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Note

The heats of deaquation and anation of $[Cr(NH_3)_5H_2O]X_3$ complexes

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The heats of deaquation and anation for the reaction,

$$[Cr(NH_3)_5H_2O]X_3(c) \xrightarrow{\Delta} [Cr(NH_3)_5X]X_2(c) + H_2O(g) \qquad (1)$$

were first obtained by Wendlandt and Bear[1] using a DTA technique. They found ΔH values of 6.1 ± 0.5, 7.8 ± 0.6, and 6.3 ± 0.5 kcal/mole, for the chloride, bromide, and iodide complexes, respectively. Also using DTA, Tsuchiya *et al.*[2] obtained somewhat higher ΔH values, 6.1, 9.0, and 10.8 kcal/mole for the above complexes, respectively. Still higher values were obtained for the nitrate, sulfate, and sulfite complexes.

We whish to report here new ΔH values for the deaquation–anation reactions which reveal new information concerning the nature of these reactions. The ΔH measurements were obtained by conventional quantitative differential thermal analysis (QDTA) using open and sealed-capillary tube sample holders[3].

EXPERIMENTAL

Apparatus

The DTA apparatus has previously been described[3]. Sample sizes ranged in mass from 3 to 4 mg and were studied using a heating rate of 5 °C/min. The calibration procedure and peak-area determination have previously been described[3].

Preparation of compounds

The complexes were prepared according to previously described methods[4]. Water contents of the complexes were determined by mass-loss on the thermobalance. The water contents found were: chloride, 6.68% found, 6.88% theor.; bromide, 4.54% found, 4.56% theor.; iodide, 3.50% found, 3.36% theor.; nitrate, 5.32% found, 5.27% theor.

RESULTS AND DISCUSSION

The open and sealed-capillary tube DTA curves of $[Cr(NH_3)_5H_2O]Br_3$ are shown in Fig. 1. The curves for the other complexes were similar to those for the bromide complex so they will not be shown here.

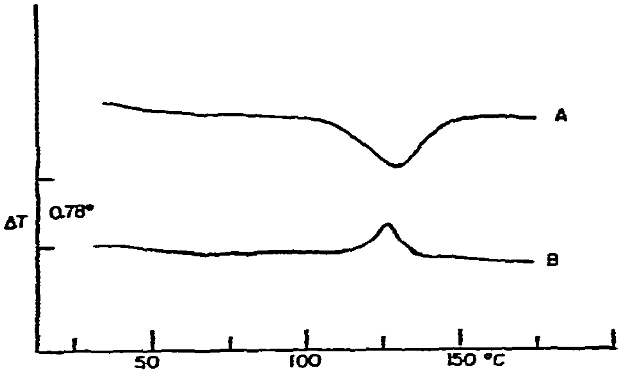

Fig. 1. Open and sealed-tube DTA curves of $[Cr(NH_3)_5H_2O]Br_3$; (A) open tube; (B) sealed tube.

The open-tube DTA curves show the characteristic single endothermic peak for the deaquation–anation reaction which is similar to those previously reported[1,2]. The reaction involved is that given by Eqn. (1). In the sealed-tube curve, instead of an endothermic peak, and *exothermic* peak was obtained. Because of the sealed tube, which prevents the escape of the evolved water, the reaction involved is:

$$[Cr(NH_3)_5H_2O]X_3(c) \xrightarrow{\Delta} [Cr(NH_3)_5X]X_2(c) + H_2O\ (l) \qquad (2)$$

The ΔH values obtained and the ΔT_{min} and ΔT_{max} values for each system are given in Table I.

TABLE I

HEATS OF DEAQUATION AND ANATION OF CHROMIUM COMPLEXES

Compound	*Open tube*		*Sealed tube*	
	ΔT_{min}(°C)	ΔH(*kcal/mole*)	ΔT_{max}(°C)	ΔH(*kcal/mole*)
$[Cr(NH_3)_5H_2O]Cl_3$	116	4.2±0.4	117	−3.1±0.3
$[Cr(NH_3)_5H_2O]Br_3$	130	5.9±0.4	127	−1.4±0.1
$[Cr(NH_3)_5H_2O]I_3$	150	4.8±0.4	140	−1.3±0.1
$[Cr(NH_3)_5H_2O](NO_3)_3$	115	3.8±0.4	115	3.1±0.3

The open-tube QDTA ΔH values were somewhat lower than those previously obtained[1,2]. The values are all within the general range of 4–6 kcal/mole and do not change very much with change in anion. However, in the case of the sealed-tube systems, there was a pronounced change in the ΔH values obtained. The sealed-tube results clearly indicated the nature of the deaquation–anation reactions in that there is a Cr^{3+}——OH_2 bond-breaking reaction which is endothermic and a Cr^{3+}——X bond-making reaction which is exothermic. Assuming little or no change in the crystal lattice energies for the aquo- and aniono-pentammine-complexes, the latter reaction has a much larger ΔH than the former. Contrary to the halo-compounds, the nitrate complex has a positive ΔH for both systems.

At the present time, the mechanism of the deaquation–anation reaction is not known. If the rate determining step is the Cr^{3+}——OH_2 bond breaking, then the reaction is of the S_N1 type. Tsuchiya *et al.*[2] stated that based on the E_a values obtained for the overall reaction, there was a tendency for a S_N2 reaction in the case of the complexes containing the larger anions, such as bromide, sulfate, and sulfite.

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