A THERMOANALYTICAL INVESTIGATION OF THE THERMAL DEAQUATION OF $BaCl_2 \cdot 2H_2O$ AND $BaBr_2 \cdot 2H_2O$

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SUMMARY

The thermal deaquation reactions of $BaCl_2 \cdot 2H_2O$ and $BaBr_2 \cdot 2H_2O$ were studied by TG, high sensitivity DTA, and open and sealed tube DTA. In each of the TG curves, only two mass-losses were observed. The DTA curves, however, were more complex in that more than one peak was observed for each deaquation reaction. An attempt was made to interpret the DTA deaquation peaks and also to determine the ΔH of the water evolution process for both compounds.

A number of investigations have been reported[1-5] concerning the thermal deaquation reactions of the barium halide hydrates, $BaCl_2 \cdot 2H_2O$ and $BaBr_2 \cdot 2H_2O$. For each compound, the water molecules were evolved in separate steps in which the second water molecule was removed at a considerably higher temperature than the first. There has been some disagreement in the literature concerning the exact nature of the first deaquation reaction. In 1957, on the basis of DTA measurements, Borchardt and Daniels[1] reported the presence of a quadruple point during the deaquation of the bromide salt. Three DTA peaks were observed, the first of which corresponded to the reaction,

$$BaBr_2 \cdot 2H_2O(s) \rightarrow BaBr_2 \cdot H_2O(s) + H_2O(l)$$

The second peak was due to the vaporization of the liquid water and the third to the simultaneous deaquation and vaporization of the remaining water of hydration. No analogous quadruple point was observed for the compound, $BaCl_2 \cdot 2H_2O$. Only two DTA peaks were observed, each due to the simultaneous deaquation and vaporization of one molecule of water of hydration.

Recent DTA data, however, revealed only two peaks for both $BaCl_2 \cdot 2H_2O$ and $BaBr_2 \cdot 2H_2O$[2]. In this same investigation, electrical conductivity curves showed that liquid water was present over a short temperature range during the deaquation of the first molecule of water for both salts. Thus the existence of a quadruple point was confirmed for both systems. The deaquation and vaporization temperatures, however, were so close together that the two reactions were not resolved by DTA measurements at atmospheric pressure. The temperatures and pressures of the quadruple points were[6]: $BaCl_2 \cdot 2H_2O$, 101.9°C, 684 mm; $BaBr_2 \cdot 2H_2O$, 107.9°C,

664 mm. At low pressures, $BaCl_2 \cdot 2H_2O$, $BaCl_2 \cdot H_2O$, $BaCl_2$, and liquid water may coexist[7]. At higher pressures, quadruple points for the $BaCl_2 \cdot 2H_2O$ system can be detected although the system is more complicated since two crystalline forms of each of the 2-hydrate and the 1-hydrate are obtained[8]. Apparently, even a 1/2-hydrate exists[9].

Because of the disagreement concerning the exact nature of the deaquation reactions of $BaCl_2 \cdot 2H_2O$ and $BaBr_2 \cdot 2H_2O$ at atmospheric pressure, these reactions were reinvestigated by the use of TG, quantitative DTA, and high sensitivity DTA techniques.

EXPERIMENTAL

Metal salt hydrate samples

Finely ground $BaCl_2 \cdot 2H_2O$ and $BaBr_2 \cdot 2H_2O$ of analytical reagent grade quality were used in this investigation.

DTA apparatus

The high sensitivity block-type DTA apparatus was a modified DuPont Thermograph. The DTA curves were displayed on a X–Y recorder rather than the conventional multiplexed strip-chart recorder. The samples, contained in 1.6–1.8 mm I.D. glass capillary tubes, ranged in mass from 10 to 20 mg. A heating rate of about 5°C/min was employed.

The quantitative DTA studies were carried out on the apparatus previously described[14].

Thermobalance

The thermogravimetry studies were carried out using a DuPont Model 950 thermogravimetric analyzer. A dynamic atmosphere of either dry or water saturated nitrogen and heating rates of 2.5, 5, and 10°C/min were employed. The samples ranged in mass from 5 to 10 mg.

