Thermochemistry of Bis(tropolonato)copper(II)

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The standard enthalpy of formation of crystalline bis(tropolonato)copper(II) has been determined at 298.15 K by solution calorimetry: $\Delta H_f^\circ[\mathrm{Cu(trop)_2}]$ (c) $= -102.47\pm0.42$ kcal mol^{-1}. Enthalpy changes at 298.15 K for the following hypothetical gaseous reactions have been subsequently derived:

$$\mathrm{Cu(g)} + 2\,\mathrm{trop^{\cdot}(g)} = [\mathrm{Cu(trop)_2}](\mathrm{c}) \qquad \Delta H = -150.4 \pm 14.1 \text{ kcal mol}^{-1}$$

$$\mathrm{Cu^{2+}(g)} + 2\,\mathrm{trop^{-}(g)} = [\mathrm{Cu(trop)_2}](\mathrm{c}) \qquad \Delta H = -731.4 \pm 11.4 \text{ kcal mol}^{-1}$$

The corresponding homolytic (E) and heterolytic(E') copper(II)-oxygen bond energy parameters were calculated as

$$E_{\mathrm{Cu-O}} = 38 \pm 4 \text{ kcal mol}^{-1} \text{ and } E'_{\mathrm{Cu-O}} = 183 \pm 3 \text{ kcal mol}^{-1}$$

respectively.

The emphasis on the study of metal-complex compounds has been largely on questions of stereochemistry and reactivity, but much work has also been done on the stability of particular species in aqueous solutions. In marked contrast, however, direct information on the strength of metal-ligand bonds is scarce. The determination of the heat of formation of a coordination compound is not particulary difficult, but, using this result to calculate the metal-ligand bond strength, often needs auxiliary data which are inaccurate, and difficult, or even impossidle to determine at the present stage of the development of chemical knowledge.

In this paper we report the heat of formation of the copper(II) complex of tropolone and consider the problem of deriving the copper(II)-oxygen bond energies from it. Tropolone** forms complexes with metal ions analogous to β-diketones.[1] Many of the metal-tropolonates are crystalline, non-ionic solids, and volatile enough to sublime under reduced pressure. Stability constant studies[2] and the general behaviour of the tropolonates suggest that they are more stable than the corresponding acetylacetonates. Both complexes decompose into the metal cation and the protonated ligand in the presence of acid. We make use of this reaction to determine the enthalpy of formation of the crystalline complex bis(tropolonato) copper(II) and the corresponding Cu–O bond energies.

Experimental

The Solution Calorimeter. The LKB 8700 reaction and solution precision calorimeter was used for all the reactions. This particular calorimeter has an 18 carat gold stirrer plated with pure gold, which was not attacked by acids, and a calibrating resistance (R_h) of 50.183 Ω measured at the leads midway between the calorimeter and its jacket; thermistor resistance at 25 °C is 2000 Ω.

The molar enthalpy of reaction was calculated from the relation $\Delta H = \varepsilon\Delta R_r/nR_{mr}$, where $\Delta R_r = R_i - R_f$, $R_{mr} = (R_i + R_f)/2$, n=number of moles of reactant, and R_i and R_f are the initial and final thermistor resistances in ohms as determined by the Dickinson treatment.[3] The energy constant, ε, of the calorimetric system is given by $\varepsilon = Q_c R_{mc}/\Delta R_c$, where Q_c is an accurately defined quantity of heat supplied electrically *via* the built-in heater, $Q_c = R_h I^2 t/4.1840$ cal (R_h is the resistance of the calibrating heater in ohms, I the calibration current in amps, and t the heating time in seconds), and R_{mc} and ΔR_c have the same significance in a calibration experiment as R_{mr} and ΔR_r have in a reaction. The ratio $\Delta R_r/R_{mr}$ is directly proportional to the temperature change.

Thermochemical functions are expressed in terms of "the thermochemical calorie" (1 thermochemical calorie=4.184 J) and refer to the isothermal process at 298.15 K and the true mass, calculated with the atomic weights of 1966 based on the isotope ^{12}C. The uncertainty interval is twice the standard deviation of the mean. A check on the accuracy of the colorimeter was carried out by determining the heat of dissolution of N,N',N''-tris(hydroxymethyl)methane triamine (tham) in dilute hydrochloric acid. The result, -7.118 ± 0.006 kcal mol^{-1} is in agreement with previous results[4] (-7.120 ± 0.007 kcal mol^{-1}).

