Thermodynamics of the Actinoid Elements. Part 6.[1] The Preparation and Heats of Formation of Some Sodium Uranates(VI)

Tze Chung Tso and David Brown*
Chemistry Division, A.E.R.E., Harwell, Oxfordshire OX11 0RA
Austin I. Judge and John H. Holloway
Department of Chemistry, University of Leicester, Leicester LE1 7RH
Jean Fuger
Laboratory of Analytical Chemistry and Radiochemistry, University of Liège (Sart Tilman), B-4000 Liège, Belgium

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The preparation of sodium uranates(VI) has been investigated by heating together appropriate amounts of Na_2O_2 and UO_2 and also by the thermal decomposition of complexes such as $Na_4U(C_2O_4)_4{\cdot}3H_2O$, $Na_4UO_2(CO_3)_3{\cdot}nH_2O$, $Na_2UO_2(C_2O_4)_2{\cdot}4H_2O$, and $NaUO_2(CH_3COO)_3$. The enthalpies of solution in 1.00 mol dm^{-3} HCl of high-purity samples of β-Na_4UO_5, α- and β-Na_2UO_4, and $Na_2U_2O_7$, prepared by the latter method, are -386.6 ± 0.6, -171.9 ± 0.4, -184.2 ± 0.4 and -171.8 ± 1.0 kJ mol^{-1}, respectively. The resulting enthalpies of formation, $-2\,457.3 \pm 2.8$, $-1\,901.3 \pm 2.3$, $-1\,889.0 \pm 2.3$, and $-3\,203.8 \pm 2.8$ kJ mol^{-1}, are discussed in relationship to published values. *X*-Ray powder diffraction studies appear to confirm the existence of α-Na_4UO_5.

Alkali-metal and alkaline-earth-metal uranates(VI) have been extensively investigated, see for example ref. 2 and 3, but relatively little is known about the properties of analogous transuranium-element compounds. This is particularly true for thermodynamic properties where the first data on neptunium(VI) and plutonium(VI) alkaline-earth-metal oxides have appeared recently[4,5] or have just been determined.[6] As a preliminary to work on alkali-metal neptunates(VI) and plutonates(VI) the preparation of selected high-purity sodium uranates(VI) has been explored with the dual aims of establishing reliable preparative methods which yield stoicheiometric oxides, and providing additional thermodynamic data in those instances where either only a single value was available or a discrepancy existed.

Investigations of the Na_2O_2–UO_2 reaction under a variety of conditions are described together with results on the thermal decomposition of the uranium-(IV) and -(VI) complexes $Na_4U(C_2O_4)_4{\cdot}3H_2O$, $NaUO_2(CH_3COO)_3$, $Na_2UO_2(C_2O_4)_2{\cdot}4H_2O$, and $Na_4UO_2(CO_3)_3{\cdot}nH_2O$. Using the latter technique high-purity samples of β-Na_4UO_5, α-Na_2UO_4, β-Na_2UO_4, and $Na_2U_2O_7$ have been prepared and their enthalpies of solution in 1 mol dm^{-3} HCl determined. The resulting enthalpies of formation are compared with available literature values.

Experimental

Reagents.—Sodium peroxide, Na_2O_2 (Alpha chemicals) (>99% purity), was used as purchased. Stoicheiometric uranium dioxide was provided by M. Mignanelli (Chemistry Division, A.E.R.E., Harwell). Sodium acetate, oxalate, and carbonate (AnalaR grade materials) were used without further purification. The compounds $U(C_2O_4)_2{\cdot}6H_2O$ and $UO_2(C_2O_4){\cdot}3H_2O$ were precipitated from aqueous oxalic acid solutions on addition of UCl_4 and UO_2Cl_2, respectively; $UO_2(CH_3COO)_2{\cdot}2H_2O$ was crystallised from a solution of UO_3 in hot, glacial acetic acid.

Uranium Complexes.—The compound $U(C_2O_4)_2{\cdot}6H_2O$ (1.29 g) was added to an aqueous solution of sodium oxalate (0.69 g). Complete dissolution was achieved by heating at 80 °C. After cooling the addition of methanol resulted in a *precipitate* of $Na_4U(C_2O_4)_4{\cdot}3H_2O$ which was isolated by centrifugation, washed with methanol, and vacuum dried at room temperature. Typical product analysis: Found, Na 12.6, U 32.3, 32.4; $Na_4U(C_2O_4)_4{\cdot}3H_2O$ requires Na 12.5, U 32.3%.

