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Thermochemistry of Inner Complex Salts: Some Heats of Combustion and Bond Energies

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The heats of combustion of eleven inner complex salts have been measured with a bomb calorimeter. By using a thermochemical cycle in which all the terms but one are experimentally accessible, values of the coordinate bond energies in these complexes may be calculated. For acetylacetonates of the type $M(C_5H_7O_2)_3$, where M is Cr, Fe, and Co, the heats evolved on formation of the complexes in the gas phase from ligand and metal atom show a minimum at Fe as expected from crystal field effects.

At present very little is known about the thermochemistry of inner complex salts. In the most extensive collection of thermochemical data on solid complexes which has yet appeared,¹ there are no such data on any member of this important class of compounds. The present study was undertaken for two purposes. The first was to provide typical data on heats of formation of some representative inner complex salts. The second was to determine whether a completely empirical route to coordinate bond energies involving these compounds could be exploited. This *direct empirical route to coordinate bond energies* is possible with inner complex compounds because a complete thermochemical cycle involving their formation from gaseous metal atoms and gaseous ligand molecules can be set up in such a manner that it involves only measurable heats in addition to the formation reaction. It should be recalled that such a cycle is not possible with typical complex salts because of the impossibility of measuring the lattice energy directly.

The compounds examined in this study were the acetylacetonates of Fe(III), Cr(III), Co(III), Th(IV), Cu(II), Mg(II), VO^{2+} , and UO_2^{2+} and three complexes of Cu(II) with amino acids. In the oxygen bomb calorimeter these burn to carbon dioxide, water, nitrogen, and some species derived from the metal.

Experimental

Apparatus and Materials.—The heats of combustion were measured in a Parr Adiabatic Calorimeter, Series 1200. The instrument was calibrated before the measurements were begun, at intervals during the course of the work, and at the conclusion of the work. The calibration

was effected by the combustion of pure samples of benzoic acid. Our values for the heat capacity of the calorimeter ranged from 2463 to 2472 cal. per deg. The bomb used in this work, a Parr Model 1104, was designed for use under more severe conditions than those ordinarily employed (e.g., for explosive samples) and this allowed the use of initial oxygen pressures of 40 atm. or more to ensure complete combustion. A correction for the formation of nitric acid in the combustion was made using a standardized procedure.² In those cases where a finely divided sample was used it was necessary to pelletize the material to slow down the rate of combustion to a safe value for the bomb. Very finely divided samples were found to undergo a mild "explosion" as indicated by the jarring of the calorimeter unless this pelletizing was done. The compounds used in this study were all well known chelates. These were prepared and purified by standard methods except for the acetylacetonates of Cu(II), Mg(II), VO^{2+} , Cr(III), and Fe(III), which were obtained from the MacKenzie Chemical Works, Central Islip, N. Y. The uranyl complex was obtained from aqueous solution as the monohydrate³; this was thoroughly dehydrated to obtain the anhydrous complex for the combustion experiments. Carbon and hydrogen analyses were made and the following results were obtained: Calcd. for $Cr(C_5H_7O_2)_3$: C, 51.59; H, 6.08. Found: C, 51.32; H, 6.08. Calcd. for $Co(C_5H_7O_2)_3$: C, 50.59; H, 5.94. Found: C, 50.51; H, 5.41. Calcd. for $Fe(C_5H_7O_2)_3$: C, 51.03; H, 6.00. Found: C, 50.68; H, 6.10. Calcd. for $VO(C_5H_7O_2)_2$: C, 45.30; H, 5.32. Found: C, 45.30; H, 5.09. Calcd. for $Cu(C_5H_7O_2)_2$: C, 45.89; H, 5.40. Found: C, 45.45; H, 5.34. Calcd. for $UO_2(C_5H_7O_2)_2$: C, 25.66; H, 3.01. Found: C, 25.73; H, 3.10. Calcd. for $Mg(C_5H_7O_2)_2$: C, 53.97; H, 6.34. Found: C, 52.01; H, 6.44. Calcd. for $Cu(C_2H_4NO_2)_2$: C, 22.70; H, 3.81. Found: C, 22.34; H, 3.58. Calcd. for $Cu(C_3H_7NO_2)_2$: C, 30.06; H, 5.05. Found: C, 29.40; H, 5.48. Calcd. for $Cu(C_5H_{10}NO_2)_2$: C, 40.60; H, 6.78. Found: C, 40.12; H, 6.39.