Materials. *Tropolone*, Htrop, was prepared by a modification of the method of Stevens *et al.*,[5] recrystallised from light petroleum (40—60 °C), sublimed, and recrystallised again from light petroleum, mp=51—52 °C (lit, 50—51 °C).

Found: C, 68.7; H, 4.95%. Calcd for $C_7H_6O_2$: C, 68.8; H, 4.95%.

Bis(tropolonato)copper(II). [Cu(trop)$_2$]—A solution of "AnalaR" copper(II) sulfate pentahydrate (2.0 g) in water (30 cm^3) was slowly added to a solution of tropolone (2.5 g) in ethanol (100 cm^3). The complex was filtered off, washed with cold ethanol, dried and recrystallised from benzene. Mp=298 °C (dec) (lit, 300 °C[6]).

Found: C, 54.93; H, 3.30; Cu, 20.78%. Calcd for $C_{14}H_{10}O_4Cu$: C, 54.99; H, 3.30; Cu, 20.78%.

Copper(II) Sulfate Pentahydrate: "AnalaR" grade copper(II) sulfate pentahydrate was powdered and dried in a desiccator, over sillica gel, for 48 h. Its composition was determined by means of copper analyses and was found to be $CuSO_4\cdot5H_2O$.

Sulfuric Acid. Concentrated "AnalaR" grade sulfuric acid was diluted with distilled water, and its concentration was determined by acid-base titration against $Na_2B_4O_7\cdot10H_2O$, after convenient dilution, and found to be 2.1567 ± 0.0003 M$\langle\rangle H_2SO_4\cdot23.69\,H_2O$.[7]

Calorimetric Solvent. A molar solution of "AnalaR" grade sulfuric acid was made up, by using a "B. D. H." concentrated volumetric solution. The concentration of the prepared solution was checked by acid-base titration against $Na_2B_4O_7\cdot10H_2O$. A series of six determinations gave the

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** Tropolone(Htrop) = 2-hydroxy-2,4,6-cycloheptatrien-1-one.

result 1.0000±0.0005 M, which corresponds to the composition $H_2SO_4\cdot 53.5391H_2O$.[7)]

Analyses. All carbon and hydrogen analyses were carried out in the Microanalytical Service, University of Surrey; copper was analysed by a complexometric titration with ethylenediaminetetraacetic acid (H_4edta) and Pyrocatechol Violet as indicator.[8)] Since bis(tropolonato)copper(II) is insoluble in water, it was necessary to decompose the complex by treating samples with successive small amounts of concentrated nitric acid, followed by gentle evaporation to dryness. The residures were dissolved in the minimum possible amount of 1 M sulfuric acid, transferred to volumetric flasks and diluted with distilled water.

Calculation. The standard enthalpy of formation of the bis(tropolonato)copper(II) complex can be determined from known standard enthalpies of formation and the enthalpy change for the reaction:

$$\mathrm{2Htrop(c)} + \mathrm{CuSO_4\cdot 5H_2O} \xrightarrow{\Delta H_R} \mathrm{H_2SO_4\cdot 5H_2O(aq)} + \mathrm{[Cu(trop)_2](c)} \qquad (1)$$

The difference between the enthalpies of solution of the products and reactants in the same stoichiometric ratio gives the required enthalpy of formation, provided equilibrium is reached from either side within the period of the experiment.

