

substitution process. With only the copper complex present, however, reasonable second-order kinetic data are obtained. The sulfonation reaction also indicates that the complex is much more reactive and that the difference in reactivity is sufficiently great to be of synthetic utility. The copper complex is the most stable complex formed with any divalent metal ion of the first row transition series. It is quite insoluble in most aqueous media including acidic ones. In the case of the sulfonation reaction, the initial attack seems to be on the insoluble complex. This results in the direct sulfonation of the ligand which solubilizes the complex.

The remaining reactions fall into the same general pattern. Acetylation appears to be extremely sluggish, but this is in accord with the fact that the Friedel-Crafts reactions of 8-hydroxyquinoline are normally rather difficult to effect¹¹; alkylations, for example, are unknown.

From the temperature variation of the rate constant for mercuration, the energy of activation and the frequency factor were calculated using the Arrhenius equation. These were found to be 19 kcal./mole and 9.6×10^{12} sec.⁻¹ ($\Delta S^* = -6.9$ e.u.), respectively, for the copper complex, and 13.6 kcal./mole and 5×10^7 sec.⁻¹ ($\Delta S^* = -25$ e.u.) for 8-hydroxyquinoline itself. The frequency factor here is considerably greater for the complex and is responsible for the greater rate in this case, in spite of a higher activation energy. The strict comparison of the free and the complexed ligand in this reaction is hindered by the temperature-dependent ionizations of the free ligand. The activation energy for the complex is fairly close to that reported for simple aromatic systems.¹² For these latter, which

(11) J. P. Phillips, *Chem. Rev.*, **56**, 284 (1956).

include benzene and toluene, the activation energies are about 21 kcal./mole and the frequency factor is close to 10^{10} . The relative order of reactivity of free 8-hydroxyquinoline and its complexes toward mercuration is the same as that found for diazo coupling¹ and bromination,¹³ *i.e.*, the protonated species is less reactive than the metal complex. The relative order of aromatic ligands toward *electrophilic* reagents supports the general order of rates given by the sequence: $L > ML > HL$. Here L can be a phenolate anion, an aromatic amine, pyridine, or any other aromatic ligand. This is also found in the nitration of α, α' -dipyridyl,¹⁴ which proceeds more readily when the α, α' -dipyridyl is complexed to iron(III), cobalt(III), or chromium(III) than when the ligand is protonated on both nitrogens.

While one would expect that the reverse order of reactivity should hold for nucleophilic substitution reactions, only scattered information is available on this point. Nucleophilic reactions of pyridine derivatives are catalyzed by protonation¹⁵ and also by the formation of a coordinate bond to oxygen (*i.e.*, by the formation of pyridine N-oxides).¹⁶ Here the order of reactivity appears to be $HL > OL > L$.

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Coordinate Bond Energies and Inner Orbital Splitting in Some Tervalent Transition Metal Acetylacetonates

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The heats of combustion of the tris acetylacetonate complexes of the transition metal ions from scandium(III) through cobalt(III) have been measured in an oxygen bomb calorimeter. The heats of sublimation of these complexes were determined using a static vapor pressure method. Using these data in a suitable thermochemical cycle, the bond energies for the heterolytic cleavage of the metal to ligand bonds were calculated. These heterolytic bond energies vary with the atomic number of the central metal ion in the fashion predicted by crystal field theory. From a knowledge of the spin states of the central ions it is possible to estimate $10Dq$ for some of these complexes from thermochemical data alone. These thermochemical $10Dq$ values are in fair agreement with those obtained by spectroscopic methods.

In previous work in this laboratory coordinate bond energies in a wide variety of complexes have been determined.¹⁻³ The present work was undertaken to de-

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(2) J. L. Wood and M. M. Jones, *J. Phys. Chem.*, **67**, 1049 (1963).

(3) D. T. Farrar and M. M. Jones, *ibid.*, **68**, 1717 (1964).

termine the variations in metal to ligand bond energies in a series of closely related complexes. The complexes of the trivalent first row transition metal ions with acetylacetonate were selected for this work. These compounds are well characterized. They are known to

TABLE I
ANALYSES OF COMPOUNDS STUDIED

| Compound | % M | |
|--|--------|-------|
| | Calcd. | Found |
| Tris-(2,4-pentanediono)scandium(III) ^a | 13.13 | 13.18 |
| Tris-(2,4-pentanediono)vanadium(III) ^b | 14.63 | 14.50 |
| Tris-(2,4-pentanediono)chromium(III) ^c | 14.89 | 14.90 |
| Tris-(2,4-pentanediono)manganese(III) ^d | 15.59 | 15.44 |
| Tris-(2,4-pentanediono)iron(III) ^e | 15.81 | 15.86 |
| Tris-(2,4-pentanediono)cobalt(III) ^f | 16.54 | 16.37 |