The compound $UO_2(C_2O_4){\cdot}3H_2O$ (2.25 g) was dissolved in a hot (80 °C) aqueous solution containing a 1:3 stoicheiometric molar excess of sodium oxalate. The solution was filtered and cooled; *crystals* of $Na_2UO_2(C_2O_4)_2{\cdot}4H_2O$ formed after several days. Typical product analysis: Found, Na 8.1, U 42.1; $Na_2UO_2(C_2O_4)_2{\cdot}4H_2O$ requires Na 8.15, U 42.2%.

Sodium acetate (0.82 g) was added to a hot solution of uranyl(VI) acetate (3.85 g) in glacial acetic acid containing ammonium acetate to assist dissolution. On cooling *crystals* of $NaUO_2(CH_3COO)_3$ separated: these were isolated by filtration, washed with a mixture of diethyl ether and ethanol, and vacuum dried. Typical product analysis: Found, Na 4.8, U 50.45, 50.2; $NaUO_2(CH_3COO)_3$ requires Na 4.9, U 50.65%.

Addition of an aqueous, saturated solution of Na_2CO_3 to uranyl(VI) nitrate (5.2 g) in water initially gave a yellow precipitate. This was redissolved by addition of just sufficient of the saturated Na_2CO_3 solution to give a clear solution, from which *crystals* of $Na_4UO_2(CO_3)_3{\cdot}nH_2O$ ($1.5 < n < 3.5$) were obtained on addition of methanol. The product was washed with small volumes of 50% aqueous methanol, methanol, and finally ether and air-dried at room temperature. The variable uranium analyses were attributed to different water contents of different preparations since U:Na mol ratios of 1:4 were found (*e.g.* Na 16.05, U 41.2%) and, as described later, uranium analyses showed that β-Na_4UO_5 was obtained on thermal decomposition of the products. This is supported by the absence of impurity reflections on the high-quality *X*-ray powder photographs of the various preparations of this sodium uranate(VI).

Samples of β-Na_4UO_5, α- and β-Na_2UO_4, and $Na_2U_2O_7$ used for calorimetric studies were prepared on the 100—300 mg scale by thermal decomposition of uranium-(IV) and -(VI) complexes in gold crucibles using the conditions given in Table 1. Reactions involving stoicheiometric amounts of Na_2O_2 and UO_2 (100—200 mg scale) for the formation of Na_4UO_5 and Na_2UO_4 were also done in gold crucibles *in vacuo* or in an argon, argon–oxygen, or oxygen atmosphere. Alternatively, evacuated, sealed silica ampoules were used to contain the reactants.

Table 1. Preparative conditions and analyses of the various sodium uranates(VI)

Compound	Preparation	Method	Analysis (%)[a]	
			U	Na
β-Na_4UO_5	I	$Na_4UO_2(CO_3)_3{\cdot}nH_2O$ at 800 °C in O_2 for 21.5 h	58.0, 57.9 (58.0)	 (22.4)
	II	$Na_4U(C_2O_4)_4{\cdot}3H_2O$ at 800 °C in O_2 for 19 h	58.0	22.4
α-Na_2UO_4	I	$Na_2UO_2(C_2O_4)_2{\cdot}4H_2O$ at 760 °C in O_2 for 19.5 h	68.5, 68.2 (68.4)	 (13.2)
	II	$Na_2UO_2(C_2O_4)_2{\cdot}4H_2O$ at 720 °C in O_2 for 22 h	68.3, 68.4	13.2
	III	$Na_2UO_2(C_2O_4)_2{\cdot}4H_2O$ at 760 °C in O_2 for 21 h	68.4, 68.2	13.2
β-Na_2UO_4	I	$Na_2UO_2(C_2O_4)_2{\cdot}4H_2O$ at 880 °C in O_2 for 22.5 h	68.3, 68.4	13.2
	II	$Na_2UO_2(C_2O_4)_2{\cdot}4H_2O$ at 900 °C in O_2 for 20 h	68.4, 68.4	13.2
$Na_2U_2O_7$	I	$NaUO_2(CH_3COO)_3$ at 650 °C in O_2 for 22.5 h	75.0, 75.1 (75.1)	7.1, 7.3 (7.3)
	II	$NaUO_2(CH_3COO)_3$ at 700 °C in O_2 for 19 h	74.9, 75.1	7.1, 7.2
	III	$NaUO_2(CH_3COO)_3$ at 800 °C in O_2 for 19 h	74.9, 75.1	7.1, 7.1
	IV	$NaUO_2(CH_3COO)_3$ at 800 °C in O_2 for 22 h	75.0, 75.1	7.2, 7.2
	V	$NaUO_2(CH_3COO)_3$ at 750 °C in O_2 for 16 h	*b*	*b*
	VI	$NaUO_2(CH_3COO)_3$ at 750 °C in O_2 for 2 h	74.1	7.3
	VII	$NaUO_2(CH_3COO)_3$ at 750 °C in O_2 for 2.5 h	75.1	7.4

[a] Theoretical values in parentheses. [b] Identified by *X*-ray powder diffraction analysis which showed the absence of impurity reflections.

