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HEATS OF FORMATION OF SOME NICKEL(II) β-DIKETONATES AND NICKEL–OXYGEN BOND ENERGIES

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ABSTRACT

The standard enthalpies of formation of Ni(II) acetylacetonate (acac), benzoylacetonate (bzac) and of dibenzoylmethanate (dbzm) were determined. The enthalpy changes for several hypothetical reactions of complex formation in the gaseous state were calculated on the basis of the appropriate thermodynamical cycle. The Ni–O bond energies were determined.

INTRODUCTION

The transition element β-diketonates are very suitable for thermochemical investigations, since almost all the enthalpy changes in the thermodynamical cycle, being the basis for the metal–oxygen bond energy calculations, are known. The literature data available for the properties of Ni(II) β-diketonates concern, first of all, their structure[1–4] and equilibria in solutions[5, 6], but very few deal with the thermochemistry of those compounds. Wood et al. have determined the Ni–O and Ni–N bond energies in several square-planar Ni(II) complexes from their combustion heat measurements in a calorimetric bomb[7]. This method, contrary to the direct calorimetric measurements of the heat effect of the complex formation in solution, seems not to be precise enough, because of the difficulties in determination of the stable combustion products of a given complex.

The present paper presents the calorimetric investigations of the Ni(II) complexes with acetylacetone and its derivatives, which allow us to determine the influence of the R_1 and R_2 substituents in the R_1–CO–CH_2–CO–R_2 ligand on the properties of β-diketonates under investigation. Nakamoto[8] who has examined the IR spectra of these complexes in the solid phase has proved that their stabilities changed in the order dbzm > bzac > acac. That was confirmed also by Rao[5] using the potentiometric measurements. Holtzclaw[9] has reported the reverse order for the stability of the Ni(II) complexes i.e. acac > bzac > dbzm, on the basis of the polarographic measurements.

The discrepancy in results reported in the references quoted would seem to require measurement conditions which eliminate the intermolecular forces and also those between the solvent molecules i.e. the state of an ideal gas. For this purpose the following thermodynamical cycle was proposed for calculations of enthalpy changes in the gaseous state for reaction (1)

$$Ni_{(g)} + 2\,L_{(g)} \rightarrow NiL_{2(g)} + H_{2(g)} \quad \Delta H_{chel} \qquad (1)$$
$$NiL_{2(g)} \rightarrow NiL_{2(c)} \quad \Delta H_s$$
$$H_{2(g)} \rightarrow 2\,HCl_{(g)} \quad 2\Delta H_1$$
$$2\,HCl_{(g)} \rightarrow 2\,HCl_{\infty}H_2O_{(l)} \quad 2\Delta H_2$$
$$Ni_{(c)} \rightarrow Ni_{(g)} \quad \Delta H_{s1}$$
$$NiCl_{2(c)} \rightarrow Ni_{(c)} \quad \Delta H_3$$
$$NiCl_2 \cdot 6H_2O_{(c)} \rightarrow NiCl_{2(c)} \quad \Delta H_4$$
$$2\,L_{(g)}(\text{keto–enol}) \rightarrow 2\,L_{(g)}(\text{enol}) \quad 2\Delta H_5$$
$$2\,L_{(l)\ \text{or}\ (c)} \rightarrow 2\,L_{(g)}(\text{keto–enol}) \quad 2\Delta H_6$$
$$NiL_{2(c)} + 2\,HCl_{\infty}H_2O_{(l)} \rightarrow NiCl_2 \cdot 6H_2O_{(c)} + 2\,L_{(l)\ \text{or}\ (c)} + \infty H_2O_{(l)} \quad \Delta H_x$$

From Hess's law the following expression was derived:

$$\Delta H_{chel} = \Delta H_x + \Delta H_s + 2\Delta H_1 + 2\Delta H_2 + \Delta H_{s1} + \Delta H_3 + \Delta H_4 + 2\Delta H_5 + 2\Delta H_6$$

The enthalpy change ΔH_x was derived from the measurement of successive heats of dissolution of products and the reaction of parent substances in the appropriate solvent

$$NiL_{2(c)} + \text{solvent} \rightarrow \text{solution } A_1 \quad \Delta H_7$$
$$HCl_{\infty}H_2O_{(l)} \rightarrow 4.36\,M\ HCl \quad \Delta H_8$$
$$4.36\,M\ HCl_{(l)} + \text{solution } A_1 \rightarrow \text{solution } A_2 \quad \Delta H_9$$
$$L_{(c)} + \text{solvent} \rightarrow \text{solution } B_1 \quad \Delta H_{10}$$
$$NiCl_2 \cdot 6H_2O_{(c)} + \text{solution } B_1 \rightarrow \text{solution } B_2 \quad \Delta H_{11}$$