^a G. T. Morgan and H. W. Moss, *J. Chem. Soc.*, **105**, 189 (1914). ^b G. T. Morgan and H. W. Moss, *ibid.*, **103**, 85 (1913). ^c W. C. Fernelius and J. E. Blanch, *Inorg. Syn.*, **5**, 130 (1957). ^d R. G. Charles, *ibid.*, **7**, 183 (1963). ^e W. C. Fernelius and B. E. Bryant, *ibid.*, **5**, 105 (1957). ^f B. E. Bryant and W. C. Fernelius, *ibid.*, **5**, 188 (1957).

TABLE II
HEATS OF COMBUSTION

| Compound | Formula wt. | Oxide ^a | ΔE_{comb} , cal./g. | σ | ΔE_{comb} , kcal./mole | Δn , moles |
|---------------------------------------|-------------|---|------------------------------------|----------|---------------------------------------|--------------------|
| Tris-(2,4-pentanediono)scandium(III) | 342.30 | Sc ₂ O ₃ | -5566.7 | ±10.5 | -1905.5 | -3 |
| Tris-(2,4-pentanediono)vanadium(III) | 348.29 | V ₂ O ₅ | -5517.2 | ±21.1 | -1921.6 | -3.5 |
| Tris-(2,4-pentanediono)chromium(III) | 349.35 | Cr ₂ O ₃ | -5460.9 | ±9.7 | -1907.8 | -3 |
| Tris-(2,4-pentanediono)manganese(III) | 352.28 | MnO ₂ ·MnO 1:1 | -5420.9 | ±8.0 | -1909.7 | -3 |
| Tris-(2,4-pentanediono)iron(III) | 353.19 | Fe ₂ O ₃ + Fe ₂ O ₃ ·H ₂ O | -5293.8 | ±9.8 | -1869.7 | -3 |
| Tris-(2,4-pentanediono)cobalt(III) | 356.28 | Co ₃ O ₄ :CoO 1:1 | -5236.0 | ±12.0 | -1865.5 | -2.9 |

^a Determined from X-ray diffraction pattern of the solid combustion residues.

have an octahedral structure, they are volatile, and their vibrational and electronic spectra have been thoroughly studied. It was anticipated that study of such a closely related group of complexes would allow any stabilization of the bonds due to crystal field effects to reveal itself.⁴ The thermodynamic consequences of crystal field splitting have been thoroughly reviewed by George and McClure.⁵ While a few bond energies for some divalent metal amines⁵ and some miscellaneous bond energies for a few other complexes are available,⁶ these are insufficient to provide a satisfactory test for the occurrence of crystal field effects in bond energies.

Experimental

Apparatus and Materials.—The heats of combustion of the complex compounds were determined using a Parr oxygen bomb calorimeter and procedures similar to those described earlier.¹ In the combustions of the scandium(III), chromium(III), and cobalt(III) complexes, N.B.S. sample 39e benzoic acid was used as a combustion aid. The compounds studied were prepared by standard procedures. They were analyzed for total metal content by ignition to the metal oxide after first destroying the complex with concentrated sulfuric acid over a heat lamp. Table I gives the analytical results for the compounds studied and the method of preparation.

Several attempts were made to prepare the titanium(III) acetylacetonate by two methods.^{7,8} Both methods yielded the dark blue complex but it was almost immediately oxidized to the orange titanyl acetylacetonate complex. We were unsuccessful in our attempts to utilize the complex for combustion studies.

The vapor pressures of the compounds were determined over a range of temperatures using the isotenoscope method of Burg and

Truemper.⁹ The powdered compound was placed in a small glass vessel made by closing off one end of a 0.25-in. length of 3-mm. glass tubing. The filled vessel was then placed in the bottom of the isotenoscope by allowing it to slide down the inside of the isotenoscope walls. The reproducibility of the vapor pressures was better than that previously reported for some nickel chelates.² A calibration run with benzoic acid gave vapor pressures of 0.96 mm. at 95.8°, 1.17 mm. at 100°, 1.79 mm. at 105.3°, and 2.48 mm. at 109.7°. The literature values for these temperatures are 0.99, 1.26, 1.68, and 2.11 mm., respectively.¹⁰

Results

The heats of combustion reported represent an average of four or more runs. The reproducibility of the runs varied with the different compounds from ±21

cal./g. (standard deviation for gross heat of combustion) for the vanadium complex to ±8.0 cal./g. for the manganese complex. Table II gives the heats of combustion.