Products were removed from the reaction vessels in a nitrogen glove-box (water and oxygen <20 p.p.m.) and all subsequent handling was done in nitrogen atmospheres.

Analyses.—Uranium was determined gravimetrically by heating precipitated hydrated oxides at >700 °C in air and weighing as U_3O_8. Sodium was determined by atomic absorption spectroscopy. Results are given in Table 1.

X-*Ray Measurements*.—*X*-Ray powder photographs were recorded as described previously.[7] Unit-cell dimensions were refined using the program COHEN.[8]

Enthalpies of Solution.—Measurements were made using two calorimeters: a vacuum-jacketed isoperibol microcalorimeter with a tantalum chamber, which has been described elsewhere,[9,*] and an air-jacketed isoperibol calorimeter (model 8700-1; LKB, Bromma, Sweden) with a glass vessel, and equipped with a Hewlett-Packard (San Diego, California) model 7131 A/B strip chart recorder. Details of calibration runs have been published.[10–12]

Samples were weighed, in the appropriate calorimetric ampoules, on a model GRAM electric balance (Cahn, Paramount, California); weights were reduced to weights *in vacuo*. The sodium uranates(VI) were handled in a dry, oxygen-free nitrogen atmosphere, which contained less than 10 p.p.m. water vapour (Alnor Dewpoint meter, Casella, London) and less than 10 p.p.m. oxygen (potential drop across a ZrO_2 membrane[13]).

Merck-titrated 1.000 mol dm^{-3} hydrochloric acid solutions were used for sample dissolution.

Units and Limits of Error.—The joule (J) is used throughout as the energy unit. All literature data originally reported in calories were recalculated using the conversion factor 1 cal (thermochemical) = 4.184 J. The ^{12}C scale of atomic weights[14] was used to calculate molecular weights. All the calorimetric measurements are reported for 298.15 ± 0.05 K.

Uncertainty limits on the mean of several identical measurements and representing the consistency of the measurements are based on the 95% confidence interval[15] except where stated (*cf*., Table 2). When combining the new results with data from other sources no attempt has been made to retain this limit; the error stated by the author has been accepted. The errors quoted for the calculated enthalpies of formation were obtained from the errors on the individual terms of the thermodynamic cycle used, according to a standard procedure.[16] Unless otherwise specified, auxiliary data recommended by CODATA or values consistent with the CODATA selection were employed.[17]

Results and Discussion

Preparation of Sodium Uranates(VI).—The compounds chosen for investigation were Na_4UO_5, α- and β-Na_2UO_4, and $Na_2U_2O_7$.

Initial studies of the preparation of Na_4UO_5 involved the interaction of UO_2 and Na_2O_2, stoicheiometric amounts (1:2) of which were intimately mixed by grinding prior to being heated in gold crucibles either *in vacuo*, or in argon, argon–oxygen mixtures, or oxygen at temperatures in the range 360—800 °C. At temperatures below 400 °C the deep red products were shown by *X*-ray powder diffraction analysis to be mixtures of sodium uranates(VI). Thus, for 36-h reactions (2 × 18 h with intermediate regrinding) done *in vacuo* or under argon the major phase could be indexed on the basis of a face-centred cubic (f.c.c.) unit cell, whilst the additional very weak reflections could be attributed to $Na_2U_2O_7$. For reactions done in oxygen–argon mixtures and in oxygen the changes in relative intensities of the reflections indicated that increasing amounts of $Na_2U_2O_7$ were being formed, presumably *via* reaction (1).

$$Na_2O_2\,(s) + 2\,UO_2\,(s) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow Na_2U_2O_7\,(s) \quad (1)$$

The unit-cell dimension of the f.c.c. phase [a = 4.764(1) Å] is very close to that reported by Keller[18] for a α-Na_4UO_5 (a = 4.766 Å), which he obtained by reaction of UO_3 with Na_2O at 400—450 °C. Although the existence of this phase has been queried by Cordfunke and Loopstra,[19] who obtained only β-Na_4UO_5 under the same conditions, the present crystallographic results appear to confirm that a low-temperature modification does exist and can also be obtained by reaction (2).