At the carefully preserved stoichiometry, solutions A_2 and B_2 are thermodynamically equivalent, hence

$$\Delta H_x = \Delta H_7 + 2\Delta H_8 + 2\Delta H_9 - 2\Delta H_{10} - \Delta H_{11}$$

EXPERIMENTAL

Measurements were carried out in the sensitive calorimeter designed according to the Johansson model[10]; its accuracy was 10^{-4}°C. The calorimetric bowl was the glass Dewar, the solution volume was 100–120 ml. Corrected temperature variations were determined graphically from the calorimetric curve obtained from the recorder, according to the Dickinson method. The heat of dissolution of KCl in water was found to be equal to $+4.192 \pm 0.008$ kcal mole^{-1} which is in agreement with the literature data[11]. β-Diketonates prepared by the methods described in ref. 12 were purified by repeated recrystallizations and dried under high vacuum. The contents of Ni, C and H was determined

Ni acac$_2$	— Calc.:	22.85% Ni,	46.8% C,	5.5% H
	Found:	22.85% Ni,	47.3% C,	5.7% H

Ni $bzac_2$ — Calc.: 15.41% Ni, 63.0% C, 4.8% H
Found: 15.53% Ni, 62.5% C, 5.2% H
Ni $dbzm_2$ — Calc.: 11.62% Ni, 71.3% C, 4.4% H
Found: 11.50% Ni, 71.5% C, 4.7% H

β-Diketones

Acetylacetone analytical grade (Schuchardt) was dried over dehydrated Na_2SO_4 and distilled taking before measurements. The fraction boiling from 135 to 136°C was used.

Benzoylacetone (Schuchardt) was recrystallized repeatedly from ethanol.

Dibenzoylmethane (L. Light and Co. Ltd.) was recrystallized from methanol.

RESULTS AND DISCUSSION

β-Diketones under examination decompose in concentrated inorganic acids into the Ni^{2+} ion and the free ligand. Decomposition reactions were the basis for the calculation of the enthalpy of complex formation. 4.36 M HCl was used as solvent for Ni $acac_2$ and Ni $bzac_2$ and for Ni $dbzm_2$ a solution containing 75% by volume dioxane and 25% by volume 70% H_2SO_4. The results of calorimetric measurements are summarized in the Tables 1–8.

TABLE 1

HEAT OF DISSOLUTION OF Ni $acac_2$ IN 4.36 M HCl

n *(mmole)*	*Q* *(cal)*	$-\Delta H_7$ *(kcal mole^{-1})*
0.3156	0.364	1.153
0.4406	0.524	1.189
0.4608	0.551	1.195
0.5223	0.611	1.170
0.5932	0.711	1.198

$\Delta H_7 = -1.181 \pm 0.008$ kcal mole^{-1}

TABLE 2

HEAT OF DISSOLUTION OF $NiCl_2 \cdot 6H_2O$ IN 4.36 M HCl

n *(mmole*	*Q* *(cal)*	ΔH_{11} *(kcal mole^{-1})*
0.23179	1.188	5.125
0.26083	1.333	5.111
0.29305	1.495	5.101
0.30121	1.498	4.973
0.40217	2.078	5.167

$\Delta H_{11} = +5.095 \pm 0.032$ kcal mole^{-1}

TABLE 3

HEAT OF DISSOLUTION OF acac IN THE SOLUTION OF $NiCl_2\ 6H_2O$

n (*mmole*)	Q (*cal*)	$-\Delta H_{10}$ (*kcal mole*$^{-1}$)
0.5214	0.170	0.326
0.5214	0.171	0.328
0.5853	0.190	0.325
0.6023	0.197	0.328
0.8789	0.286	0.325

$\Delta H_{10} = -0.326 \pm 0.001$ kcal mole^{-1}

TABLE 4

HEAT OF DISSOLUTION OF Ni $bzac_2$ IN 4.36 M HCl

n (*mmole*)	Q (*cal*)	$-\Delta H_7$ (*kcal mole*$^{-1}$)
0.23197	4.166	17.959
0.26099	4.699	18.004
0.29308	5.270	17.981
0.30119	5.437	18.052
0.40220	7.249	18.023

$\Delta H_7 = -18.004 \pm 0.020$ kcal mole^{-1}

TABLE 5

HEAT OF DISSOLUTION OF Ni $dbzm_2$ IN A SOLVENT

n (*mmole*)	Q (*cal*)	$-\Delta H_7$ (*kcal mole*$^{-1}$)
0.02892	0.1426	4.932
0.04026	0.1908	4.740
0.05809	0.2916	5.020
0.06755	0.3126	4.628
0.06973	0.3159	4.531