The value Δn refers to the change in the number of moles of gaseous molecules within the bomb upon combustion. Then $\Delta H_{\text{comb}} = \Delta E_{\text{comb}} + nRT$ at 298°K. was used to calculate the heats of combustion at constant pressure. These values are given in Table IV. The combustion products were taken to be carbon dioxide, water, and the metal oxide. The results of the X-ray analyses on the metal oxide residues are also given in Table II. The mixed oxide ratios for the manganese and cobalt residues represent a best estimate obtained from the relative intensities of the X-ray scattering peaks. More sophisticated methods have been employed in the past to arrive at the Co₃O₄:CoO ratios¹¹ but upon examination of the relatively small spread in the heats of oxidation calculated using varying ratios of Co₃O₄ to CoO, we felt it unnecessary to use these. For example, an error of 50% in determining the ratio of Co₃O₄ to CoO would give as one result 1 Co₃O₄ to 0.5 CoO. The heat of oxidation calculated using this ratio is -2194.16 kcal./mole. The difference between this value and -2193.0 kcal./mole calculated using the 1:1 ratio is much less than the experimental error in the heat of combustion of the compound. Similar calculations were carried out for the manganese complex with similar results. No correction was attempted in the case of the iron oxides since we had no way of knowing

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TABLE III
VAPOR PRESSURES^a

| Compound | Vapor pressure, mm. (°C.) | | |
|---------------------------------------|---------------------------|---------------|---------------|
| | I | II | III |
| Tris-(2,4-pentanediono)scandium(III) | 0.711 (114.4) | 0.677 (109.3) | 0.532 (103.6) |
| Tris-(2,4-pentanediono)vanadium(III) | 4.15 (114.6) | 2.98 (105.8) | 2.54 (101.7) |
| Tris-(2,4-pentanediono)chromium(III) | 0.254 (123.5) | 0.235 (120.1) | 0.219 (115.9) |
| Tris-(2,4-pentanediono)manganese(III) | 5.14 (117.6) | 3.73 (113.9) | 3.26 (110.3) |
| Tris-(2,4-pentanediono)iron(III) | 2.09 (114.6) | 1.71 (109.8) | 1.30 (104.8) |
| Tris-(2,4-pentanediono)cobalt(III) | 1.56 (119.6) | 0.913 (110.6) | 0.631 (105.0) |

^a The temperature of measurement is given in parentheses.

TABLE IV
THERMOCHEMICAL PROPERTIES OF SOME TERVALENT ACETYLACETONATES

| Metal | ΔH_{sub}^a Metal | $\sum_{i=1}^3 I_i^b$ Metal | $\Delta H_{\text{sub}} \pm \sigma$ Complex | $\Delta H_{\text{comb}} \pm \sigma$ Complex | ΔH_{ox} Complex | ΔH_f Complex | $\Delta H(\text{M:L}) \pm \sigma$ Homolytic | Total heterolytic bonding energy $\pm \sigma$ |
|-----------|------------------------------------|-------------------------------|---|--|-----------------------------------|-------------------------|--|---|
| | | | | | | | | |
| Scandium | 82 | 1019.0 | 11.9 ± 0.6 | -1907.3 ± 3.6 | -2331.8 | -424.5 | 66.6 ± 0.6 | -1320.6 ± 3.9 |
| Titanium | 112.6 | 1120.4 | | | | | | |
| Vanadium | 122.8 | 1167.5 | 10.6 ± 0.6 | -1923.8 ± 7.3 | -2317.8 | -394.1 | 67.0 ± 1.2 | -1471.5 ± 7.5 |
| Chromium | 95.0 | 1249.6 | 6.64 ± 0.7 | -1909.6 ± 3.4 | -2263.2 | -353.8 | 56.3 ± 0.6 | -1489.5 ± 3.8 |
| Manganese | 66.73 | 1308.6 | 18.6 ± 0.2 | -1911.5 ± 2.8 | -2236.4 | -325.0 | 44.8 ± 0.5 | -1479.4 ± 3.1 |
| Iron | 99.83 | 1261.5 | 15.6 ± 0.4 | -1871.5 ± 3.5 | -2226.9 | -355.1 | 55.9 ± 0.6 | -1498.9 ± 3.8 |
| Cobalt | 101.6 | 1346.4 | 17.9 ± 1.1 | -1867.0 ± 4.3 | -2193.0 | -326.1 | 50.9 ± 0.7 | -1553.9 ± 4.7 |

^a D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," Advances in Chemistry Series, No. 18, American Chemical Society, Washington, D. C., 1956. ^b National Bureau of Standards, Circular 467, "Atomic Energy Levels," U. S. Government Printing Office, Washington, D. C., 1952.