$$2Na_2O_2\,(s) + UO_2\,(s) \xrightarrow{360\,^{\circ}C} Na_4UO_5\,(s,\alpha) + \tfrac{1}{2}\,O_2\,(g) \quad (2)$$

For reaction periods of 100—120 h in an oxygen atmosphere the α-Na_4UO_5 was contaminated with β-Na_4UO_5 and larger amounts of $Na_2U_2O_7$ than in 36-h reactions, presumably due to reaction (3).

$$Na_2U_2O_7\,(s) + 3Na_2O_2\,(s) \longrightarrow 2Na_4UO_5\,(s,\beta) + \tfrac{3}{2}\,O_2\,(g) \quad (3)$$

Additional studies at 360 °C in evacuated, sealed silica ampoules yielded α-Na_4UO_5 mixed with $Na_2U_2O_7$ after 36 h,

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[*] Although the calorimeter chamber has remained unchanged, many modifications to the circuitry (timer, power source, *etc*.) have been made throughout the years.

Table 2. Enthalpies of solution of various sodium uranates(VI) in 1 mol dm^{-3} hydrochloric acid at 298.15 ± 0.10 K

Compound	Preparation	Experiment	Calorimeter[a]	Sample weight (mg)	Concentration of compound in solution (10^{-3} mol dm^{-3})	Enthalpy effect (J)	ΔH^b/kJ mol^{-1}
β-Na_4UO_5	I	1	A	4.024	1.155	3.8053	−387.7
		2		3.284	0.942	3.1005	−387.1
		3		3.952	1.134	3.7387	−387.9
		4		3.399	0.975	3.2074	−386.9
		5		5.048	1.449	4.7457	−385.4
		6		5.203	1.493	4.9084	−386.8
	II	1	B	11.930	1.164	11.253	−386.7
		2		13.630	1.330	12.827	−385.8
		3		16.430	1.603	15.464	−385.9
		4		16.425	1.602	15.464	−386.0
						Average:	−386.6 ± 0.6
α-Na_2UO_4	I	1	A	8.457	2.850	4.1692	−171.7
		2		9.406	3.180	4.6605	−172.4
		3		7.642	2.583	3.8022	−173.1
		4		6.556	2.216	3.2538	−172.7
		5		7.594	2.567	3.7595	−172.3
	II	1	A	5.767	1.950	2.8412	−171.5
		2		9.011	3.046	4.4512	−171.9
		3		5.971	2.019	2.9470	−171.8
		4		6.076	2.054	3.0220	−172.0
		5		5.744	1.942	2.8227	−171.0
	III	1	B(1)	37.175	1.068	18.322	−171.5
		2		34.600	0.994	17.118	−172.2
		3		29.600	0.880	14.514	−170.6
						Average:	−171.9 ± 0.4
β-Na_2UO_4	I	1	A	7.005	2.385	3.7290	−183.9
		2		5.508	1.862	2.9097	−183.8
		3		7.909	2.674	4.1853	−184.2
	II	1	B(1)	33.120	0.952	17.529	−184.2
		2		24.980	0.718	13.254	−184.6
		3		38.795	1.115	20.575	−184.6
						Average:	−184.2 ± 0.4
$Na_2U_2O_7$	I	1	B	10.650	0.672	2.866	−170.6
		2		19.910	1.256	5.372	−171.1
		3		20.905	1.319	5.612	−170.2
		4		18.215	1.149	4.896	−170.4
	II	1	B(1)	28.025	0.442	7.549	−170.8
	IV	1	B(1)	53.16	0.838	14.434	−172.2
		2		56.76	0.895	15.491	−173.0
		3		52.42	0.827	14.326	−173.3
		4		47.83	0.754	13.053	−173.0
		5		72.22	1.139	19.679	−172.8
	V	1	B(1)	41.61	0.656	11.194	−170.6
		2		48.84	0.770	13.329	−173.0
		3		39.16	0.618	10.571	−171.2
	VI	1	B(1)	46.53	0.734	12.585	−171.5
		2		40.14	0.633	10.923	−172.5
	VII	1	B(1)	49.57	0.782	13.504	−172.7
		2		53.63	0.846	14.519	−171.6
		3		60.87	0.960	16.480	−171.7
						Average:	−171.8 ± 1.0[c]

