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Thermochemistry of dioxouranium(VI) β-diketonates. Pentane-2,4-dionate and 1-phenylbutane-1,3-dionate

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Abstract

The standard molar enthalpies of formation of crystalline dioxouranium(VI) (uranyl(VI)) chelate complexes with pentane-2,4-dione (acetylacetone, HACAC) and 1-phenylbutane-1,3-dione (benzoylacetone, HBZAC) were determined by a solution–reaction calorimetry method. The following values of $\Delta H^{\ominus}_{f(c)}$ (kJ mol^{-1}) were obtained: $UO_2(ACAC)_2 \cdot H_2O$: -2260.1 ± 3.2; $UO_2(BZAC)_2 \cdot H_2O$: -1959.2 ± 6.0.

The enthalpies of the hypothetical gas phase dissociation reactions $UO_2L_2(g) = UO_2(g) + 2L^{\cdot}(g)$ and $UO_2L_2(g) = UO_2^{2+}(g) + 2L^-(g)$ were determined, and uranium–ligand bond energies in the equatorial plane were derived.

INTRODUCTION

Our routine calorimetric investigations of the thermodynamic properties of the first-row transition metal β-diketonates were extended over the f-electron element chelates [1]. The present paper is the first of a series devoted to the studies of uranyl(VI) β-diketonates. The physicochemical and structural properties of uranyl acetylacetonate have been widely studied, beginning with its first synthesis [2]. Interest in uranium compounds intensified because of the development of nuclear techniques. Discovery of synergism in the solvent extraction of uranyl ion with β-diketone [3] was followed by studies in appropriate directions. The practical and theoretical aspects of investigations require the knowledge of the basic thermodynamic properties of chemical compounds. However, strikingly few papers deal with that problem. The thermochemical investigations of solid uranyl acetylacetonate undertaken by Wendlandt et al. [4] and extended by Sacconi and Paoletti [5] covered its heat of solvation. Jones et al. for the first time determined the standard enthalpy of formation of solid uranyl(VI) acetylacetonate by a static bomb

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calorimetry method [6]. That method, when applied to organometallic compounds, did not always lead to satisfactory results. For that reason, in the study reported here we have applied solution–reaction calorimetry to examine uranyl acetylacetonate and benzoylacetonate.

EXPERIMENTAL

The solution–reaction calorimeter, the precise isoperibol calorimeter, its equipment, testing and operation were described in [7].

Materials

AnalaR $UO_2(NO_3)_2 \cdot 6H_2O$ (Chemapol, Czechoslovakia) was recrystallized several times from water and stored over 40 wt% $H_2SO_{4(aq)}$.

$HNO_3 \cdot 34.159H_2O$ obtained by dilution of the concentrated acid was analysed alkalimetrically ($c_m = 1.5451$) and its density was determined pyknometrically ($d_{25} = 1.0482$).

4.36 M HCl was obtained by dilution of the concentrated acid and analysed alkalimetrically.

1,4-Dioxane was purified by a routine method [8].

Acetylacetone (Schuchardt) was purified by drying over anhydrous sodium sulphate, followed by distillation. The fraction boiling at 407–408 K was used for synthesis and measurements.

Benzoylacetone (Fluka AG) was repeatedly recrystallized from ethanol.

Chelates

Uranyl(VI) acetylacetonate monohydrate

To an aqueous solution of uranyl nitrate, $UO_2(NO_3)_2 \cdot 6H_2O$ (5 g), buffered by sodium acetate (1.64 g), was added dropwise acetylacetone (2.05 ml) with continuous stirring, followed by concentrated ammonia solution. The precipitated yellow complex was filtered off, dried in air at room temperature and then recrystallized from a water–ethanol mixture. The results (wt%) of the elemental analysis were U, 49.16; C, 24.60; H, 3.40; calculated for $UC_{10}H_{16}O_7$ were U, 48.95; C, 24.70; H, 3.32.

