Thermochemistry of Copper(II) β-Diketonates. II.[†] Bis(benzoylacetonato)copper(II)

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(Received July 22, 1978)

The standard enthalpy of formation of crystalline bis(benzoylacetonato)copper(II) has been determined at 298.15 K by solution calorimetry: $\Delta H_f^\circ[\mathrm{Cu(bzac)_2}]\ (\mathrm{c}) = -143.6 \pm 2.2\ \mathrm{kcal\ mol^{-1}}$. Enthalpy changes at 298.15 K for the following hypothetical gaseous reactions have been subsequently derived:

$$\mathrm{Cu(g)} + 2\mathrm{bzac}^{\bullet}\mathrm{(g)} = [\mathrm{Cu(bzac)_2}]\mathrm{(g)} \qquad \Delta H = -165.9 \pm 14.3\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{Cu^{2+}(g)} + 2\mathrm{bzac^{-}(g)} = [\mathrm{Cu(bzac)_2}]\mathrm{(g)} \qquad \Delta H = -747.3 \pm 14.4\ \mathrm{kcal\ mol^{-1}}$$

The corresponding homolytic($\bar{E}$) and heterolytic($\bar{E}'$) copper(II)-oxygen mean bond energy parameters were calculated as

$$\bar{E}_{\mathrm{Cu-O}} = 41 \pm 3\ \mathrm{kcal\ mol^{-1}} \quad \text{and} \quad \bar{E}'_{\mathrm{Cu-O}} = 187 \pm 3\ \mathrm{kcal\ mol^{-1}}$$

respectively.

In a previous paper,[1)] the standard enthalpy of formation of bis(tropolonato)copper(II) and the Cu(II)–O homolytic and heterolytic bond energies were presented. As it was pointed out in the discussion, the lack of knowledge of similar parameters for the Cu(II)–O bonds of other compounds, made it very difficult to discuss the calculated values of the Cu(II)–O bonds.

To close the gap we examine here the corresponding benzoylacetonate[††] complex in order to compare the ligand structural effects in the copper–oxygen bond. The crystal structure of bis(benzoylacetonato)copper(II) has been determined[2)] and shows that the crystals are formed from separate components and that in each molecule the four oxygen atoms lie in the same plane as the copper atoms.

Experimental

The Solution Calorimeter. The LKB 8700 Reaction and Solution Precision Calorimeter was used for all solution reactions. The operation and calculation methods have been described before.[1)]

Thermochemical functions are expressed in terms of the thermochemical calorie (defined as 4.184 J exactly) and refer to the isothermal process at 298.15 K and the true mass, calculated using the atomic weights of 1966 based on the isotope ^{12}C. A check on the accuracy of the calorimeter was carried out by determining the enthalpy of solution of *N,N′,N″*-tris(hydroxymethyl)methanetriamine, (tham) in excess 0.1 M hydrochloric acid. The result, -7110.2 ± 0.7 cal mol^{-1} is in excellent agreement with previous results[3)] (-7115.4 ± 0.6 cal mol^{-1}).

The uncertainty range is twice the standard deviation of the mean (five determinations were made for each compound).

Materials. *Benzoylacetone (Hbzac)*: 'AnalaR' Koch-Light benzoylacetone was recrystallized from ethanol-water and dried over silica gel; mp=55 °C (lit, 56 °C[4)]).

Found: C, 73.87; H, 6.26%. Calcd for $\mathrm{C_{10}H_{10}O_2}$: C, 74.06; H, 6.22%.

Bis(benzoylacetonato)copper(II): [Cu(bzac)$_2$] was prepared by a modification of the method of Hammond *et al*:[5)] a solution of 'AnalaR' copper(II) sulfate (2.5 g) in water (100 cm^3) was buffered with sodium acetate (7.5 g) and then mixed with a solution of benzoylacetone (5 g) in ethanol (80 cm^3). The precipitated complex was washed on the filter with water and cold ether, filtered off, dried in the air, recrystallised from chloroform and stored in a desiccator over silica gel; mp=189—190 °C.

Found: C, 62.00; H, 4.68; Cu, 16.41%. Calcd for $\mathrm{C_{20}H_{18}O_4Cu}$: C, 62.25; H, 4.70; Cu, 16.46%.