$\Delta H_7 = -4.770 \pm 0.073$ kcal mole^{-1}

TABLE 6

HEAT OF DISSOLUTION OF 4.36 M HCl IN A_1 SOLUTION

n (*mmole*)	Q (*cal*)	$-\Delta H_9$ (*kcal mole*$^{-1}$)
0.05668	0.9958	17.568
0.07848	1.3999	17.837
0.08720	1.5295	17.540
0.11336	1.9974	17.620
0.13516	2.4175	17.886

$\Delta H_9 = -17.690 \pm 0.07$ kcal mole^{-1}

TABLE 7

HEAT OF DISSOLUTION OF dbzm IN A SOLVENT

n (*mmole*)	*Q* (*cal*)	ΔH_{10} (*kcal mole*$^{-1}$)
0.05596	0.2997	5.356
0.08008	0.4238	5.292
0.09801	0.5325	5.433
0.12601	0.6665	5.289
0.13239	0.6810	5.144

$\Delta H_{10} = +\ 5.303 \pm 0.048$ kcal mole^{-1}

TABLE 8

HEAT OF DISSOLUTION OF $NiCl_2 \cdot 6H_2O$ IN B_1 SOLUTION

n (*mmole*)	*Q* (*cal*)	ΔH_{11} (*kcal mole*$^{-1}$)
0.05120	0.0603	1.178
0.06609	0.0795	1.203
0.06870	0.0765	1.113
0.08136	0.0948	1.165
0.09583	0.1086	1.133

$\Delta H_{11} = +\ 1.158 \pm 0.016$ kcal mole^{-1}

Benzoylacetone is insoluble in 4.36 M HCl and hence, for Ni bzac$_2$ $\Delta H_{10} = 0$. From the available literature data:

ΔH_f^0 $NiCl_2 \cdot 6H_2O_{(c)} = -505.8$ kcal mole^{-1} [13]
ΔH_f^0 acac$_{(l)} = -101.32 \pm 0.36$ kcal mole^{-1} [14]
ΔH_f^0 bzac$_{(c)} = -81.2 \pm 1.1$ kcal mole^{-1} [13]
ΔH_f^0 dbzm$_{(c)} = -53.60 \pm 0.40$ kcal mole^{-1} [15]
ΔH_f^0 $HCl_{\infty}H_2O_{(l)} = -39.96 \pm 0.05$ kcal mole^{-1} [13]
ΔH_f^0 HCl 4.36 $M_{(l)} = -38.90 \pm 0.05$ kcal mole^{-1} [16]
ΔH_f^0 $H_2O_{(l)} = -68.314 \pm 0.01$ kcal mole^{-1} [13]

and from the calculated ΔH_x values, the standard enthalpies of formation of the complexes in the solid phase have been calculated:

ΔH_f^0 Ni acac$_{2(c)} = -215.1 \pm 0.5$ kcal mole^{-1}
ΔH_f^0 Ni bzac$_{2(c)} = -157.4 \pm 1.0$ kcal mole^{-1}
ΔH_f^0 Ni dbzm$_{2(c)} = -73.4 \pm 1.5$ kcal mole^{-1}

TABLE 9

THE LITERATURE DATA AND CALCULATED ΔH_{chel} VALUES IN KCAL MOLE^{-1}

Complex	ΔH_s	ΔH_1	ΔH_2	ΔH_{s1}	ΔH_3	ΔH_4	ΔH_5	ΔH_6	ΔH_{chel}
Ni acac$_2$	-16.5^a	-22.6^c	-17.9^d	102.8^e	75.5^f	20.42^g	-0.20^h	9.82^j	-116.9
Ni bzac$_2$	-10.1^a	-22.6^c	-17.9^d	102.8^e	75.5^f	20.42^g	-0.20^i	20.0^k	-126.2
Ni dbzm$_2$	-7.0^b	-22.6^c	-17.9^d	102.8^e	75.5^f	20.42^g	-0.20^i	18.0^l	-96.5

[a] Ref. 17. [b] Estimated. [c, d, g] Ref. 13. [e] Ref. 18. [f] Ref. 19. [h] Ref. 20. [i] Assumed to be equal to that for acac. [j] Ref. 21. [k] Ref. 22. [l] Ref. 23.

The available literature data (Table 9) enabled us to calculated the heat of the hypothetical process of complex formation (1) in gaseous state — ΔH_{chel}.

