

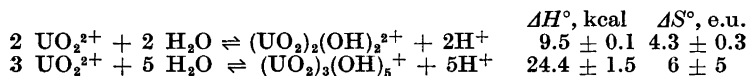
## Thermochemical Studies of Hydrolytic Reactions

### 8. A Recalculation of Calorimeter Data on Uranyl Hydrolysis

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The calorimeter data, reported in 1962 by one of the authors (K.S.), on uranyl hydrolysis in the medium 3 M NaClO<sub>4</sub> at 25°C have been recalculated by means of the computer program LETAGROPVRID. The following results were obtained (deviations 3σ):



In the preceding paper in this series<sup>1</sup> a recalculation of data from enthalpy titrations on hydrolysed iron(III) perchlorate solutions was reported. Similar titrations were made on hydrolysed uranyl perchlorate solutions, in the concentration range 5–100 mM (UO<sub>2</sub>)<sub>total</sub>, in the medium 3 M NaClO<sub>4</sub> at 25°C.<sup>2</sup> Using the preliminary equilibrium constants given by Hietanen<sup>3</sup> the heats of formation of the different uranyl hydrolysis products were calculated by successive approximations, using graphical methods. The uranyl data have now been recalculated in the same manner as the iron(III) data, by means of the computer program LETAGROPVRID.<sup>4,5</sup>

#### THE LETAGROPVRID TREATMENT

We write  $\beta_{p,q}$  for the equilibrium constant and  $\Delta H_{p,q}$  for the enthalpy change of



The formulas and equilibrium constants of the complexes in the medium 3 M NaClO<sub>4</sub> at 25°C have been determined with emf methods by Hietanen and Sillén.<sup>6</sup> They explained their emf data by assuming the complexes (UO<sub>2</sub>)<sub>q</sub>(OH)<sub>p</sub><sup>(2q-p)+</sup> with the (p,q) values (2,2), (4,3), (5,3) and (6,4) and the equilibrium constants  $\beta_{2,2} = 9.6 \times 10^{-7}$  M,  $\beta_{4,3} = 1.5 \times 10^{-14}$  M<sup>2</sup>,  $\beta_{5,3} = 2.9 \times 10^{-17}$  M<sup>3</sup> and  $\beta_{6,4} = 6 \times 10^{-20}$  M<sup>3</sup>.

By means of the computer program LETAGROPVRID we tried to find the enthalpies  $\Delta H_{pq}$ , and the corrections,  $\delta H_0$ , to the analytical hydrogen excess  $H_0$  in the initial solutions, that minimized the error square sum:

$$U = \sum (Q_{\text{calc}} - Q_{\text{exp}})^2$$

$Q_{\text{exp}}$  is the measured heat. The results of the LETAGROPVRID treatment are summarized in Table 1. The deviations given in the table are  $\sigma$ , the standard deviation calculated by LETAGROPVRID.  $\sigma_Q$  is the standard deviation in the measured quantity,  $Q_{\text{exp}}$ .

Table 1. Results of LETAGROPVRID treatment.

Calculation No.	a) $\Delta H_{pq}$ , $\beta_{pq}$ and $\sigma_Q$					Schlyter (1962)
	I	II	III	IV		
$\Delta H_{22}$ , kcal	9.52 $\pm$ 0.03	9.52 $\pm$ 0.02	9.47 $\pm$ 0.01	9.46 $\pm$ 0.02	9.44 $\pm$ 0.11	
$\Delta H_{53}$ , kcal	24.4 $\pm$ 0.5	24.4 $\pm$ 0.4	24.6 $\pm$ 0.5	24.6 $\pm$ 0.1	25 $\pm$ 2	
$\Delta H_{43}$ , kcal	1 $\pm$ 8	15.9 $\pm$ 0.7	—	—	18 $\pm$ 5	
$\Delta H_{64}$ , kcal	28 $\pm$ 3.4	—	22.6 $\pm$ 1.5	—	24 $\pm$ 5	
$10^7 \beta_{22}$	9.6	9.2	9.6	9.5 $\pm$ 0.3	9.3	
$10^{17} \beta_{53}$	2.9	2.9	2.9	2.9 $\pm$ 0.2	2.8	
$10^{14} \beta_{43}$	1.5	9	—	—	6.3	
$10^{20} \beta_{64}$	6	—	7	—	3.8	
$\sigma_Q$ , cal	0.055	0.055	0.056	0.056		