Each of the heats of combustion reported is the average of three or more runs. The reproducibility of the meas-

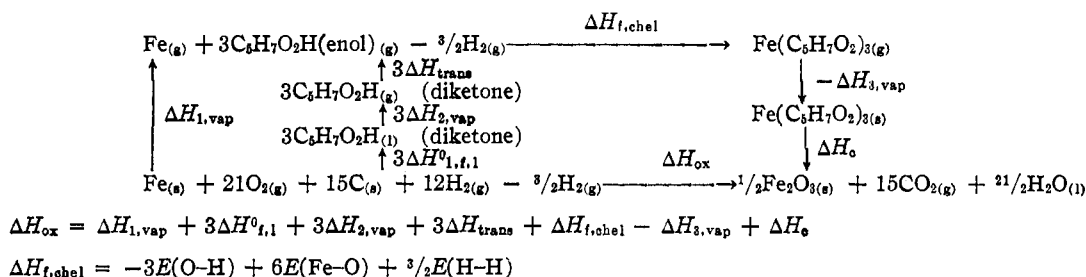
(1) K. B. Jazimirsky, "Thermochemie von Komplexverbindungen," Akademie-Verlag, Berlin, 1956.

(2) "Oxygen Bomb Calorimetry and Combustion Method," Parr Instrument Co., Moline, Illinois, 1960, p. 22.

(3) W. Biltz and J. Clinch, *Z. anorg. u. allgem. Chem.*, **40**, 218 (1904).

TABLE I
 HEATS OF COMBUSTION OF SOME INNER COMPLEX SALTS

Compound	Formula weight	ΔE		Δn Moles	ΔH Combustion kcal./mole
		Combustion cal./g.	Combustion kcal./mole		
Fe(C ₅ H ₇ O ₂) ₃	353.04	-5308	-1874	-3	-1876
Cr(C ₅ H ₇ O ₂) ₃	349.20	-5393	-1883	-3	-1885
Co(C ₅ H ₇ O ₂) ₃	356.13	-5134	-1828	-3	-1830
Th(C ₅ H ₇ O ₂) ₄	628.54	-3996	-2512	-4	-2514
Cu(C ₅ H ₇ O ₂) ₂	261.75	-4851	-1269	-1.92	-1270
Mg(C ₅ H ₇ O ₂) ₂	222.53	-5600	-1246	-2	-1247
VO(C ₅ H ₇ O ₂) ₂	265.16	-4808	-1275	-1.75	-1276
UO ₂ (C ₅ H ₇ O ₂) ₂	468.18	-2688	-1258	-2.83	-1260
Cu(glycinate) ₂	211.66	-2113	-447.2	0.75	-446.8
Cu(alaninate) ₂	239.72	-2929	-702.1	-0.25	-702.3
Cu(valinate) ₂	295.81	-4542	-1344	-2.25	-1345


 Fig. 1.—Thermochemical cycle for the empirical evaluation of coördinate bond energies in Fe(C₅H₇O₂)₃.

ured heats of combustion is of the order of $\pm 0.4\%$. The principal factors responsible for this limit are (1) the use of mercury thermometers which did not allow temperature changes to be estimated closer than 0.001° and (2) the purity of the materials which were used. The analytical methods available for these compounds allow a lower limit of only $\pm 0.1\%$ to be attained in customary analyses for some of the constituents. Unlike many of the compounds which have been studied by more sophisticated calorimetric methods, there are no established criteria for determining the absolute purity of the sample used. Since the primary aim of this study was to obtain coördinate bond energies to within a few kilocalories it was felt that the ultimate in precision calorimetry was not essential to the conduct of this investigation, however desirable it might be. The combustion products were taken as CO₂, H₂O, N₂, and the following metal oxides which were identified as products: Fe₂O₃, Cr₂O₃, Co₃O₄, ThO₂, MgO, V₂O₅, and U₃O₈. Considerable difficulty was experienced in effecting complete combustion of the copper chelates and amino acid complexes. An X-ray powder pattern of the solid residue from the combustion of Cu(C₅H₇O₂)₂ showed it to be CuO. The products of the combustion of the glycine and alanine complexes were found in the same manner to be a mixture of Cu₂O and CuO in the ratio of 1:2 and this composition was used in the calculations for these materials. The valinate complex yielded small balls of metallic copper on combustion. Attempts to oxidize these products further by the use of initial oxygen pressures of up to 44 atm. were unsuccessful. Higher pressures were not used for safety reasons. The heat of vaporization of acetylacetone was determined by measuring its vapor pressure over a range of temperatures using the Ramsay-Young