From the suggestions by Berg et al.[17], that the heat of sublimation of the Ni(II) chelates depends on the type of substituent in the R_1–CO–CH_2–CO–R_2 ligand and increases in the series: methyl > thionyl > phuryl > phenyl, the heat of sublimation of Ni dbzm$_2$ was estimated to be equal to 7.0 ± 3.0 kcal mole^{-1}.

The complex formation process in the gaseous phase could be considered either as a radical process

$$Ni_{(g)} + 2\,L^{\cdot}_{(g)} \rightarrow NiL_{2(g)} \qquad \Delta H_{fR} \tag{2}$$

or an ionic one

$$Ni^{2+}_{(g)} + 2\,L^{-}_{(g)} \rightarrow NiL_{2(g)} \qquad \Delta H_{fI} \tag{3}$$

Enthalpy changes ΔH_{fR} can be calculated from the known heat of formation of radicals. Hill et al.[24] have calculated the heat of formation of the acetylacetone radical as equal to −38.6 kcal mole^{-1} assuming the dissociation energy of the O–H bond in acetylacetone D($C_5H_7O_2$–H) to be 105 ±5 kcal mole^{-1}. This estimation was made on the basis of the known dissociation energy of the O–H bond in acetic acid and methanol D(CH_3COO–H) and D(CH_3O–H) equal to 110 kcal mole^{-1} and 100 kcal mole^{-1}, respectively.

The detailed analysis of the influence of the aromatic ring on the O–H bond energy in numerous aromatic compounds[15, 25, 26] led us to the general conclusion that its presence results in a decrease of the bond dissociation energy in comparison with the aliphatic compounds. On this basis the dissociation energy of the O–H bond in benzoylacetone and dibenzoylmethane was calculated as 98±5 kcal mole^{-1} and 92±5 kcal mole^{-1}, respectively. The heats of formation of radicals calculated from the above values are equal to $\Delta H_f\ C_{10}H_9O^{\cdot}_{2(g)} = -15.3 \pm 6.0$ kcal mole^{-1}, $\Delta H_f\ C_{15}H_{11}O^{\cdot}_{2(g)} = 4.3 \pm 5.4$ kcal mole^{-1}.

The enthalpy change ΔH_{fI} of process (3) was defined from the relation[27]:

$$\Delta H_{fI} = \Delta H_{fR} + \sum_{i=1}^{2} I_i + 2.\frac{5}{2}RT - 2\,E_L$$

TABLE 10

THE ΔH_{fR}, ΔH_{fI} VALUES AND Ni–O BOND ENERGIES IN KCAL MOLE^{-1}

Complex	$-\Delta H_{fR}$	$-\Delta H_{fI}$	E_R(Ni–O)	E_I(Ni–O)
Ni $acac_2$	224.2	899.4	56.0	224.8
Ni $bzac_2$	219.5	894.7	54.9	223.7
Ni $dbzm_2$	177.8	853.0	44.4	213.2

where

$\sum_{i=1}^{2} I_i$ is the overall ionization potential of Ni (610.63 kcal mole^{-1}) and E_L is the electron affinity of the ligands assumed to be equal to the electron affinity of oxygen 33.78 kcal mole^{-1} [28].

The ΔH_{fR} and ΔH_{fI} values are summarized in the Table 10.

The Me(II) β-diketonates exhibit the tendency for polymerisation[29]. The non-aqueous Ni(II) acetylacetonate is a trimer in the solid phase[4] and in concentrated solutions[30] at room temperature. The Ni(II) complexes formed with benzoylacetone and dibenzoylmethane are also trimers in the solid phase, which was confirmed by spectrophotometric analysis and molecular weight measurements[31, 6]. Since the calculated enthalpy changes of complex formation ΔH_{fR} and ΔH_{fI}, being the measure of the Ni–O bond energy, are related to the gaseous phase processes, it is necessary to know the structure of the examined complexes in that phase. The Ni(II) acetylacetonate is a monomer in the gaseous phase[2, 32]. Since the trimers Ni_3bzac_6 and Ni_3dbzm_6 are less stable than Ni_3acac_6 [6] and have a tendency to be transformed into monomers at slight changes in temperature and when the solution is diluted[33], these complexes in the gaseous phase should also be considered as monomers. Assuming the equivalency of all four bondings, the Ni–O bond energy was calculated for the radical E_R and ionic E_I complex formation process (Table 10).

The E_R(Ni–O) bond energy value, lower than that of E_I(Ni–O), seems to illustrate that complex dissociation is more probably a radical process and should be considered as a real measure of the Ni–ligand bond stability.

The determined bond energy values indicate that the presence of an aromatic ring in a ligand reduces the Ni–O bond energies in the order Ni $acac_2$ > Ni $bzac_2$ > Ni $dbzm_2$.

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