Copper(II) Sulfate Pentahydrate: 'AnalaR' grade copper(II) sulfate pentahydrate was powdered and dried in a desiccator over silica gel for 48 h. Its composition was determined by means of a electrogravimetric copper analyses and found to be $\mathrm{CuSO_4 \cdot 5.00\,H_2O}$. Periodical analyses showed no change in composition.

Sulfuric Acid: A molar solution of 'AnalaR' grade sulfuric acid was made up, by using a BDH concentrated volumetric solution; the concentration was checked by acid-base titration against $\mathrm{Na_2B_4O_7 \cdot 10H_2O}$ and found to be (series of six titrations) 1.0000 ± 0.0004 M which corresponds[4)] to the composition $\mathrm{H_2SO_4 \cdot 53.539(1)\ H_2O}$.

1,4-Dioxane: 'AnalaR' dioxane was purified according to Refs. 6 and 7.

Constant Boiling Hydrochloric Acid, was prepared from 'AnalaR' HCl by dilution with distilled water. The concentration of the HCl solution was determined by titration against $\mathrm{Na_2B_4O_7 \cdot 10H_2O}$. A series of six different determinations gave the result of 4.2172 ± 0.0004 M *i.e.* $\mathrm{HCl \cdot 11.911\ H_2O}$.[4)]

Analyses: All carbon and hydrogen analyses were carried out in the Microanalytical Service of the University of Surrey; copper in the complex was analysed by atomic absorption spectroscopy.

Method for Solution Calorimetry: Preliminary tests of solubility showed that although some species would dissolve very slowly in dilute acid solutions, satisfactory results were obtained using a solution of dioxane (75%) and 4.2 M HCl (25%) as calorimetric solvent, and dissolving stoichiometric quantities of the reactants and products in this mixed solvent.

Calculation: The standard enthalpy of formation of the bis(benzoylacetonato)copper(II) complex can be determined from reaction between the benzoylacetone and the copper(II) sulfate pentahydrate to give a solution of the copper(II) complex and sulfuric acid:

$$2\mathrm{Hbzac(c)} + \mathrm{CuSO_4 \cdot 5H_2O(c)} \xrightarrow{\Delta H_\mathrm{R}} [\mathrm{Cu(bzac)_2}]\mathrm{(c)} + \mathrm{H_2SO_4 \cdot 5H_2O(aq)}. \qquad (1)$$

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

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[†] Part I is Ref. 1.

[††] Benzoylacetone(Hbzac) = 1-phenyl-1,3-butanedione.

reached from either side within the period of the experiment.

To the calorimetric solvent (100.0 cm^3) ampoules with the appropriate amounts of water, benzoylacetone and $CuSO_4 \cdot 5H_2O$ were added consecutively and ΔH_1, ΔH_2, and ΔH_3 were measured. To a second portion of the same solvent (100.0 cm^3) were added consecutively ampoules of $H_2SO_4 \cdot 53.54\ H_2O$ and bis(benzoylacetonato)copper(II) and ΔH_4 and ΔH_5 were measured. The general procedure together with the general thermochemical cycle, is given in the Scheme. The quantities of reactants in a series of experiments were determined by the amount of bis(benzoylacetonato)copper(II) in a particular ampoule (about 2.5×10^{-4} mol); exact 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 of the validity of this, ampoules of solutions (B_2) were broken into solution (A_3) in the calorimeter; no detectable heat exchange occurred.

Results and Discussion

The experimental data are presented in Table 1, leading to the value $\Delta H_R = +10.13 \pm 0.31$ kcal mol^{-1}. The following values were taken from the literature:

$\Delta H^\circ_f[CuSO_4 . 5H_2O(c)] = -544.85$ kcal mol^{-1},8)

$\Delta H^\circ_f[Hbzac(c)] = -81.2 \pm 1.1$ kcal mol^{-1},9)

$\Delta H^\circ_f[H_2SO_4 \cdot 53.54H_2O(aq)]$

$= -3869.5509$ kcal mol^{-1},10)

$\Delta H^\circ_f[H_2O(l)] = -68.315$ kcal mol^{-1},10)

and, according to the first line of the Scheme, the standard enthalpy of formation of crystalline bis(benzoylacetonato)copper(II) at 25 °C was calculated to be $\Delta H^\circ_f[Cu(bzac)_2](c) = -143.6 \pm 2.2$ kcal mol^{-1}.