Expt. No.	b) $\delta H_0$					
	1	2	3	4	5	6
$\delta H_0$ , mM (LETAGROPVRID)	-1.7 $\pm$ 0.1	-1.3 $\pm$ 0.1	-0.8 $\pm$ 0.05	-0.5 $\pm$ 0.05	-0.3 $\pm$ 0.05	-0.2 $\pm$ 0.05
$\delta H_0$ , mM (Schlyter, 1962)	-1.6	-1.4	-0.7	-0.4	-0.3	-0.3

## DISCUSSION

When all four  $\Delta H_{pq}$  were treated as unknown constants together with the  $\delta H_0$ , then  $\Delta H_{43}$  and  $\Delta H_{64}$  came out with high  $\sigma$  (column I, Table 1a). Calculations were then performed with different combinations of the complexes, leaving out one or both of the minor species (4,3) and (6,4). In these calculations the  $\beta_{pq}$  of the remaining complexes were either taken from the LETAGROPVRID treatment of the emf data in Ref. 8 or were treated as unknown parameters. The results are given in columns II, III, and IV in Table 1a. It should be noted that the equilibrium constants  $\beta_{22}$  and  $\beta_{53}$  could be determined independently from the enthalpy titrations (column IV) when the species (4,3) and (6,4) were neglected.

The corrections  $\delta H_0$  obtained from the LETAGROPVRID treatment are given in Table 1b. They agree very well with those estimated graphically by Schlyter.

From the results in Table 1a we may conclude that  $\Delta H_{22}$  and  $\Delta H_{53}$  have the values  $\Delta H_{22} = 9.5 \pm 0.1$  kcal/mole and  $\Delta H_{53} = 24.4 \pm 1.5$  kcal/mole (with  $3\sigma$ ), irrespective of what assumptions are made about the presence of additional minor species. These values agree very well with those reported in 1962. Further Baes and Meyer <sup>7</sup> have obtained  $\Delta H_{22} = 10.2$  and  $\Delta H_{53} = 25.1$  kcal/mole from the temperature coefficient between 25°C and 94.4°C in 0.5 M (K)NO<sub>3</sub> medium.

Before discussing the values for  $\Delta H_{43}$  and  $\Delta H_{64}$  it should be pointed out that the emf data on uranyl hydrolysis <sup>6</sup> could be interpreted in several alternative ways with approximately the same fit (for discussion see Ref. 8): with only the (4,3) species, with only the (6,4) species, or with both (4,3) and (6,4). In this situation it is of course somewhat dubious to try to calculate  $\Delta H_{43}$  and  $\Delta H_{64}$ . The values  $\Delta H_{43} = 15.9$  kcal and  $\Delta H_{64} = 22.6$  kcal obtained in calculations II and III in the table could perhaps be regarded as minimum values;  $\Delta H_{43}$  was calculated neglecting (6,4) and  $\Delta H_{64}$  was calculated neglecting (4,3). Considering that the values for  $\Delta H_{22}$  and  $\Delta H_{53}$  suggest a constancy of  $\Delta H$  per OH<sup>-</sup> bound (or H<sup>+</sup> ion produced) of about 5 kcal/mole for the uranylhydroxocomplexes we might perhaps expect  $\Delta H_{43} \approx 20$  kcal and  $\Delta H_{64} \approx 30$  kcal.

The thermochemical data for the two main hydrolytic reactions of the uranyl ion in 3 M (Na)ClO<sub>4</sub> at 25°C are:

Reaction	$\Delta G^\circ$ , kcal	$\Delta H^\circ$ , kcal	$\Delta S^\circ$ , e.u.
$2\text{UO}_2^{2+} + 2\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_2(\text{OH})_2^{2+} + 2\text{H}^+$	$8.21 \pm 0.03$	$9.5 \pm 0.1$	$4.3 \pm 0.3$
$3\text{UO}_2^{2+} + 5\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$	$22.56 \pm 0.04$	$24.4 \pm 1.5$	$6 \pm 5$

The entropy changes associated with the reactions above are small; the position of the equilibria are almost entirely determined by the enthalpy terms.

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