4 solution, for which the enthalpy change is derived from tabulated integral heats of formation[7] to be -211.33 kcal/mole.

The algebraic summation $-H(1) + H(2) - H(3) + H(4) - H(5)$ gives the following reaction

$$Mg(c) + 2C_5H_6(l) \longrightarrow Mg(C_5H_5)_2(c) + H_2(g) \quad (6)$$

with an enthalpy change of -34.05 ± 0.7 kcal. The standard enthalpy of formation of $C_5H_6(g)$ is calculated to be 31.82 ± 0.3 kcal/mole from the heat of hydrogenation to $C_5H_{10}(g)$,[8] corrected to 298°K using calculated ideal gas heat capacities. Subtracting the heat of vaporization, 6.78 ± 0.06 kcal/mole at 298°K,[5] gives $\Delta H_{f,298}C_5H_6(l) = 25.04 \pm 0.3$ kcal/mole. Substitution of this value in reaction 6 allows the evaluation of the standard enthalpy of formation of $Mg(C_5H_5)_2(c)$, $\Delta H_f°_{298} = 16.0 \pm 0.8$ kcal/mole. Adding the heat of vaporization, 16.3 ± 0.3 kcal/mole, found from vapor pressure studies,[5] gives $\Delta H_f°_{298}Mg(C_5H_5)_2(g) = 32.3 \pm 0.9$ kcal/mole.

TABLE I

HEAT OF REACTION OF $Mg(C_5H_5)_2(c)$ WITH 120 G OF 1 *N* H_2SO_4 AT 25°

Sample wt, g	Q_{obsd}, cal	Q_{vap}, cal	$-\Delta H$, kcal/mole
0.1216	61.37	0.44	78.5
0.0848	42.59	0.43	78.3
0.1372	69.05	0.25	78.0
0.1500	74.40	0.30	76.9
0.1912	96.59	0.25	78.2
		Av	78.0 ± 0.6

For $Fe(C_5H_5)_2(c)$ low-temperature heat capacities[3] give $\Delta S_f°_{298} = -124.4$ cal/deg mole, and this value may be used with little error to calculate preliminary values of $\Delta G_{f,298}$ for the other compounds (Table II).

TABLE II

PROPERTIES OF BIS(CYCLOPENTADIENYL)METAL COMPOUNDS

	$Mg(C_5H_5)_2$	$Ni(C_5H_5)_2$	$Fe(C_5H_5)_2$	Ref
$\Delta H_f°_{298}(c)$, kcal	16.0 ± 0.8	62.8 ± 0.5	33.8 ± 1.3	1
$\Delta H_f°_{298}(g)$, kcal	32.3 ± 0.9	80.4 ± 1.0	51.4 ± 1.3	2
$\Delta H_{f,298}M(g)$, kcal	35.3 ± 0.3	81.0 ± 1	100.2 ± 0.5	15–18
$\bar{B}$, kcal	54.5 ± 12	53 ± 12	77 ± 12	Calcd
$\bar{B}_M$, kcal	78	77	106	*a*
f, mdynes/A	1.7	1.5	2.7	Calcd
f_1, mdynes/A	1.83	1.68	3.11	*b*
$\Delta G_f°_{298}(c)$, kcal	53.1 ± 2	99.9 ± 2	70.9 ± 1.5	Calcd

[a] L. Friedman, A. P. Irsa, and G. Wilkinson, *J. Am. Chem. Soc.*, **77**, 3689 (1955). [b] P. Fritz, *Advan. Organometal. Chem.*, **1**, 239 (1964).

Bond Energy.—The mean bond energy $\bar{B}$ at 298°K is defined by the equation

$$Mg(C_5H_5)_2(g) \xrightarrow[2\bar{B}]{} Mg(g) + 2C_5H_5(g) \quad (7)$$

For use in eq 7, $\Delta H_f°_{298}C_5H_5(g)$ may be evaluated from recently reported mass-spectroscopic appearance potentials.[10] For the process

$$C_5H_6(g) + e \longrightarrow C_5H_5^+(g) + H(g) + 2e \quad (8)$$

a potential of 11.9 ± 0.5 ev was found, in agreement with <12.6 ev reported by Harrison, *et al.*,[11] but differing from the early value of 10.7 ev.[12] Also, for the process

$$C_5H_5(g) + e \longrightarrow C_5H_5^+(g) + 2e \quad (9)$$

an appearance potential of 8.73 ± 0.1 ev has been reported,[11] in satisfactory agreement with the molecular orbital calculation giving 8.82 ev.[13] Combining the above processes gives

$$C_5H_6(g) \longrightarrow C_5H_5(g) + H(g) \quad (10)$$

with a heat of 3.17 ev or 73 ± 12 kcal. This is in good agreement with the dissociation of C_7H_8 to C_7H_7 + H for

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[8] G. B. Kistiakowski, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **58**, 146 (1936).

[9] G. Becker and W. A. Roth, *Chem. Ber.*, **67B**, 627 (1934).

[10] F. Dorman, *J. Chem. Phys.*, **43**, 3507 (1965).

[11] A. G. Harrison, L. R. Honnen, H. J. Dauben, and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960).

[12] J. Hissel, *Bull. Soc. Roy. Sci. Liege*, **21**, 457 (1952).

