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Note

THE MEAN ZINC–OXYGEN BOND ENTHALPY IN BIS(2,4-PENTANEDIONATO)ZINC(II)

CLAUDIO AIROLDI

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13.100 Campinas, São Paulo (Brasil)

Coordination compounds involving β-diketonates are widely covered in the literature and the apperarance of significant reviews [1–4] certainly reflects the increasing importance of this field. The great ability of this class of ligand in coordinating metals is illustrated by the number of compounds studied [4]. In particular, our interest is mainly driven to 2,4-pentanedione (acacH) and zinc group elements. The reaction of this ligand with zinc salts produces monoaquobis(acetylacetonato)zinc(II) [5], where the coordinated water can be easily replaced by heterocyclic bases and amines, forming 1 : 1 adducts [6–8]. The derivative compounds of heterocyclic ligands dissociate in benzene solution, probably giving a metal with a coordination number of five [6].

Some thermochemical data of the anhydrous chelate were reported in a recent publication [9], which was extracted from an international conference [10]. Taking into consideration the thermochemistry of the zinc group elements, we decided to restudy this system using a different approach, by the use of a calorimetric replacement reaction, taking into account the previous results obtained with bis(diethyldithiocarbamato)zinc(II) chelate [11].

EXPERIMENTAL

All chemicals were of analytical reagent grade, which were rigorously purified for the preparations and calorimetric determinations.

The monohydrated chelate, $Zn(acac)_2 \cdot H_2O$, was prepared as before, and became anhydrous after subliming in vacuo, with a melting point of 128°C [5]. Bis(diethyldithiocarbamato)zinc(II) was obtained by reacting zinc chloride with diethylammonium diethyldithiocarbamate in ethanol [11].

A precision calorimeter system (LKB 8700-1) was used for all solution reactions [12]. For each enthalpy determination a series of ampoules containing ca. 10^{-4} mol of reactant was broken into a glass reaction vessel at 298.15 ± 0.02 K, charged with 100 cm^3 of calorimetric solvent. A dry-box was used for preparing ampoules of air-sensitive compounds.

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RESULTS AND DISCUSSION

The determination of the standard enthalpy of formation of bis (acetylacetonato)zinc(II) was based on the following calorimetric replacement reaction

$$Zn(acac)_2(s) + 2[NH_2Et_2][S_2CNEt_2](s)$$
$$= Zn(S_2CNEt_2)_2(s) + 2acacH(l) + 2Et_2NH(l); \Delta H_R^\ominus$$

The standard enthalpy change, $\Delta H_R^\ominus$, for this reaction was made in acetone due to its ability to dissolve the five components of the reaction. For this determination a calorimetric sequence of reactions is presented below, and the results are summarized in Table 1

$Zn(acac)_2(s)$ + acetone = solution A $\quad \Delta H_1^\ominus$

Solution A + $2[Et_2NH_2][S_2CNEt_2](s)$ = solution B $\quad \Delta H_2^\ominus$

$Zn(S_2CNEt_2)_2(s)$ + acetone = solution C $\quad \Delta H_3^\ominus$

Solution C + $2[Et_2NH](l)$ = solution D $\quad \Delta H_4^\ominus$

Solution D + 2acacH(l) = solution E $\quad \Delta H_5^\ominus$

Solution B = solution E $\quad \Delta H_6^\ominus$

For this series of reactions a strict control of the stoichiometry of the individual reactions was made throughout the cycle, to give a zero $\Delta H_6^\ominus$ value. The application of the first law of thermodynamics to the cycle gave: $\Delta H_R^\ominus = \Delta H_1^\ominus + \Delta H_2^\ominus - \Delta H_3^\ominus - \Delta H_4^\ominus - \Delta H_5^\ominus$, which from the data listed in Table 1 produced $\Delta H_R^\ominus = +49.46 \pm 1.05$ kJ mol^{-1}.

The standard enthalphy of formation of the solid chelate was calculated through the expression: $\Delta H_f^\ominus$ [Zn(acac)$_2$,s] $= \Delta H_R^\ominus - \Delta H_f^\ominus$ [acacH,l] $+ 2\Delta H_f^\ominus$ ([NH$_2$Et$_2$][S$_2$CNEt$_2$],s). By the use of the values -289.65 ± 4.9, -101.29 ± 0.37, -425.5 ± 1.0 and -248.9 ± 2.1 kJ mol^{-1}, for bis(diethyldithiocarbamato)zinc(II) [11], diethylamine [13], acetylacetone [14] and dieth-

TABLE 1

Enthalpies of dissolution at 298.15 K

Compound	Calorimetric solvent	No. of experiments	i	$\Delta H_i^\ominus$ (kJ mol^{-1})
$Zn(acac)_2(s)$	Acetone	5	1	$+29.41 \pm 0.42$
$[NH_2Et_2][S_2CNEt_2](s)$	$Zn(acac)_2$–acetone	5	2	$+46.94 \pm 0.89$
$Zn(S_2CNEt_2)_2(s)$	Acetone	6	3	$+35.03 \pm 0.22$
$Et_2NH(l)$	$Zn(S_2CNEt_2)_2$–acetone	5	4	-9.73 ± 0.28
acacH(l)	$Zn(S_2CNEt_2)_2$–Et_2NH–acetone	4	5	$+1.59 \pm 0.02$

ylammonium diethyldithiocarbamate [15], respectively, the value $\Delta H_f^{\ominus}$ [Zn(acac)$_2$,s] = -849.89 ± 6.88 kJ mol^{-1} was found which, combined with its enthalpy of sublimation [16] (ΔH_{sub} [Zn(acac)$_2$] = 117 ± 3 kJ mol^{-1}) gave $\Delta H_f^{\ominus}$ [Zn(acac),g] = 777.9 ± 7.5 kJ mol^{-1}.

The enthalpy of the zinc–oxygen bond must refer to the breaking of the chelate molecule in the gaseous phase. The homolytic parameter [17] can be related to the equation

$$\mathrm{Zn(g)} + 2\mathrm{aca\dot{c}(g)} = \mathrm{Zn(acac)_2(g)};\ \Delta H_{\mathrm{fr}}$$

As the coordination sites are equivalent, the mean zinc–oxygen bond enthalpy is equated to one-quarter of the enthalpy of the above equation. Thus, $\bar{D}(\mathrm{Zn{-}O}) = -1/4\Delta H_{\mathrm{fr}}$. By using the enthalpy of sublimation of zinc [18] and the enthalpy of the radical in the gaseous phase [19] (130.73 and -182.42 ± 21.34 kJ mol^{-1}, respectively) $\bar{D}(\mathrm{Zn{-}O}) = 136 \pm 11$ kJ mol^{-1} is derived.

In comparing our result with that available from the literature [9] (138 ± 4 kJ mol^{-1}) a close agreement can be noted between them, but they clearly differ in the uncertainty. The calculation in the uncertainty used by the authors of ref. 10 is unknown; however, our result has a large uncertainty attached to $\bar{D}$(Zn–O), which comes from the enthalpy of formation of the radical.

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