Uranyl(VI) benzoylacetonate monohydrate was obtained by the analogous route. An ethanol solution of ligand was applied. The results (wt%) of the elemental analysis were U, 39.12; C, 39.22; H, 3.40; calculated for $UC_{20}H_{20}O_7$: U, 39.00; C, 39.35; H, 3.30.

The compounds were analysed for uranium by gravimetry after conversion into U_3O_8 at 1173 K.

RESULTS AND DISCUSSION

The standard molar enthalpies of formation of monohydrates of the crystalline complexes studied were determined from the thermochemical formal decomposition reactions in nitric acid

$$\mathrm{UO_2L_2 \cdot H_2O(s) + 2HNO_3 \cdot 34.159H_2O(l) =}$$
$$\mathrm{UO_2(NO_3)_2 \cdot 6H_2O(s) + 2HL(l) \text{ or } (s) + 63.318H_2O(l)} \qquad (1)$$

The changes of enthalpy ΔH_r were calculated from the calorimetrically measured heats of the successive dissolution of stoichiometric amounts of the products and substrates of reaction (1) in the appropriate solvents (Table 1).

In the routine experiment the concentration of each complex was of the order of 3×10^{-4}–8×10^{-4} mol dm^{-3} and the heat capacity of the calorimeter was 430.0–440.0 J K^{-1}. With strictly preserved stoichiometry of reaction (1) the solutions A_2 and B_3 are thermodynamically equivalent. This was checked experimentally by mixing of solutions A_2 and B_3; no heat effect was observed. On that basis, from the Hess law the following values were calculated

$$\Delta H(1)_{(\mathrm{ACAC})} = \Delta H_1 + 2\Delta H_2 - \Delta H_3 - 2\Delta H_4 - 63.318\Delta H_5$$
$$= -15.69 \pm 0.21 \text{ kJ mol}^{-1}$$

$$\Delta H(1)_{(\mathrm{BZAC})} = \Delta H_6 + 2\Delta H_2 - \Delta H_3 - 2\Delta H_7 - 63.318\Delta H_5$$
$$= -53.75 \pm 0.36 \text{ kJ mol}^{-1}$$

The ΔH_2 and ΔH_5 values were found to be independent of the composition of solutions A_1 and B_2, respectively.

In the calculations of the standard molar enthalpies of formation of the complexes, the literature data of $\Delta H_f^{\ominus}$ (kJ mol^{-1}) were used, viz.

TABLE 1

Results of calorimetric measurements at 298.15 K

Reactant	Solvent	Solution	ΔH_i (kJ mol^{-1})[a]
1. $\mathrm{UO_2(ACAC)_2 \cdot H_2O(s)}$	HCl–dioxane	A_1	25.44 ± 0.12
2. $\mathrm{HNO_3 \cdot 34.159H_2O(l)}$	A_1	A_2	−43.50 ± 0.05
3. $\mathrm{UO_2(NO_3)_2 \cdot 6H_2O(s)}$	HCl–dioxane	B_1	23.16 ± 0.05
4. HACAC(l)	B_1	B_2	2.714 ± 0.007
5. $\mathrm{H_2O(l)}$	B_2	B_3	−1.176 ± 0.003
6. $\mathrm{UO_2(BZAC)_2 \cdot H_2O(s)}$	HCl–dioxane	A_1	37.65 ± 0.23
7. HBZAC(s)	B_1	B_2	27.85 ± 0.09

[a] The mean values from at least five measurements with the standard deviation of the mean.

$UO_2(NO_3)_2 \cdot 6H_2O(s)$: −3189.5 [9]; HACAC(l): −425.5 ± 1.0 [10]; HBZAC(s): −335.1 ± 2.8 [11]; $H_2O(l)$: −285.83 ± 0.04 [12]; $HNO_3 \cdot 34.159H_2O(l)$: −9931.46 [12]. The results are listed in Table 2.