[13] A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960).

which Harrison, *et al.*,[11] found 74 kcal by a similar argument. The bond energy of the weakest C–H bond in C_5H_6 is estimated to be 98 kcal from the Bernstein correlations.[14] However, molecular orbital calculations suggest 30 kcal more resonance stabilization in C_5H_5 than in C_5H_6.[13] Thus a dissociation energy of 68 kcal is estimated, in reasonable agreement with the expermental value. Using $\Delta H_{298}(10) = 73$ kcal, $\Delta H_f{}^\circ{}_{298}H(g) = 52$ kcal/mole, and $\Delta H_f{}^\circ{}_{298}C_5H_6(g) = 31.8$ kcal/mole in reaction 10 gives $\Delta H_f{}^\circ{}_{298}C_5H_5(g) = 53 \pm 12$ kcal. This is then used in eq 7, with the heat of sublimation of magnesium, 35.3 ± 0.3 kcal/g-atom,[15-17] to obtain $\bar{B}$ $(Mg–C_5H_5) = 54.5 \pm 12$ kcal. Comparable values of $\bar{B}$ may be recalculated for $Fe(C_5H_5)_2$ and $Ni(C_5H_5)_2$ as shown in Table II. It should be noted that the heat of sublimation of nickel[16] used here is some 20 kcal/g-atom less than the previously accepted value,[17] but it[16] appears to be more reliable. The heats of sublimation of magnesium and iron[18] appear to be well established. Fischer and Grubert[19] reported $\bar{B}$ values of 93.5 kcal for both $Os(C_5H_5)_2$ and $Ru(C_5H_5)_2$, but these must be regarded as preliminary until accurate combustion and sublimation heats are available for the metals.

Discussion

The bond energies given by eq 7 may be conveniently considered as the sum of (a) the valence state promotion energy of the metal, (b) the rearrangement energy of C_5H_5 to its state in the compound, and (c) the "intrinsic" bond energy. Since there is no evidence of systematic changes in bond distance and planarity of C_5H_5, the rearrangement term may be taken as small and constant for all metal–biscyclopentadienyl compounds. The bond energies may then be qualitatively related to molecular orbital studies of the bond types involved.

For iron, nickel, ruthenium, and osmium there is thought to be π-bond formation between the p orbitals of C_5H_5 and hydridized ds orbitals of suitable symmetry on the metal.[20] Although nickel has a slightly lower promotion energy than iron the two extra electrons occupy an antibonding orbital, thus accounting for the lower observed bond energy.[20] Ruthenium has a lower promotion energy than iron[21] so that the higher observed bond energy is understandable.

For magnesium there is still disagreement on the exact type of bonding, but it has been shown[22] that the promotion energy involved is much higher than for iron, suggesting a lower bond energy as is found in the present work and a bonding system having a moderate degree of charge separation. The partial covalent nature of the bonding system is shown by the occurrence of a metal–ring stretching vibration with an absorption intensity inconsistent with a completely ionic bond.[23] For manganese, the bond may also be mainly ionic due to the stabilization of the half-filled d electron shell, giving a low bond energy similar to that of magnesium.

Where metal–ring stretching vibrations are observed, it is expected that the force constants should be closely related to the corresponding bond strengths. From frequencies assigned to the asymmetric metal–ring stretch,[23] approximate force constants, f, are obtained which show the same trend as the bond energies (Table I). Alternatively, from slightly different assignments of all three vibrations of the metal–ring system, Fritz[24] found force constants, f_1, also showing the same trend as the bond energies (Table I).

The thermochemical bond energies $\bar{B}$ may be compared with values $\bar{B}_M$ derived by Friedman, Irsa, and Wilkinson[25] from mass spectroscopic appearance potentials for the process

$$M(C_5H_5)_2(g) + e \longrightarrow M^+(g) + 2C_5H_5(g) + 2e \qquad (11)$$

As shown in Table II the $\bar{B}_M$ values are 22–29 kcal higher than the $\bar{B}$ values. This cannot be due to too low a heat of formation of C_5H_5 in calculating $\bar{B}$, since the value used is probably an upper limit. Excess kinetic energy of the product ions and their formation in excited states would both cause the $\bar{B}_M$ values to be too high. There was also difficulty in calibrating the energy scales for the appearance potentials, since the ionization efficiency curves had long tails of 3.0 ± 0.5 ev.[25] Thus the absolute values of $\bar{B}_M$ are probably too high, but they show the expected trend across the transition series. In particular, manganese has a similar low value (76 kcal) to magnesium, and cobalt has a value (96 kcal) intermediate between iron and nickel. The use of an average correction of 25 kcal to the $\bar{B}_M$ values leads to $\bar{B}$ values for vanadium, 115 kcal, chromium, 84 kcal, manganese, 51 kcal, and cobalt, 71 kcal.

Bis(cyclopentadienyl)magnesium is a useful intermediate for preparing other metal–cyclopentadienyl compounds either in the molten state[26] or in tetrahydrofuran solution.[27]

$$Mg(C_5H_5)_2 + MCl_2 \longrightarrow M(C_5H_5)_2 + MgCl_2 \qquad (12)$$

Neglecting the fusion or solution energies, which tend to cancel out, the free energy change of eq 12 may now be evaluated for the compounds in the solid state. For iron $\Delta G_{298}(12) = -51.4$ kcal/mole and for nickel $\Delta G_{298}(12) = -29.5$ kcal/mole, confirming the quantitative reactions observed. The calculation shows that although $Mg(C_5H_5)_2$ is the most stable compound with respect to the elements, the high free energy of formation of $MgCl_2$ causes the metatheses to be favorable. The use of metal fluorides, bromides, and iodides also gives large negative free energy changes for reaction 12.

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