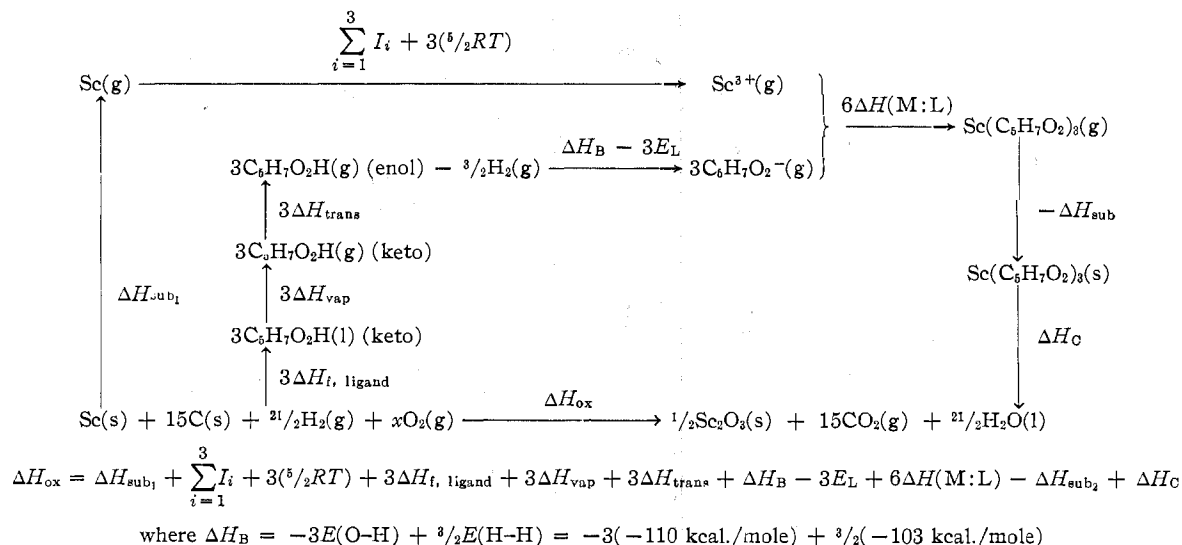


Fig. 1.—Thermochemical cycle for the empirical evaluation of heterolytic bonding energies in tris-(2,4-pentanediono)scandium(III).

the conditions under which the hydrated oxide was formed.

The heats of sublimation of the compounds studied were obtained from an average of three plots of $\log P$ vs. $1/T$. Table III contains a representative set of vapor pressure measurements used to obtain ΔH_{sub} . The ΔH_{sub} values are given in Table IV.

Discussion

With experimental values for the heat of combustion and heat of sublimation available, we may calculate the coordinate bond energies using the type of thermochemical cycle given earlier.¹⁻³ These bond energies, however, are for a homolytic cleavage of the metal-to-ligand bond, *i.e.*, $\text{M:L} \rightarrow \text{M}\cdot + \text{L}\cdot$. Most of the

thermodynamic properties used thus far to demonstrate the crystal field stabilization have depended upon a separation of charge or heterolytic type bond cleavage, *i.e.*, $\text{M:L} \rightarrow \text{M}^+ + \text{:L}^-$. The two types of bond energies are related to each other in the following way

$$6\Delta H(\text{M:L})_{\text{homo}} = 6\Delta H(\text{M:L})_{\text{hetero}} +$$

$$\sum_{i=1}^3 I_i + 3(^{5/2}RT) = 3E_L$$

where $\sum_{i=1}^3 I_i$ is the ionization potential summation and E_L is the electron affinity of the ligand. In order to calculate the heterolytic metal-to-ligand bonding energies in these acetylacetonates, a thermochemical cycle

TABLE V
 STABILIZATION ENERGIES AND THERMOCHEMICAL $10Dq$ VALUES (KCAL./MOLE)

| Compound | $-\delta H$ | n_t | n_e | Dq | $10Dq$ | Spect. $10Dq^b$ |
|---------------------------------------|-------------|----------------|-------|------|--------|--------------------|
| Tris-(2,4-pentanediono)scandium(III) | ... | 0 | 0 | ... | ... | ... |
| Tris-(2,4-pentanediono)titanium(III) | (97) | 1 | 0 | (26) | (270) | 40.0 |
| Tris-(2,4-pentanediono)vanadium(III) | 80 | 2 | 0 | 10.0 | 100 | 51.5 |
| Tris-(2,4-pentanediono)chromium(III) | 62.5 | 3 | 0 | 5.21 | 52.1 | 51.8 |
| Tris-(2,4-pentanediono)manganese(III) | 15.5 | 3 | 1 | 2.58 | 25.8 | 48.6 |
| Tris-(2,4-pentanediono)iron(III) | ... | 3 | 2 | ... | ... | 46.9 |
| Tris-(2,4-pentanediono)cobalt(III) | 20 | 6 ^a | 0 | 8.33 | 83.3 | 60.1 |