method.⁴ The vapor pressure measurements resulted in the following data: at 48° , $p = 15.2$ mm.; 88° , $p = 130.2$ mm.; 118° , $p = 327.8$ mm.; 124° , $p = 443.8$ mm.; 130° , $p = 545.8$ mm.; 139° , $p = 725$ mm. From these, the heat of vaporization of acetylacetone is estimated to be 11.5 kcal./mole from a plot of $\log p$ vs. $1/T$.

Results and Discussion

The heats of combustion obtained are listed in Table I. In order to obtain bond energies from such data a suitable thermochemical cycle must be used. The cycle used for ferric acetylacetonate is shown in Figure 1. This compound is used as an example because experimental values for the enthalpy changes associated with each step but one are available. This step involves the formation of the chelate in the gas phase and can be obtained from the other steps. This information is summarized in the first line of Table II. The coördinate bond energy for the iron(III) to oxygen bond has an average value of 59.4 kcal. for this compound. The subsequent lines of Table II contain comparable data for the other compounds studied here. The coördinate bond energies for the chromium(III) to oxygen and the cobalt(III) to oxygen bonds were evaluated using the assump-

(4) F. Daniels, J. H. Mathews, and J. W. Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co. Inc., New York, N. Y., 1941, pp. 20-23.

TABLE II
THERMOCHEMICAL VALUES USED IN CALCULATIONS AND THEIR SOURCES (KCAL./MOLE OR KCAL.)

Complex	ΔH_{ox}^a	ΔH_1 vap	$\Delta H_{i,1}^b$	ΔH_{trans}	ΔH_2 vap	ΔH_3 vap	ΔH_{hel}^d	Bond energy
Fe(C ₅ H ₇ O ₂) ₃	-2225.1	96.68 ^a	-100.95 ^b	2.61 ^c	11.5 ^d	-4.67 ^e	-180.60	(Fe-O) = 59.4
Cr(C ₅ H ₇ O ₂) ₃	-2261.7 ^a	80.5 ^a	-100.95 ^b	2.61 ^c	11.5 ^d	-4.67 ^f	-192.02	(Cr-O) = 61.3
Co(C ₅ H ₇ O ₂) ₃	-2196.9	105 ^a	-100.95 ^b	2.61 ^c	11.5 ^d	-4.67 ^f	-206.67	(Co-O) = 63.7
Ti(C ₅ H ₇ O ₂) ₄	-3127.8 ^a	136.6 ^g	-100.95 ^b	2.61 ^c	11.5 ^d	-20 ^h	-383.06	(Ti-O) = 77.1
Cu(C ₅ H ₇ O ₂) ₂	-1455.0 ^a	81.52 ^a	-100.95 ^b	2.61 ^c	11.5 ^d	-15 ⁱ	-77.85	(Cu-O) = 48.7
Mg(C ₅ H ₇ O ₂) ₂	-1561.8	35.9 ^a	-100.95 ^b	2.61 ^c	11.5 ^d	-15 ⁱ	-161.8	(Mg-O) = 69.7
VO(C ₅ H ₇ O ₂) ₂	-1604.4	52 ^j	-100.95 ^b	2.61 ^c	11.5 ^d	-15 ⁱ	-191.7	(VO-O) = 77.2
UO ₂ (C ₅ H ₇ O ₂) ₂	-1717.2	-121.2 ^k	-100.95 ^b	2.61 ^c	11.5 ^d	-15 ⁱ	-147.36	(UO ₂ -O) = 66.1
Cu(glycinate) ₂	-632.57	81.52 ^a	-126.69 ^l	0.0	20 ^m	-20 ⁿ	-34.0	(Cu-N) = 26.8 ^o
Cu(alaninate) ₂	-957.24	81.52 ^a	-135.26 ^l	.0	20 ^m	-20 ⁿ	-85.9	(Cu-N) = 52.8 ^o
Cu(valinate) ₂	-1622.9	81.52 ^a	-144.79 ^m	.0	20 ^m	-20 ⁿ	-89.8	(Cu-N) = 54.7 ^o