The measured enthalpy values of addition of a water molecule to the solid uranyl acetylacetonate molecule

$$UO_2(ACAC)_2(s) + H_2O(l) = UO_2(ACAC)_2 \cdot H_2O(s) \qquad (2)$$

were equal to −13.47 [4] and $-16.11\ \text{kJ mol}^{-1}$ [5]. On the assumption of an average value of $-14.8 \pm 1.3\ \text{kJ mol}^{-1}$, the standard enthalpy of formation of the anhydrous chelate was calculated. The enthalpy of reaction (2) for uranyl dibenzoylmethanate is equal to $-16.57\ \text{kJ mol}^{-1}$ [5], which is indicative of the very weak effect of replacement of a methyl substituent by a phenyl moiety in the chelate ring of the complex on the addition enthalpy value. That was why the standard enthalpy of formation of the non-aqueous uranyl benzoylacetonate was calculated from the estimated $\Delta H(2) = -16.3 \pm 2.0\ \text{kJ mol}^{-1}$. The results are presented in Table 2.

The enthalpy value of formation of uranyl acetylacetonate calculated by us, ($-1959.4 \pm 3.5\ \text{kJ mol}^{-1}$) is drastically different from that originally reported by Jones, ($-1913\ \text{kJ mol}^{-1}$) [6]. In fact, this difference becomes larger if we use the newest recommended enthalpies of formation of U_3O_8, CO_2 and H_2O, together with the experimental original value of the heat of combustion, $5272.7\ \text{kJ mol}^{-1}$; the recalculated value is then $\Delta H_f^\ominus(UO_2(ACAC)_2) = -1855.7\ \text{kJ mol}^{-1}$.

Interesting information about the energy of metal–ligand interactions could be found from the heat effects of reaction in the gaseous phase. We refer especially to the enthalpies of complex dissociation reactions into the appropriate components

$$\text{radicals:} \quad UO_2L_2(g) = UO_2(g) + 2L^\cdot(g) \qquad (3)$$

$$\text{or ions:} \quad UO_2L_2(g) = UO_2^{2+}(g) + 2L^-(g) \qquad (4)$$

being measures of the mean uranyl–oxygen bond dissociation energy, $\bar{D}(UO_2\text{–}O)$, and that of the coordination bond, $\bar{D}_{CB}(UO_2\text{–}O)$, respectively.

TABLE 2

Thermochemical properties of uranyl(VI) β-diketonates (values in kJ mol^{-1})

Complex	$-\Delta H_{f(s)}^\ominus$	$-\Delta H_{f(g)}^\ominus$	ΔH_3	$\bar{D}(UO_2\text{–}O)$	ΔH_4	$\bar{D}_{CB}(UO_2\text{–}O)$
$UO_2(ACAC)_2 \cdot H_2O$	2260.1 ± 3.2					
$UO_2(ACAC)_2$	1959.4 ± 3.5	1619 ± 12	958 ± 42	246 ± 10	2595 ± 46	649 ± 12
$UO_2(BZAC)_2 \cdot H_2O$	2041.0 ± 6.2					
$UO_2(BZAC)_2$	1738.9 ± 6.3	1599 ± 12	1030 ± 42	257 ± 10	2640 ± 46	660 ± 12

Calculation of these enthalpies requires the knowledge of the sublimation enthalpy of the studied complexes. Because these values were unavailable, they were estimated to be 140 ± 5 kJ mol^{-1}. In the light of new reports [13], the ΔH_{sub} value estimated for $UO_2(ACAC)_2$ as 63 kJ mol^{-1} [6] seems indubitably to be too low. Enthalpies of reactions (3) and (4) were calculated using additionally the literature data for $\Delta H_f^{\ominus}$ (kJ mol^{-1}) UO_2(g): −466.3 ± 5.0 [14]; $ACAC^{\cdot}$(g): −184 ± 20 [15]; $BZAC^{\cdot}$(g): −51 ± 20 [15]; UO_2^{2+}(g): 1210 ± 20 [16]; $ACAC^{-}$(g): −217 ± 20 [15]; $BZAC^{-}$(g): −84 ± 20 [15].