[a] A, microcalorimeter; B, LKB, 25 cm^3; B(1), LKB, 100 cm^3. [b] Represents ΔH_5, ΔH_6, $\Delta H_{6'}$, and ΔH_7, respectively, for the dissolution of β-Na_4UO_5, α-Na_2UO_4, β-Na_2UO_4, and $Na_2U_2O_7$. [c] Uncertainty limits increased to account for a slight discrepancy between the solution data for preparation I and for the others.

but with reaction periods of 94 h α-Na_2UO_4 was also present, probably due to the interaction of α-Na_4UO_5 and the diuranate, according to reaction (4).

$$Na_4UO_5\,(s,\alpha) + Na_2U_2O_7\,(s) \longrightarrow 3Na_2UO_4\,(s,\alpha) \quad (4)$$

The interaction of Na_2O_2 and UO_2 at 800 °C in oxygen gave salmon coloured β-Na_4UO_5 but according to *X*-ray powder diffraction analysis the product was always contaminated with a small amount of β-Na_2UO_4. The reaction of 630 °C *in vacuo* gave a mixture of β-Na_4UO_5, $Na_2U_2O_7$, and α-Na_2UO_4.

Although β-Na_4UO_5 appears to be stable up to 950 °C in oxygen, it decomposes in argon at temperatures as low as 750 °C, with the formation of α-Na_2UO_4.

The direct preparation of Na_2UO_4 has been examined *via* the interaction of equimolar amounts of Na_2O_2 and UO_2. At temperatures between 600 and 760 °C α-Na_2UO_4 was formed in both argon and oxygen but the products were contaminated with $Na_2U_2O_7$, the amount of impurity being less in an oxygen atmosphere. The compound β-Na_2UO_4, which is formed at *ca.* 860 °C in oxygen, was essentially pure according to the *X*-ray powder pattern of the product. An alternative reaction involving 1:1 mol ratios of β-Na_4UO_5 and UO_2 at 700 °C in oxygen resulted in the formation of almost pure α-Na_2UO_4 after 63 h, only traces of unreacted β-Na_4UO_5 being indicated by *X*-ray powder diffraction analysis; β-Na_2UO_4 of similar purity was obtained at *ca.* 800 °C.

The somewhat lower temperature observed for the formation of β-Na_2UO_4 (*ca.* 800 °C) than reported previously[19–21] (*ca.* 900 °C) may be attributed to the prolonged heating periods during the present study during which the α ⟶ β conversion was found to be complete only after >40 h.

Attempts to repeat the reported preparation[19,22] of Na_2UO_4 by heating together UO_3 and Na_2CO_3 in dry air have been unsuccessful. Thus, even after >120 h at temperatures in the range 760—800 °C the product was still contaminated with $Na_2U_2O_7$ and Na_2CO_3.

Although 'almost pure' phases have been obtained in certain instances, it is apparent from the foregoing discussion that oxide interactions and, in the case of Na_2UO_4, uranium oxide–sodium carbonate reactions, are not completely satisfactory for the preparation of sodium uranates(VI) of the high purity required for thermodynamic studies. This may be attributed to factors such as difficulties in ensuring intimate mixing of the reagents, the relative ease with which $Na_2U_2O_7$ is formed, and the side reactions it may undergo with, for example, Na_2O_2 and Na_4UO_5. In addition, the various UO_2–Na_2O_2 reactions all involve prolonged reaction periods, often at elevated temperatures, and require frequent regrinding of the mixture.

In view of the difficulties encountered in obtaining pure sodium uranates(VI) from the above reactions, and since in subsequent studies it is intended to extend the scope of the investigations to include other alkali metals as well as the actinide elements neptunium and plutonium, alternative preparative routes have been explored. These involved the preparation of uranium-(IV) and -(VI) complexes with different Na:U ratios followed by thermal decomposition in oxygen.

The complexes studied, all of which were prepared by crystallisation as opposed to precipitation as fine powders, were $Na_4U(C_2O_4)_4 \cdot 3H_2O$, $Na_4UO_2(CO_3)_3 \cdot nH_2O$ (*n* varied between 1.5 and 3.5 depending on the extent of drying), $Na_2UO_2(C_2O_4)_2 \cdot 4H_2O$, and $NaUO_2(CH_3COO)_3$. Preliminary d.t.a. and t.g.a. studies indicated that these compounds decomposed in the temperature range 300—400 °C. In order to obtain highly crystalline sodium uranates(VI) the temperatures chosen for decomposition in oxygen were somewhat higher than these as indicated in Table 1, which also gives the heating periods employed. The products, β-Na_4UO_5, α- and β-Na_2UO_4, and $Na_2U_2O_7$, were all single phases according to *X*-ray powder diffraction analysis and, as shown in Table 1, the analytical results were in good agreement with theoretical values.