^a Circular 500, U. S. Bureau of Standards, Washington, D. C. ^b G. R. Nicholson, *J. Chem. Soc.*, 2431 (1957) and (a). ^c B. Jakuszewski and M. Lazniewski, *Bull. Acad. Polon. Sci., Ser. Sci., Chim., Geol. et Geograph.*, 7, 177 (1959); *Chem. Abstr.*, 54, 16161. ^d This paper. ^e E. W. Burg and J. W. Truempfer, *J. Phys. Chem.*, 64, 487 (1960) and J. W. Truempfer, Thesis, Louisiana State University, Baton Rouge, 1959, Mic 59-5529, University Microfilms, Ann Arbor, Mich. ^f Estimated to be the same as that for Fe(C₅H₇O₂)₃. ^g A. J. Darnell, W. A. McCollum, and T. A. Milne, *J. Phys. Chem.*, 64, 341 (1960). ^h Estimated. ⁱ Estimated on the basis of values for analogous complexes given in (e). ^j This is the value for the heat of formation of gaseous VO from (a). ^k This is the sum of the heat of formation and heat of vaporization of UO₂ from (a). ^l H. M. Huffman, S. W. Fox, and E. L. Ellis, *J. Am. Chem. Soc.*, 59, 2199 (1937). ^m Calculated from data of E. Werde, *Z. Physik. Chem.*, 75, 81 (1910) and (a). ⁿ Estimated from data on analogous organic compounds. ^o Some difficulty was encountered in obtaining consistent ΔH_2 values and products for these complexes resulting in a range of values for the (Cu-N) bond energy.

tion that the heats of vaporization of these complexes were the same as that for ferric acetylacetonate. This assumption is based upon the very similar molecular volumes and stereochemistry of these three compounds. The bond energies for the remaining acetylacetonates were evaluated using the assumption that their heats of sublimation amounted to 15 kcal./mole with the exception of thorium acetylacetonate, which was taken as 20 kcal./mole. It is probable that the less symmetrical structure or greater molecular weights of these compounds will result in values close to these estimates. The heats of vaporization of the amino acids all were taken as 20 kcal./mole, an estimate based upon the heats of vaporization of some analogous organic compounds. The values and sources of the other terms used in the thermochemical cycles are listed in Table II. A generalized thermochemical cycle of the type used with the amino acid complexes of copper(II) is presented in Figure 2. The coordinate bond energies derived from these are collected and listed in the last column of Table II. The Cu-N bond energies were calculated from the data on the amino acids using the Cu-O bond energy obtained with the acetylacetonate. In the calculations the O-H bond energy was taken as 110 kcal./mole and the H-H bond energy as 103 kcal./mole.

It must be emphasized that from what little is known about coordinate bond energies, they may be expected to be very strongly dependent upon the nature of the central species. It also should be recalled that crystal field effects should show up most obviously in the ΔH_{hel} term where the ferric acetylacetonate is expected and found to have a lower value than either the Cr(III) or the Co(III) acetylacetonates.⁵

It is obvious that an attempt to set up a table of coordinate bond energies will result in a useful compilation only if the central atom and its ($n - 1$) neighbors prior to coordination are specified. The coordinate bond energy of the n th bond then probably will be reasonably constant for a given type of donor atom aside from steric factors.⁶

When charged ligands interact with ions the bond energies are large, as can be seen from the values collected by Basolo and Pearson. The values of the coordinate bond energies in such

(5) P. George and D. S. McClure, *Progr. in Inorg. Chem.*, 1, 416 (1959).

(6) Work up to 1954 is collected by H. C. Brown, D. M. McDaniel, and O. Hafiger in "Determination of Organic Structures by Physical Methods," ed. by E. A. Braude and F. C. Nachod, Academic Press, Inc., New York, N. Y., 1955, Chapter 14.