Uranyl acetylacetonate monohydrate was the first example of a chelate of the unusual coordination number 7. Structural investigations revealed [17] that in $UO_2(ACAC)_2 \cdot H_2O$ the U–O bond lengths are 2.51 ± 0.07 Å for the oxygen atoms in the rings, 2.48 ± 0.07 Å for water oxygen and 1.60 ± 0.07 Å for the oxygen atoms in the uranyl group. However, in uranyl(VI) acetylacetonebis(acetylacetonate), $UO_2(ACAC)_2 \cdot HACAC$, the mean U–O bond distances are 2.401 Å in the chelate rings and 1.772 Å in the uranyl group [18].

No structural data are available for anhydrous uranyl acetyloacetonate, but the above results of structural investigations allowed us to assume the equivalence of uranium–oxygen bonds in the equatorial plane of $UO_2(ACAC)_2$, and to calculate their energies as one quarter of the enthalpy of the homolytic dissociation process (3). The formalism of such a definition of the bond energy results from the necessity of assumption that the U–O bond energies in UO_2 and uranyl chelates are transferable. Such an assumption is, however, controversial, because

(1) the U–O distances in the uranyl group of acetylacetonate are dissimilar to the U–O distances in UO_2 (2.36 Å); and

(2) the U–O bond energies in uranium oxides depend on their oxidation state, and in UO, UO_2 and UO_3 are equal to 828, 741 and 708 kJ mol^{-1}, respectively [19].

The "formal" bond energies listed in Table 2 were calculated for verification of the energy estimated by Jones et al. as 276 kJ mol^{-1} [6]. The discrepancy between our value and that calculated by Jones follows from the difference in the experimental standard enthalpies of formation of the complexes and from difference in auxiliary values used in the calculations.

A more realistic method of calculation of energy seems to be one based upon the following decomposition reaction

$$UO_2L_2(g) = U(g) + 2O(g) + 2L^{\cdot}(g) \qquad (5)$$

The enthalpies of reaction (5) calculated from $\Delta H_f^{\ominus}(U(g)) = 546.8 \pm 9.2$ kJ mol^{-1} [20] and $\Delta H_f^{\ominus}(O(g)) = 249.17 \pm 0.10$ kJ mol^{-1} [21] are the energies of all six uranium–oxygen bonds, and then $\Delta H(5) = 2\bar{D}(U\text{–}O)_{ox} + 4\bar{D}(U\text{–}O)_{comp}$.

The assumption that the oxidation state of uranium is the U–O bond energy determining factor in the uranyl group, i.e. $\bar{D}(\text{U–O})_{\text{ox}} = 708\ \text{kJ mol}^{-1}$ (average dissociation U–O bond energy in UO_3), allowed us to determine the U–O bond energy in the complexes as $\bar{D}(\text{U–O})_{\text{ACAC}} = 270 \pm 10\ \text{kJ mol}^{-1}$ and $\bar{D}(\text{U–O})_{\text{BZAC}} = 282 \pm 10\ \text{kJ mol}^{-1}$. The metal–oxygen bond energy values in the acetylacetonates of oxovanadium(IV) and dioxomolybdenum(VI) are available in the literature. After recalculation with the $\Delta H_f^{\ominus}(\text{ACAC}^{\cdot}(\text{g}))$ applied herein, these values would be equal to: $\bar{D}(\text{V–O})_{\text{ACAC}} = 252 \pm 10\ \text{kJ mol}^{-1}$ [22] and $\bar{D}(\text{Mo–O})_{\text{ACAC}} = 206 \pm 10\ \text{kJ mol}^{-1}$ [23]. Oxovanadium(IV) acetylacetonate has a different oxidation state and coordination number, and thus the energy of the V–O bond cannot be compared with that of the Mo–O and U–O bonds.