Although the enthalpy of sublimation of the bis(benzoylacetonato)copper(II) has not yet been experimentally and accurately measured, the consideration of the existing data on similar compounds (other metal β-diketonates11,12)) makes possible a reasonable estimate1); however, the uncertainty must be large, but if we take the upper value of ±10 kcal mol^{-1}, this only produces an uncertainty of *ca.* 2.5 kcal in the bond energy. Accordingly, if we assume $\Delta H^\circ_{subl}[Cu(bzac)_2](c) = 32.0 \pm 10.0$ kcal mol^{-1}, the standard enthalpy of formation of the gaseous complex is $\Delta H^\circ_f[Cu(bzac)_2](g) = -111.6 \pm 10.2$ kcal mol^{-1}.

As discussed previously,11,12) the metal–oxygen bond strength can be equated to be the energy needed to break the molecule into the metal and ligand radicals, all referred to the gaseous state (Eq. 2), in order to remove the condensed state effects.

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

Since the oxygens in β-diketonates are known to be equivalent,13) which is again supported by the crystal structure of this particular complex2), the mean copper(II)–oxygen homolytic bond energy $\overline{E}$(Cu–O), is $\Delta H^\circ_f(r)/4$.

The value of the standard enthalpy of formation of the benzoylacetone radical itself can be calculated from the knowledge of the dissociation energy of the enolic hydrogen of benzoylacetone, that is the enthalpy of reaction of process(3)

$$Hbzac(g) \longrightarrow H\cdot(g) + bzac\cdot(g) \qquad (3)$$

According to previous work1,11,14,15) we take 100±5 kcal mol^{-1} for the enolic hydrogen dissociation energy of gaseous Hbzac. Hence, from $\Delta H^\circ_{subl}(Hbzac) =$

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

(a) Addition of H_2O to solvent (dioxane-HCl)

10^2 H_2O amount/mol	$10^3(\Delta R/R_m)$	ε	ΔH_1/kcal mol^{-1}
1.2446	1.8124	1566.2	−0.228
1.2416	1.7986	1569.0	−0.227
1.2463	1.6979	1565.6	−0.213
1.2111	1.7363	1562.4	−0.224
1.2102	1.7262	1570.4	−0.224

Mean: $\Delta H_1 = -0.223 \pm 0.006$ kcal mol^{-1}

(b) Addition of Hbzac to solution A_1

10^4 Hbzac amount/mol	$10^3(\Delta R/R_m)$	ε	ΔH_2/kcal mol^{-1}
5.0046	2.0179	1567.7	+6.321
5.0583	2.0686	1575.2	+6.442
5.0348	2.0417	1576.6	+6.393
4.9824	2.0318	1564.6	+6.380
4.9676	2.0275	1568.2	+6.400

Mean: $\Delta H_2 = +6.39 \pm 0.04$ kcal mol^{-1}

(c) Addition of $CuSO_4 \cdot 5H_2O$ to solution A_2

10^4 $CuSO_4 \cdot 5H_2O$ amount/mol	$10^4(\Delta R/R_m)$	ε	ΔH_3/kcal mol^{-1}
2.4860	9.9760	1562.4	+6.270
2.5276	9.9381	1558.7	+6.129
2.5152	9.8559	1577.7	+6.182
2.4824	9.6201	1575.7	+6.106
2.5124	9.6803	1606.5	+6.190

Mean: $\Delta H_3 = +6.18 \pm 0.06$ kcal mol^{-1}

(d) Addition of $H_2SO_4 \cdot 53.54H_2O$ to solvent (dioxane-HCl)

10^4 $H_2SO_4 \cdot 53.54H_2O$ amount/mol	$10^3(\Delta R/R_m)$	ε	ΔH_4/kcal mol^{-1}
2.5172	2.0177	1574.2	−12.618
2.6236	2.1124	1574.4	−12.676
2.5076	2.0235	1575.2	−12.711
2.5078	2.0625	1557.1	−12.806
2.5223	2.0371	1573.5	−12.708