To 100.0 cm³ of calorimetric solvent, ampoules of bis(tropolonato)copper(II) were added consecutively, and ΔH_2 was measured. To a second portion of the same solvent (100.0 cm³) were added consecutively ampoules of tropolone and copper(II) sulfate pentahydrate, and ΔH_4 and ΔH_5 were measured. The thermochemical cycle and the general procedure used are given in the following scheme. The values of ΔH_1 and ΔH_3 were calculated from literature data,[9)] and they were found to be $\Delta H_1 = +0.001 \pm 0.001$ kcal mol⁻¹ and $\Delta H_3 = 0.000 \pm 0.001$ kcal mol⁻¹. In order to maintain the necessary stoichiometry of the reaction, the appropriate amounts of sulfuric acid and water were added to the calorimetric solvents by means of a calibrated microsyringe.

$$\begin{tikzcd}[column sep=small]
\mathrm{CuSO_4\cdot 5.00\,H_2O(c)} \arrow[d, "\Delta H_5"] & + & \mathrm{2Htrop(c)} \arrow[d, "\Delta H_4"] & + & \mathrm{18.69\,H_2O}(l) \arrow[d, "\Delta H_3"] \arrow[r, "\Delta H_R"] & {} \\
\mathrm{Calorimetric\ solvent} & & \mathrm{(H_2SO_4\cdot 53.5391\ H_2O)} & & {} & \\
& & \mathrm{Solution\ A_3} & & &
\end{tikzcd}$$

$$\begin{tikzcd}[column sep=small]
\mathrm{[Cu(trop)_2](c)} \arrow[d, "\Delta H_2"] & + & \mathrm{H_2SO_4\cdot 23.69\,H_2O}(l) \arrow[d, "\Delta H_1"] \\
\mathrm{Calorimetric\ solvent} & & \mathrm{(H_2SO_4\cdot 53.5391\ H_2O)} \\
& \mathrm{Solution\ B_2} &
\end{tikzcd}$$

$$\mathrm{Solution\ A_3} \xrightarrow{\Delta H_6 = 0} \mathrm{Solution\ B_2}$$

$$\mathrm{Solvent} + \mathrm{H_2SO_4\cdot 23.69\,H_2O} \xrightarrow{\Delta H_1} \mathrm{Solution\ B_1}$$

$$\mathrm{Solution\ B_1} + \mathrm{[Cu(trop)_2]} \xrightarrow{\Delta H_2} \mathrm{Solution\ B_2}$$

$$\mathrm{Solvent} + \mathrm{H_2O} \xrightarrow{\Delta H_3} \mathrm{Solution\ A_1}$$

$$\mathrm{Solution\ A_1} + \mathrm{Htrop} \xrightarrow{\Delta H_4} \mathrm{Solution\ A_2}$$

$$\mathrm{Solution\ A_2} + \mathrm{CuSO_4\cdot 5.00\,H_2O} \xrightarrow{\Delta H_5} \mathrm{Solution\ A_3}$$

$$\Delta H_R = 18.69\Delta H_3 + 2\Delta H_4 + \Delta H_5 - \Delta H_1 - \Delta H_2 + \Delta H_6$$

Scheme.

The quantities of reactants in a particular series of experiments were determined by the amount of bis(tropolonato)copper(II) in the particular ampoule; strict control of stoicheiometry was maintained throughout each series.

When this procedure is used, the value calculated for ΔH_R refers to the reaction indicated in the first line of the scheme, provided that solutions A_3 and B_2 are identical, and that the value of ΔH_6 is zero. As a check on the validity of this assumption, ampoules of solution B_2 were broken into A_3 in the calorimeter; no detectable heat change occured.

Results and Discussion

The experimental data are given in Table 1, leading to the value $\Delta H_R = +6.88 \pm 0.06$ kcal mol⁻¹.

The following values were taken from the literature: $\Delta H_f^\circ[\mathrm{CuSO_4\cdot 5.00\ H_2O\ (c)}] = -544.85$ kcal mol⁻¹,[10)] $\Delta H_f^\circ[\mathrm{Htrop(c)}] = -57.18 \pm 0.21$ kcal mol⁻¹ [11,12)] and $\Delta H_f^\circ[\mathrm{H_2SO_4\cdot 5.00\ H_2O\ (aq)}] = -549.863 \pm 0.001$ kcal mol⁻¹.[9)] The standard enthalpy of formation of crystalline bis(tropolonato)copper(II), at 25 °C, was calculated from relationship (1) to be $\Delta H_f^\circ[\mathrm{Cu(trop)_2}]\mathrm{(c)} = -102.47 \pm 0.42$ kcal mol⁻¹.