Enthalpies of Solution and Formation.—Table 2 shows the results obtained for dissolution of the various sodium uranates(VI) in 1 mol dm^{-3} hydrochloric acid. The dissolution reactions can be represented by equations (5), (6), (6′) and (7),

$$Na_4UO_5\,(s,\beta) + \{a\,HCl, b\,H_2O\} \longrightarrow \{4\,NaCl, UO_2Cl_2, (a-6)HCl, (b+3)H_2O\};\ \Delta H_5 \quad (5)$$

$$\begin{array}{l} Na_2UO_4\,(s,\alpha) + \{a\,HCl, b\,H_2O\} \searrow \\ Na_2UO_4\,(s,\beta) + \{a\,HCl, b\,H_2O\} \nearrow \end{array} \{2\,NaCl, UO_2Cl_2, (a-4)HCl, (b+2)H_2O\};$$

$$\Delta H_6 \text{ for the } \alpha \text{ phase, } \Delta H_{6'} \text{ for the } \beta \text{ phase} \quad (6), (6')$$

$$Na_2U_2O_7\,(s) + \{a\,HCl, b\,H_2O\} \longrightarrow \{2\,NaCl, 2\,UO_2Cl_2, (a-6)HCl, (b+3)H_2O\};\ \Delta H_7 \quad (7)$$

respectively, with $b/a = 54.4$ and *a* ranging from *ca.* 400 to 2 500.

The enthalpy of formation at 298 K of the various uranates(VI), according to reactions (8), (9), (9′), and (10),

$$4\,Na\,(s) + U\,(s,\alpha) + \tfrac{5}{2}\,O_2\,(g) \longrightarrow Na_4UO_5\,(s,\beta);\ \Delta H_8 \quad (8)$$

$$2\,Na\,(s) + U\,(s,\alpha) + 2\,O_2\,(g) \begin{array}{l} \nearrow Na_2UO_4\,(s,\alpha);\ \Delta H_9 \quad (9) \\ \searrow Na_2UO_4\,(s,\beta);\ \Delta H_{9'} \quad (9') \end{array}$$

$$2\,Na\,(s) + 2\,U\,(s,\alpha) + \tfrac{7}{2}\,O_2\,(g) \longrightarrow Na_2U_2O_7\,(s);\ \Delta H_{10} \quad (10)$$

respectively, are calculated from the enthalpies of solution and the relationships (11)—(16). In these calculations, ΔH_{11}, the

$$Na\,(s) + \tfrac{1}{2}\,Cl_2\,(g) \longrightarrow NaCl\,(s);\ \Delta H_{11} \quad (11)$$

$$NaCl\,(s) + \{a\,HCl, b\,H_2O\} \longrightarrow \{NaCl, a\,HCl, b\,H_2O\};\ \Delta H_{12} \quad (12)$$

$$U\,(s,\alpha) + O_2\,(g) + Cl_2\,(g) \longrightarrow UO_2Cl_2\,(s);\ \Delta H_{13} \quad (13)$$

$$UO_2Cl_2\,(s) + \{a\,HCl, b\,H_2O\} \longrightarrow \{UO_2Cl_2, a\,HCl, b\,H_2O\};\ \Delta H_{14} \quad (14)$$

$$H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) + \{a\,HCl, b\,H_2O\} \longrightarrow \{a\,HCl, (b+1)H_2O\};\ \Delta H_{15} \quad (15)$$

$$\tfrac{1}{2}\,H_2\,(g) + \tfrac{1}{2}\,Cl_2\,(g) + \{a\,HCl, b\,H_2O\} \longrightarrow \{(a+1)HCl, b\,H_2O\};\ \Delta H_{16} \quad (16)$$

standard enthalpy of formation of NaCl (s),[23] −411.26 ± 0.11 kJ mol^{-1}, and ΔH_{13}, the standard enthalpy of formation of UO_2Cl_2 (s),[24] −1 243.6 ± 1.2 kJ mol^{-1}, are taken from the literature; ΔH_{15} and ΔH_{16} represent the partial molar enthalpy of formation of water and hydrochloric acid in 1 mol dm^{-3} HCl, respectively, −285.85 ± 0.04 and −164.36 ± 0.10 kJ mol^{-1}.[24] All these data are compatible with the CODATA selections.[17]