^a Pairing energy = 60 kcal.: F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p. 569. ^b T. S. Piper and R. L. Carlin, *Inorg. Chem.*, **2**, 260 (1963).

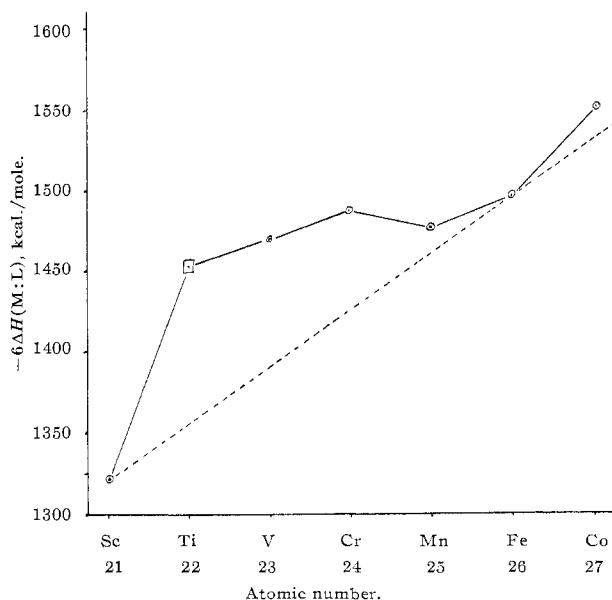


Fig. 2.—Bonding energies of some first transition series acetylacetonates.

such as the one shown in Fig. 1 was used. The only parameter that must be estimated here is E_L , the electron affinity of the ligand. In these calculations, it was estimated to be the same as that of oxygen, 34 kcal./mole. Any variation between this estimated value and the true value is a constant applied equally to every calculation. The term $3(\frac{5}{2}RT)$ is used to correct the ionization potentials to 298°K.⁵ In the calculation of the bonding energies, the heat of formation of the acetylacetonate ligand was taken to be -100.95 kcal./mole,¹² its heat of vaporization was 16.5 kcal./mole,⁸ and the heat of transition from keto to enol form was taken to be -3.9 kcal./mole.¹³ Table IV gives the calculated thermochemical properties of the metal acetylacetonates studied along with the experimentally derived quantities used to obtain them. The total bonding energies were calculated directly from the data given in the tables. The heats of oxidation of the complexes were calculated using the standard heats of formation of water and carbon dioxide¹⁴ and the stand-

ard heats of formation of the metal oxide.¹⁵ The heats of formation of the complexes were calculated from the heat of oxidation and the heat of combustion in the normal manner. The seventh column contains the homolytic coordinate bond energies calculated according to methods given in previous papers.¹⁻³ The standard deviations reported for the total heterolytic bonding energy were calculated by methods given by Rossini.¹⁶

An estimation of the heat of combustion of the Ti(III) compound was made. On the basis of the values given in Table II, a value of ΔH_{comb} of about -1920 ± 100 kcal./mole would be reasonable. The heat of oxidation would be -2355 kcal./mole assuming TiO_2 was formed upon combustion. A white oxide was found after some preliminary combustions of a wet Ti(III) acetylacetonate paste covered with wax. Using these values and estimating a heat of sublimation of about 12 kcal./mole, we can calculate the total bonding energy to be -1454 kcal./mole.

When a plot of these heterolytic total bonding energies is made against atomic number of the metal ion, a curve such as the one shown in Fig. 2 is obtained. The dotted line in Fig. 2 was used as a basis of determining the net stabilization brought about by the splitting of the d electron orbitals. Using the notation of George and McClure,⁵ we will call this stabilization $-\delta H$ and relate this to the splitting parameter Dq by the equation

$$-\delta H = -(4n_t - 6n_e)Dq$$

Table V gives the results of these calculations; the values of $-\delta H$ were obtained graphically.

When it is considered that the $10Dq$ values listed in the last two columns of Table V were obtained by completely independent methods, the agreement is very heartening. Only in the case of vanadium(III) is the difference extremely large.

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