Enthalpies of sublimation of few coordination compounds have been accurately measured, but from con-

Table 1. Calorimetric study of [Cu(trop)$_2$]

(a) Addition of [Cu(trop)$_2$] to Solution B_1.

[Cu(trop)$_2$] (10⁴amount/mol)	$10^3(\Delta R/R_m)$	ε	ΔH_2/kcal mol⁻¹
5.0013	1.4018	2586.1	+7.249
5.0033	1.4099	2583.5	+7.280
4.9892	1.3992	2584.3	+7.248
5.0213	1.3967	2580.1	+7.177
5.0033	1.4276	2572.8	+7.341
4.9882	1.4046	2584.0	+7.276

Mean: $\Delta H_2 = +7.26 \pm 0.04$ kcal mol⁻¹

(b) Addition of Htrop to Solution A_1.

Htrop (10⁴amount/mol)	$10^3(\Delta R/R_m)$	ε	ΔH_4/kcal mol⁻¹
10.0266	1.7224	2585.0	+4.441
10.0373	1.7189	2588.3	+4.433
10.0234	1.7153	2582.5	+4.420
10.1241	1.7332	2584.7	+4.425
10.0266	1.6952	2580.8	+4.364
9.9972	1.7134	2585.5	+4.431

Mean: $\Delta H_4 = +4.42 \pm 0.02$ kcal mol⁻¹

(c) Addition of $CuSO_4\cdot 5.00\ H_2O$ to Solution A_2.

$CuSO_4\cdot 5.00\,H_2O$ (10⁴amount/mol)	$10^3(\Delta R/R_m)$	ε	ΔH_5/kcal mol⁻¹
4.9962	1.0114	2588.9	+5.240
5.0043	1.0266	2578.3	+5.289
4.9958	1.0266	2577.4	+5.296
5.0010	1.0343	2582.5	+5.332
5.0039	1.0297	2574.1	+5.297
4.9938	1.0237	2593.1	+5.316

Mean: $\Delta H_5 = +5.30 \pm 0.03$ kcal mol⁻¹

sideration of the existing data it is possible to make a reasonable estimate for the bis(tropolonato)copper(II) complex;[13] the uncertainty must be of the order of 10 kcal mol^{-1}, but this only produces an uncertainty of *ca.* 2.5 kcal in the bond energy. Accordingy, if we take $\Delta H^\circ_{sub}[Cu(trop)_2](c) = +35.0 \pm 10.0$ kcal mol^{-1}, the standard heat of formation of the geseous complex is $\Delta H^\circ_f[Cu(trop)_2](g) = -67.5 \pm 10.0$ kcal mol^{-1}.

The metal-oxygen bond strengh can be related to the energy needed to break the molecule into metal and ligands, and all referred to the gaseous state (Eq. 2), in order to remove the condensed state effects

$$[Cu(trop)_2](g) \xrightarrow{\Delta H_f(r)} Cu(g) + 2\,trop\cdot(g) \qquad (2)$$

Since the oxygens in β-diketonates are known to be equivalent,[14] which is supported by the crystal structure of this particular complex,[15] the copper(II)-oxygen homolytic bond strengh E(Cu–O), is $\Delta H^\circ_f(r)/4$.

Calculating the heat of formation of the tropolone radical itself presupposes a knowledge of the dissociation energy of the tropolone, that is, the heat of reaction of process (3)

$$Htrop(g) \longrightarrow H\cdot(g) + trop\cdot(g) \qquad (3)$$

For acetylacetone (2,4-pentanedione),[16] trifluoroacetylacetone (1,1,1-trifluoro-2,4-pentanedione)[17] and dipivaloylmethane (2,2,6,6-tetramethyl-2,4-pentanedione)[17] we assumed a value of 100 ± 5 kcal mol^{-1}, but, because of the resonating tropolone ring, there is reason to suggest that a value closer to phenol (85 kcal mol^{-1} [18]) is more appropriate,[19] Accordingly we take 90 ± 5 kcal mol^{-1} [20] for the dissociation eneregy of Htrop. In this way, from the literature values of ΔH°_f[H trop] (c) = -57.18 ± 0.21 kcal mol^{-1} [11,12] and ΔH°_{sub}[H trop](c) = $+20.1 \pm 0.1$ kcal mol^{-1},[21] we calculate ΔH°_f[H trop](g) = -37.08 ± 0.23 kcal mol^{-1} and, using the value ΔH°_f H·(g) = 52.095 kcal mol^{-1},[9] we calculate ΔH°_f[trop·](g) = 1 ± 5 kcal mol^{-1},[20]