For ΔH_{12}, the enthalpy of solution of NaCl (s) in 1 mol dm^{-3} HCl, the average of 4.60 ± 0.40 kJ mol^{-1} (for a final solution *ca.* 10^{-2} mol dm^{-3} in NaCl), as given by O'Hare *et al.*[25] and 4.31 ± 0.40 kJ mol^{-1} (for a final solution *ca.* 3 × 10^{-3} mol dm^{-3} in NaCl), as obtained in the present study from three concordant measurements, has been used; thus ΔH_{12} = 4.46 ± 0.40 kJ mol^{-1}. The enthalpy of solution of UO_2Cl_2 (s) in 1 mol dm^{-3} HCl, ΔH_{14}, is taken as −101.7 ± 1.7 kJ mol^{-1} as recommended by Parker[24] for a solution <10^{-3} mol dm^{-3} in UO_2Cl_2.

Table 3. Crystallographic data for sodium uranates(VI)

Compound	Preparation[a]	Symmetry[b]	Unit-cell dimensions a/Å	b/Å	c/Å	β/°
α-Na_4UO_5		C	4.764(1)			
β-Na_4UO_5	I	T	7.556(1)		4.639(1)	
	II		7.557(1)		4.638(1)	
α-Na_2UO_4	I	O	9.767(1)	5.731(1)	3.498(1)	
β-Na_2UO_4	II	O	5.979(1)	5.813(1)	11.726(1)	
$Na_2U_2O_7$	IV	M	12.794(3)	7.828(2)	6.888(3)	111.44(3)

[a] Preparation number refers to Table 1. [b] C = Cubic, T = tetragonal, O = orthorhombic, and M = monoclinic.

In combining equations (11)—(16) with (5), (6), (6′), and (7) to obtain the standard enthalpies of formation of the various uranates, the small dilution effects due to the water and HCl formation or depletion in 1 mol dm^{-3} HCl have been assumed to be negligible: this customary practice is quite acceptable in view of the fact that in all instances the uranium concentration in the solutes remains quite low ($< 3 \times 10^{-3}$ mol dm^{-3}). The influence of the presence of these small uranium concentrations on the various terms (ΔH_{12}, ΔH_{15}, and ΔH_{16}) of the thermodynamic cycle used to obtain the enthalpies of formation of the uranates has also been neglected. These are obtained according to relations (A)—(D).

$$\Delta H_f^\circ (Na_4UO_5, s,\beta) = \Delta H_8 = 4\,\Delta H_{11} + 4\,\Delta H_{12} + \Delta H_{13} + \Delta H_{14} + 3\,\Delta H_{15} - 6\,\Delta H_{16} - \Delta H_5 = -2\,457.3 \pm 2.8 \text{ kJ mol}^{-1} \quad \text{(A)}$$

$$\Delta H_f^\circ (Na_2UO_4, s,\alpha) = \Delta H_9 = 2\,\Delta H_{11} + 2\,\Delta H_{12} + \Delta H_{13} + \Delta H_{14} + 2\,\Delta H_{15} - 4\,\Delta H_{16} - \Delta H_6 = -1\,901.3 \pm 2.3 \text{ kJ mol}^{-1} \quad \text{(B)}$$

$$\Delta H_f^\circ (Na_2UO_4, s,\beta) = \Delta H_{9'} = 2\,\Delta H_{11} + 2\,\Delta H_{12} + \Delta H_{13} + \Delta H_{14} + 2\,\Delta H_{15} - 4\,\Delta H_{16} - \Delta H_{6'} = -1\,889.0 \pm 2.3 \text{ kJ mol}^{-1} \quad \text{(C)}$$

$$\Delta H_f^\circ (Na_2U_2O_7, s) = \Delta H_{10} = 2\,\Delta H_{11} + 2\,\Delta H_{12} + 2\,\Delta H_{13} + 2\,\Delta H_{14} + 3\,\Delta H_{15} - 6\,\Delta H_{16} - \Delta H_7 = -3\,203.8 \pm 2.8 \text{ kJ mol}^{-1} \quad \text{(D)}$$

