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LETTER

Thermodynamics of the Aqueous Coordination of Thorium with the Iodate Anion

P. M. GRANT, W. F. KINARD* and P. A. BAISDEN

Nuclear Chemistry Division, L-234, Lawrence Livermore National Laboratory, Livermore, CA 94550 (U.S.A.)

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Recent calorimetric measurements in our laboratory have resulted in enthalpy and entropy values for three thorium complexes with fluoride [1] as well as for thorium complexes with a variety of amine-*N*-polycarboxylic acids [2]. The study of thorium coordination thermodynamics is of interest to us because Th(IV) is a useful model for Pu(IV) chemistry [3, 4] without the attendant radiation hazards.

The ligand under investigation in the present work is iodate. Iodic acid belongs to an important group of intermediate-strength electrolytes [5], and we report here the results of a study of the aqueous complexation of the thorium cation with iodate species.

Experimental

A 0.02 M Th^{4+} working solution was synthesized from 99.99%-pure starting material (Spex Industries), acidified to pH 1.2 with $HClO_4$, and adjusted to ionic strength $\mu = 0.5$ M with $NaClO_4$. The titrant employed was 0.1 M $NaIO_3$ at pH 7.0 and $\mu = 0.5$ M ($NaClO_4$). Details of solution synthesis and characterization have been given elsewhere [6], and all materials were of analytical reagent-grade quality or better.

The quasi-adiabatic titration calorimeter used in this work has been described previously [7]. The initial volume of the Th^{4+} calorimeter solution was 50.0 ml, while the titrant was typically added in 0.20 to 0.50 ml aliquots. The complete range of metal–ligand speciation up to the point of $Th(IO_3)_4$ precipitation was sampled in these experiments, and precipitation occurred at an average ligand number $\bar{n} \sim 0.25$ in this system.

Experiments were also performed to measure the enthalpy of formation of HIO_3: the $NaIO_3$ solution was titrated into $\mu = 0.5$ M, pH = 1.4 $HClO_4$ to determine ΔH_{011}. (The indices '011' refer to the number of atoms of metal, hydrogen and ligand, respectively, in the complex; thus, '101' indicates the reaction $M + L \rightleftharpoons ML$, '011' indicates $H + L \rightleftharpoons HL$, etc.) Heat of dilution or blank runs were accomplished by titrating 0.5 M $NaClO_4$ solution with iodate.

All calorimetry experiments were conducted at 25.00 ± 0.01 °C, with temperature stability of the thermostat maintained to ±0.0003 °C.

Results and Discussion

Low solution pH was required to prevent metal hydrolysis reactions, and HIO_3 formation could thus compete with thorium–ligand reactions during calorimeter experiments. The apportionment of measured heats into dilution, acid and metal contributions has been described in detail elsewhere, as has the requisite computation of detailed solution speciation by non-linear regression [1]. Stability constants for three thorium iodate complexes at $\mu = 0.5$ M ($NaClO_4$) and $T = 25$ °C were taken from Day and Stoughton [8]. The HIO_3 acid constant was obtained from Bonner and Prichard, and is the average of two ion-exchange determinations at $\mu = 0.45$ M [9]. All stability constant data utilized for the speciation calculations are summarized in Table 1.

TABLE 1. Stability constants used to calculate general solution speciation at $\mu = 0.5$ M and $T = 25$ °C

Constant	Value	Reference
HIO_3 $\log \beta_{011}$	0.46 ± 0.02	9
$Th(IO_3)^{3+}$ $\log \beta_{101}$	2.88 ± 0.05	8
$Th(IO_3)_2^{2+}$ $\log \beta_{102}$	4.79 ± 0.07	8
$Th(IO_3)_3^{+}$ $\log \beta_{103}$	7.15 ± 0.1	8
pK_w	13.74 ± 0.02	10

Empirical heats were corrected for HIO_3 formation from the computed change in moles of acid (Δn_{011}) and the value $\Delta H_{011} = (7.1 \pm 1.2)$ kJ/mol. The latter datum was obtained in separate calorimeter runs in our laboratory and is the result of 20 independent measurements. Previous literature values for ΔH_{011} are (2.8 ± 0.5) kJ/mol at $\mu = 0$ [5, 10]

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*Permanent address: Department of Chemistry, College of Charleston, Charleston, SC 29424, U.S.A.

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and (4.6 ± 0.02) kJ/mol in an ideal 1 M standard state [11].

Under the experimental conditions reported here, empirical heats generated by the thorium iodate system were small and fell in the nonlinear-response region of the calorimeter below 200 mJ [7]. Thus, as previously described [1, 7], normalization of the thorium iodate data to the protonation enthalpy of the Tris primary calibration standard was effected. Reaction enthalpies were then calculated from the calorimeter and speciation data via multivariate, non-linear least-squares analysis [1].

The thermodynamic data for the thorium iodate system at $\mu = 0.5$ M are summarized in Table 2. The enthalpy data are the results of 33 independent determinations, and are from five separate calorimeter runs that spanned a range of a factor of six in measured heat. The errors reported here are 1σ standard deviation and reflect only uncertainties in the calorimeter temperature measurements. Specific detail on analysis techniques and error propagation has been given elsewhere [6, 7]. Since uncertainties in the speciation-computation input parameters have not been included, our reported errors are minimum values associated with these experiments.

We were able to reliably extract only the first two reaction enthalpies from our data, probably the result of the onset of $Th(IO_3)_4$ precipitation occurring at such small $\bar{n}$ values. While reasonable confidence is placed in the value for ΔH_{101} (6% reported uncertainty), a similar statement cannot be made for ΔH_{102} (>100% error). The only prior literature reference to $Th(IO_3)_x$ enthalpy measurements of which we are aware is an unpublished value [12] for ΔH_{101} at 25 °C and $\mu = 1$ M cited in ref. 13. That value of 6.5 ± 0.4 kJ/mol is more endothermic by a factor of two than the result reported here.

TABLE 2. Thermodynamic parameters for the $Th(IO_3)_x$ system at $T = 25$ °C and $\mu = 0.5$ M ($NaClO_4$)

Complex	i	$-\Delta G_{10i}$[a] (kJ/mol)	ΔH_{10i} (kJ/mol)	ΔS_{10i} (J/mol K)
$Th(IO_3)^{3+}$	1	16.4 ± 0.3	3.3 ± 0.2	66 ± 1
$Th(IO_3)_2^{2+}$	2	27.3 ± 0.4	4 ± 5	100 ± 20
$Th(IO_3)_3^{+}$	3	40.8 ± 0.6		

[a] Ref. 8.

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