Mean: $\Delta H_4 = -12.70 \pm 0.06$ kcal mol^{-1}

(e) Addition of $[Cu(bzac)_2]$ to solution B_1

10^4 $[Cu(bzac)_2]$ amount/mol	$10^3(\Delta R/R_m)$	ε	ΔH_5/kcal mol^{-1}
2.4739	1.6856	1576.8	+10.744
2.4104	1.6284	1572.3	+10.622
2.5369	1.7427	1566.8	+10.763
2.5188	1.7096	1569.0	+10.649
2.5146	1.7138	1580.5	+10.772

Mean: $\Delta H_5 = +10.71 \pm 0.06$ kcal mol^{-1}

$$\begin{array}{ccccccc}
\mathrm{CuSO_4\cdot 5H_2O(c)} & + & 2\mathrm{Hbzac(c)} & + \; 48.54\mathrm{H_2O(l)} & \xrightarrow{\Delta H_\mathrm{R}} & \mathrm{H_2SO_4\cdot 53.54H_2O(l)} & + \; [\mathrm{Cu(bzac)_2}](\mathrm{c}) \\
\downarrow{\scriptstyle \Delta H_3} & & \downarrow{\scriptstyle \Delta H_2} & \downarrow{\scriptstyle \Delta H_1} & & \downarrow{\scriptstyle \Delta H_4} & \downarrow{\scriptstyle \Delta H_5} \\
\multicolumn{4}{c}{\text{Solvent (75\% Dioxane+25\% HCl, 4.2 M)}} & & \multicolumn{2}{c}{\text{Solvent (75\% Dioxane+25\% HCl, 4.2 M)}}
\end{array}$$

$$\begin{array}{lcl}
\text{Solution } \mathrm{A_3} & \xrightarrow{\Delta H_6=0} & \text{Solution } \mathrm{B_2} \\
\text{Solvent} + \mathrm{H_2O} & \xrightarrow{\Delta H_1} & \text{Solution } \mathrm{A_1} \\
\text{Solution } \mathrm{A_1} + \text{Hbzac} & \xrightarrow{\Delta H_2} & \text{Solution } \mathrm{A_2} \\
\text{Solution } \mathrm{A_2} + \mathrm{CuSO_4\cdot 5H_2O} & \xrightarrow{\Delta H_3} & \text{Solution } \mathrm{A_3} \\
\text{Solvent} + \mathrm{H_2SO_4\cdot 53.54H_2O} & \xrightarrow{\Delta H_4} & \text{Solution } \mathrm{B_1} \\
\text{Solution } \mathrm{B_1} + [\mathrm{Cu(bzac)_2}] & \xrightarrow{\Delta H_5} & \text{Solution } \mathrm{B_2}
\end{array}$$

$$\Delta H_\mathrm{R} = 48.54\Delta H_1 + 2\Delta H_2 + \Delta H_3 - \Delta H_4 - \Delta H_5 + \Delta H_6$$

Scheme 1.

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

Complex	$\Delta H_f^\circ(\mathrm{c})$	$\Delta H_\mathrm{r}(\mathrm{r})$	$\bar{E}(\mathrm{Cu\text{-}O})$	$\Delta H_f'(\mathrm{i})$	$\bar{E}'(\mathrm{Cu\text{-}O})$
$[\mathrm{Cu(trop)_2}]$[24]	-99.13 ± 0.42	-146.9 ± 14.1	37 ± 3	-728.0 ± 11.4	182 ± 3
$[\mathrm{Cu(bzac)_2}]$	$-143.6\ \pm2.2$	-165.9 ± 14.3	41 ± 3	-747.3 ± 14.4	187 ± 3

20.02 ± 0.10[16] kcal mol^{-1} one calculates $\Delta H_f^\circ(\mathrm{Hbzac, g}) = -61.2\pm1.1$ kcal mol^{-1} and from the above values and $\Delta H_f^\circ(\mathrm{H\cdot, g}) = 52.095$ kcal mol^{-1},[10] the standard enthalpy of formation of the gaseous benzoylacetone radical, is derived as $\Delta H_f^\circ(\mathrm{bzac\cdot, g}) = -13.3\pm5.1$ kcal mol^{-1}.