The present result for ΔH_f° (Na_4UO_5, s,β), $-2\,457.3 \pm 2.8$ kJ mol^{-1}, is in very moderate agreement with the value of $-2\,450.6 \pm 2.1$ kJ mol^{-1} based on the enthalpy of solution of this compound in 6 mol dm^{-3} HNO_3 obtained by Cordfunke and Loopstra[19] and recalculated by Cordfunke and O'Hare[26] using CODATA-compatible auxiliary values. Our value for ΔH_f° (Na_2UO_4, s,α), $-1\,901.3 \pm 2.3$ kJ mol^{-1}, compares with the value $-1\,897.3 \pm 1.1$ kJ mol^{-1} recently reported by Cordfunke *et al.*[22] based on measurements in 1.505 mol dm^{-3} H_2SO_4. The latter result superseded two earlier literature values, obtained by the same group of authors, which, after recalculation using CODATA compatible auxiliary values yielded $-1\,889.9 \pm 2.1$ kJ mol^{-1} (based on a cycle involving 6 mol dm^{-3} HNO_3)[19] and $-1\,887.8 \pm 2.1$ kJ mol^{-1} (based on a cycle involving 0.1 mol dm^{-3} HCl).[27] According to Cordfunke *et al.*[22] the less negative value obtained for the data in 0.1 mol dm^{-3} HCl is due to the fact that the UO_2Cl_2 sample used in that cycle was hydrated.

The difference between the enthalpies of solution of α- and β-Na_2UO_4, obtained in this study, $+12.3 \pm 0.6$ kJ mol^{-1}, which reflects the difference in the enthalpies of formation of the two crystallographic forms of this compound, is in marginal agreement with the value of 13.85 ± 0.04 reported by O'Hare *et al.*[25] In view of the use of the same media by these authors and ourselves, it appears obvious that the small difference in the two sets of data may be due to small variations in the sample nature. The present data and the result of O'Hare *et al.*[25] establish with a reasonable accuracy the enthalpy difference between β- and α-Na_2UO_4, a question which required resolution[26] in view of the early value given by Cordfunke and Loopstra,[19] $+6.2 \pm 0.4$ kJ mol^{-1}.

Our value for ΔH_f° ($Na_2U_2O_7$, s), $-3\,203.8 \pm 2.8$ kJ mol^{-1}, diverges somewhat from the values published earlier by Cordfunke and Loopstra[19] and Cordfunke *et al.*[22] Those investigations, using CODATA-compatible auxiliary data, yield $-3\,194.5 \pm 2.1$ kJ mol^{-1} (based on a cycle[19] involving 6 mol dm^{-3} HNO_3) and $-3\,194.8 \pm 1.8$ kJ mol^{-1} (based on cycle[22] involving 1.505 mol dm^{-3} H_2SO_4). In view of the care taken to characterise the samples used in the various studies and in our case to report data based on multiple (six) preparations, we believe that the difference between our results and the previous data may be due to unidentified inconsistencies in the auxiliary data used in the various thermodynamic cycles. This opinion is supported by the fact that recently O'Hare[28] obtained a value of -172.4 ± 2.0 kJ mol^{-1} for the enthalpy of solution in 1 mol dm^{-3} HCl, of part of the $Na_2U_2O_7$ sample employed by Cordfunke *et al.*[22] for their determination in 1.505 mol dm^{-3} H_2SO_4. This value in 1 mol dm^{-3} HCl is in excellent agreement with our own result of -171.8 ± 1.0 kJ mol^{-1} for the same medium.

Crystallographic Results.—Unit-cell dimensions obtained for 'α-Na_4UO_5' prepared by the interaction of UO_2 and Na_2O_2 at *ca.* 360 °C and for α-Na_2UO_4, β-Na_2UO_4, and $Na_2U_2O_7$ samples prepared by this method and by thermal decomposition of the complexes are in good agreement with published values.[3] The results listed in Table 3 for samples used for determination of enthalpies of solution are typical of those obtained.

Conclusions

Thermal decomposition of uranium-(IV) and -(VI) complexes such as $Na_4UO_2(CO_3)_3{\cdot}nH_2O$ ($1.5 < n < 3.5$), $Na_4U(C_2O_4)_4{\cdot}3H_2O$, $Na_2UO_2(C_2O_4)_2{\cdot}4H_2O$, and $NaUO_2(CH_3COO)_3$ in oxygen provides convenient routes to the high-purity sodium uranates(VI), β-Na_4UO_5, α- and β-Na_2UO_4, and $Na_2U_2O_7$. This method appears to be more convenient and more reliable than Na_2O_2–UO_2 interactions.

The enthalpies of formation reported, based on enthalpies of solution of compounds prepared by thermal decomposition methods, reveal small differences compared with literature data either as assessed by Cordfunke and O'Hare[26] or published more recently;[22] it is unlikely, however, in view of the efforts to characterise the samples fully, that in all instances sample variation is the major cause for these differences.

The results for α- and β-Na_2UO_4 agree reasonably well with those recalculated[26] on the basis of the results of O'Hare *et al.*[25] and therefore provide confirmation of the enthalpy of the α ⟶ β transition for this compound.

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