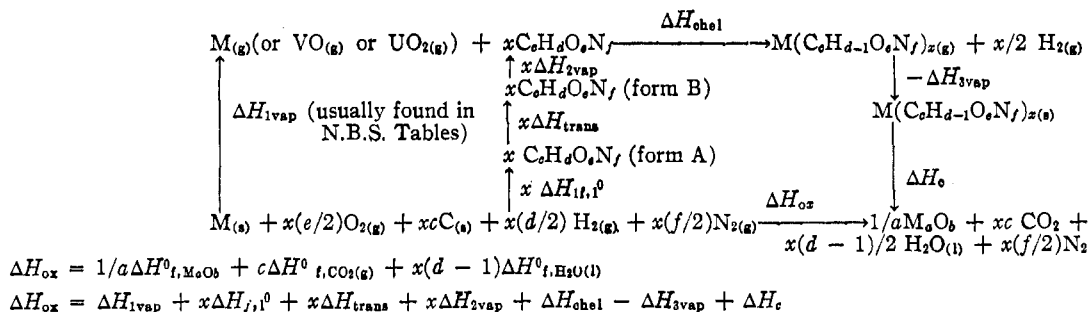


Fig. 2.—Generalized thermochemical cycle.

cases⁷ (calculated) go up to over 400 kcal., but average nearer 100 kcal. It is possible to evaluate coördinate bond energies in volatile carbonyls from their heats of combustion.⁸ From such data coördinate bond energies are found to be E (Fe-C) = 28.7 kcal.; E (Ni-C) = 35.2 kcal.; E (Cr-C) = 29.9 kcal.; E (Mo-C) = 38.7 kcal.; and E (W-C) = 45.1 kcal. It also is possible to determine the Fe-halogen bond energies in the iron carbonyl halides using the Fe-C bond energy obtained here and data of Hieber and Woerner.⁹ These are: Fe-Cl = 37.3 kcal.; Fe-Br = 31.5 kcal.; and Fe-I = 22.9 kcal. The values are for the bonds in $(CO)_4Fe-X_2$ and probably are much smaller than the corresponding values for Fe^{2+} or Fe^{3+} in ionic complexes.

For coördinate bonds in complexes which form ionic lattices, cycles similar to the Born-Haber cycle may be used to estimate coördinate bond energies.^{5,10} These require, however, that the lattice energy be calculated using some suitable model.

It is still too early to answer some very impor-

tant questions on coördinate bond energies. These include the following: (1) How closely must one specify the central atom-donor atom combination to approximate to a constant bond energy (e.g., how many different kinds of copper-nitrogen coördinate bonds must be considered)? (2) How do coördinate bond energies vary when pi bonding contributions vary? (3) Are there relations between internuclear distances and coördinate bond energies such as have been found for covalent bonds?¹¹ It seems reasonable to hope that when enough data become available, it will be possible to devise a system for predicting the energies of formation of inner complex salts by a scheme similar to one of those used for organic compounds.¹² It must be recognized that the number of types of coördinate bond energy for each central atom or ion may be almost as great as the number of types of covalent bonds (energy-wise) found for carbon.

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(7) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1958, pp. 50, 62-72.

(8) F. A. Cotton, A. K. Fisher, and G. K. Wilkinson, *J. Am. Chem. Soc.*, **78**, 5168 (1956); **79**, 2044 (1957); F. A. Cotton and R. R. Monchamp, *J. Chem. Soc.*, 533, 1438 (1960).

(9) W. Hieber and A. Woerner, *Z. Elektrochem.*, **40**, 287 (1934).

(10) W. Biltz and H. G. Grimm, *Z. anorg. u. allgem. Chem.*, **145**, 63 (1925); W. Hieber and E. Levy, *Z. Elektrochem.*, **39**, 26 (1933); **40**, 291, 608 (1934); K. B. Yatsimirskii and L. L. Pankhova, *Zhur. Obshchei Khim.*, **19**, 617 (1949); *Chem. Abstr.*, **43**, 7805; F. A. Cotton, *Acta Chem. Scand.*, **10**, 1520 (1956); D. H. Busch, *J. Chem. Educ.*, **33**, 376, 498 (1956); H. Yamatera, *J. Inorg. & Nuclear Chem.*, **15**, 50 (1960).

(11) M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4125 (1953); F. A. Cotton and J. R. Leto, *J. Chem. Phys.*, **30**, 993 (1959).

(12) I. Klotz, "Chemical Thermodynamics," Prentice-Hall, Inc., New York, N. Y., 1950, pp. 53-57; M. W. Wolkenstein, "Struktur und Physikalische Eigenschaften Der Moleküle," B. G. Teubner Verlags., Leipzig, 1960, Ch. V. A table of bond energies for transition metal halides has been published by T. L. Allen, *J. Chem. Phys.*, **26**, 1644 (1957).