The octahedral structure of dioxomolybdenum(VI) acetylacetonate is strongly distorted. The compound contains the non-linear molybdyl group with an O–Mo–O angle equal to 105° [24]. This geometric hindrance is the reason why the Mo–O bond energy in the chelate ring is much lower than that of the U–O bond, although the Mo–O bonds (1.97–2.21 Å) are shorter than the U–O bonds. Observed changes in the metal–oxygen bond energy in oxides of the above discussed metals according to the oxidation state were similar to those in complexes with acetylacetone: $\bar{D}(\text{Mo–O})_{\text{MO}_3} = 590\ \text{kJ mol}^{-1}$; $\bar{D}(\text{V–O})_{\text{VO}_2} = 623\ \text{kJ mol}^{-1}$ and $\bar{D}(\text{U–O})_{\text{UO}_3} = 708\ \text{kJ mol}^{-1}$ [19].

REFERENCES

1 E. Giera and W. Kąkołowicz, J. Therm. Anal., 33 (1988) 977.
2 W. Biltz and J.A. Clinch, Z. Anorg. Chem., 40 (1904) 218.
3 J.R. Ferraro and T.V. Healy, J. Inorg. Nucl. Chem., 24 (1962) 1429, 1449, 1463 and references therein.
4 W.W. Wendlandt, J.L. Bear and G.R. Horton, J. Phys. Chem., 64 (1960) 1289.
5 L. Sacconi and P. Paoletti, J. Chem. Soc., (1961) 4250.
6 M.M. Jones, B.J. Yow and W.R. May, Inorg. Chem., 1 (1962) 166.
7 W. Kąkołowicz and E. Giera, J. Chem. Thermodyn., 15 (1983) 203.
8 A.I. Vogel, Practical Organic Chemistry, 3rd edn., Longman, London, 1956.
9 E.H.P. Cordfunke, J. Phys. Chem., 68 (1964) 3353.
10 J.M. Hacking and G. Pilcher, J. Chem. Thermodyn., 11 (1979) 1015.
11 M.L.C.C.H. Ferrao, M.A.V. Ribeiro da Silva, S. Suradi, G. Pilcher and H.A. Skinner, J. Chem. Thermodyn., 13 (1981) 567.
12 D.D. Wagman, W.H. Evans, V.B. Parker, I. Halow, S.B. Bailey and R.H. Schumm, US National Bureau of Standards, Selected Values of Chemical Thermodynamic Properties, US Government Printing Office, Washington, DC, 1968.
13 P.M. Burkinshaw and C.T. Mortimer, J. Chem. Soc. Dalton Trans., (1984) 75.
14 D.W. Green, Int. J. Thermophys., 1 (1980) 61.
15 E. Giera and W. Kąkołowicz, J. Therm. Anal., 33 (1988) 977.
16 Y. Marcus, J. Inorg. Nucl. Chem., 37 (1975) 493.
17 E. Frasson, G. Bombieri and C. Panattoni, Coord. Chem. Rev., 1 (1966) 145.
18 M. Lenner, Acta Crystallogr., Sect B, 35 (1979) 2396.
19 C. Glidewell, Inorg. Chim. Acta, 24 (1977) 149.

20 K. Klingerich, J. Chem. Phys., 51 (1969) 4433.
21 CODATA No. 6 (1971), No. 7 (1972).
22 E.H. Jamea and G. Pilcher, Thermochim. Acta, 97 (1986) 77.
23 G. Pilcher, K.J. Cavell, C.D. Garner and S. Parkes, J. Chem. Soc. Dalton Trans., (1978) 1311 and the attached errata.
24 O.H. Krasochka, Yu.A. Sokolova and L.O. Atovmyan, Zh. Strukt. Khim., 16 (1975) 696.