As ΔH°_f[Cu(g)] = 80.86 kcal mol^{-1},[10] the value of $\Delta H_f(r) = 150.4 \pm 14.1$ kcal mol^{-1} and, hence, the copper(II)-oxygen homolytic bond energy E(Cu–O) = 38 ± 4 kcal mol^{-1} was calculated.

It is sometimes convenient to consider the bond energy in terms of the ions, as defined by equation(4)

$$[Cu(trop)_2](g) \xrightarrow{\Delta H_f(i)} Cu^{2+}(g) + 2trop^-(g) \qquad (4)$$

Estimating the electron affinity of the ligands to be approximately equal to that of the oxygen atom, $E_L = 33.8$ kcal mol^{-1},[22] the enthalpy of formation of the gaseous tropolone ion was calculated to be -33 ± 5 kcal mol^{-1} [20] and using the literature value of ΔH°_f [Cu^{2+}](g) = 729.93 kcal mol^{-1} [10] the value of $\Delta H_f(i)$ for the ionic gas reaction (4) was calculated to be $\Delta H_f(i) = 731.4 \pm 11.2$ kcal mol^{-1} and, thence, the so-called heterolytic copper(II)-oxygen bond energy E'(Cu–O) = $\Delta H_f(i)/4$ is calculated as E'(Cu–O) = $= 183 \pm 3$ kcal mol^{-1}.

In the present work, careful and precise measurements of molar enthalpies of solution led to a new value of the standard enthalpy of formation of the crystalline complex of bis(tropolonato)copper(II), with an accuracy better than 0.4%.

In attempting a rigorous determination of bond energies of complexes of tropolone, estimations of some enthalpies of sublimation have had to be made and, in addition, it has also been necessary to estimate the dissociation energy of the enolic hydrogen from tropolone. The resulting bond energies, therefore, have a large uncertainty attached to them.

Table 2. (all values in kcal mol^{-1})

Complex	$\Delta H_f(r)$	E(M-O)	$\Delta H_f(i)$	E'(M-O)
[Be(trop)$_2$][23]	263±11	66±3	833±11	208±3
[Al(trop)$_3$][20]	368±15	61±3	1468±15	250±3
[Al(4-Metrop)$_3$][20]	357±15	60±3	1487±15	248±3
[Cu(trop)$_2$]	150±14	38±4	731±11	183±3

However, as is summarized in Table 2, the beryllium-oxygen bond is stronger than the aluminium-oxygen bond as one would expect from a simple electrostatic model. The copper(II) complex has been studied because it contains the metal in a planar environment of ligands. In spite of all the assumptions that were required to obtain the metal-oxygen bond parameters, it seems to provide a clear evidence that the copper(II) complex has considerably weaker bonds than the aluminium and beryllium complexes.

The value we obtained for the copper(II)-oxygen bond energy of the tropolonato complex (38 ± 4 kcal mol^{-1}) is very close to the value found by Jones and co-workers[24] for the copper complex of acetylacetone (2,4-pentanedione): 42 kcal mol^{-1}. One would expect to find a higher value for the tropolonato complex as a direct result of the interaction of the bulky seven membered ring of the ligand and the chelate rings. However, it must be pointed out that the value of Jones *et al.* has been derived from the measured heat of combustion of the metal complex. This method has two major disadvantages for coordination compounds with organic ligands: (a) a very large heat of combustion of the organic ligand, which tends to swamp the metal-ligand bond energy; (b) the difficulty of deciding the exact thermodynamic state of the combustion products at the reference temperature. Neither of these is encountered in solution calorimetry where the formation reaction $M + mL \rightarrow ML_m$ is directly involved.

As the conclusion of the above discussion we might think that a further investigation with other copper(II) complexes will be needed before more reliable information about this bond energy can be obtained.

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