As $\Delta H_f^\circ(\mathrm{Cu, g}) = 80.86$ kcal mol^{-1},[8] the calculated value for the hypothetical gaseous reaction 2 is $\Delta H_\mathrm{r}(\mathrm{r}) = 165.9\pm14.3$ kcal mol^{-1} and hence, the mean copper(II)–oxygen homolytic bond energy, $\bar{E}(\mathrm{Cu\text{-}O}) = 41\pm3$ kcal mol^{-1} was calculated.

The bond energy in terms of the ions in defined by Eq. 4.

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

Estimating the electron affinity of the β-diketonates[1] to be approximately equal to that of the oxygen atom for one electron ($E_\mathrm{L} = 1.465$ eV$= 33.8$ kcal mol^{-1}),[17] the enthalpy of formation of the gaseous anion benzoylacetone is calculated as $\Delta H_f(\mathrm{bzac^-})(\mathrm{g}) = -47.1\pm5.1$ kcal mol^{-1}, and using the literature value $\Delta H_f^\circ(\mathrm{Cu^{2+}})(\mathrm{g}) = 729.93$ kcal mol^{-1},[8] one calculates the value of $\Delta H_f(\mathrm{i}) = 747.3\pm14.4$ kcal mol^{-1} and hence the so called heterolytic copper(II)–oxygen mean bond energy, $\bar{E}'_\mathrm{Cu-O} = \Delta H_f(\mathrm{i})/4$, is calculated as $\bar{E}'_\mathrm{Cu-O} = 187\pm3$ kcal mol^{-1}.

The stability of a co-ordination compound is commonly interpreted as referring to the process

$$\mathrm{M}^{n+} + n\mathrm{L}^- \longrightarrow [\mathrm{ML}_n]$$

occurring in solution, which is a Lewis acid-base reaction and therefore the stability of the compound should increase as the strength of the Lewis base increases. One would expect therefore that the stability should be in the order of increasing dissociation constant pK of the ketone, *i.e.*, in the case of copper(II) β-diketonates, tropolone(7.0)[18] and benzoylacetone (8.94).[19] There is little data from stability constant studies which related directly to this system: copper(II) tropolonate has an overall stability constant of 15.4, at 30 °C in 50% dioxane–water[20–22] and copper(II) benzoylacetonate has an overall stability constant of 17.02 at 25 °C in 75% dioxane–water,[23] from which the free energies can be derived: $\Delta G[\mathrm{Cu(trop)_2}] = -21.4$ kcal mol^{-1} and $\Delta G[\mathrm{Cu(bzac)_2}] = -23.2$ kcal mol^{-1}.

This is quite a significant difference in free energy but the lack of values for the entalpy of formation of the complexes in solution prevents other conclusions.

However, the large value for the enthalpy of formation of copper(II) benzoylacetonate from its ions in the vapour state (-747 kcal mol^{-1}) shows the large importance of solvation effects in solution processes, and so, it is apparent from this, that stability constants can give very little direct information of metal–ligand bond energies.

Table 2 summarizes the relevant parameters for the copper(II) complexes of benzoylacetone and tropolone.[24]

Whether the Cu–O bond energy is expressed in terms of dissociation into radicals or ions, the uncertainty arising from the use of the estimated auxiliary data is sufficiently large to obscure any clear difference effect of ligand parameters, but it is noteworthy that a change in the dissociation constant of the ligand by almost 2 pK units causes a change in the heterolytic bond energy of less that 5 kcal (3%). Unfortunatly, the uncertainties ascribed to the bond energy parameters (±3 kcal mol^{-1}) are big enough to prevent one to conclude that the Cu–O bond energy is definitely larger in the benzoylacetonate complex than in the tropolonate one. Nevertheless, it seems reasonable to think that these results are in agreement with the Nakamoto's[25] statement that the value of the metal–oxygen bond energy in substituted β-diketonates increases with the introduction of a phenyl group in the β-diketones and disagrees with Collman's[26] opposite statement.

Thanks are due to the Instituto Nacional de Investigação Científica, Lisboa, Portugal, for partial financial support of the research project.

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