RESULTS AND DISCUSSION

The TG curves for $BaCl_2 \cdot 2H_2O$ are illustrated in Fig. 1, while those for $BaBr_2 \cdot 2H_2O$ are shown in Fig. 2. Curves are presented for heating rates of 2.5, 5, and 10°C/min in both dry and water saturated dynamic nitrogen atmospheres. In each case, two distinct mass losses were observed; one for the loss of each of the two hydrated water molecules. As previously observed for other deaquation reactions[10], the reaction temperatures increased with increasing heating rate and the presence of water vapor in the furnace atmosphere. The reasons for these observed trends are probably similar to those previously given for other deaquation reactions[10,11]. Also, as previously observed[12], the TG curves obtained in a water saturated atmosphere were considerably more clearly resolved than those obtained using a dry atmosphere.
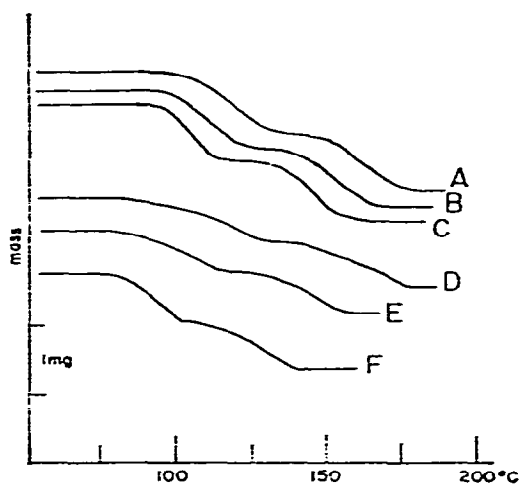
Fig. 1. TG curves of $BaCl_2 \cdot 2H_2O$. A, 10°C/min, water saturated N_2; B, 5°C/min, water saturated N_2; C, 2.5°C/min, water saturated N_2; D, 10°C/min, dry N_2; E, 5°C/min, dry N_2; F, 2.5°C/min, dry N_2.
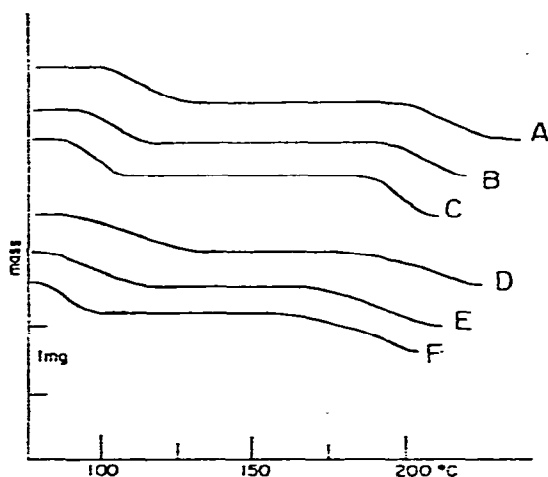
Fig. 2. TG curves of $BaBr_2 \cdot 2H_2O$. A, 10°C/min, water saturated N_2; B, 5°C/min, water saturated N_2; C, 2.5°C/min, water saturated N_2; D, 10°C/min, dry N_2; E, 5°C/min, dry N_2; F, 2.5°C/min, dry N_2.

The DTA curves for $BaCl_2 \cdot 2H_2O$ and $BaBr_2 \cdot 2H_2O$ are illustrated in Fig. 3. For $BaCl_2 \cdot 2H_2O$, two peaks can clearly be seen for the loss of the first hydrated water, while for $BaBr_2 \cdot 2H_2O$ two peaks are also present, but the first is observed as a shoulder on the second peak. Since the TG curves for both compounds indicated only a single step mass-loss, the first two DTA peaks are due to the reactions:

$$BaX_2 \cdot 2H_2O(s) \rightarrow BaX_2 \cdot H_2O(s) + H_2O(l) \qquad (X = Cl, Br) \qquad (1)$$

$$H_2O(l) \rightarrow H_2O(g) \qquad (2)$$
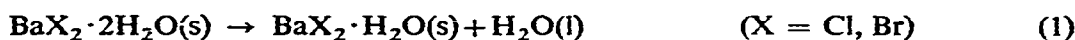
Therefore, as indicated by the previous electrical conductivity data[2], the presence of quadruple points in these systems can be detected at atmospheric pressure.
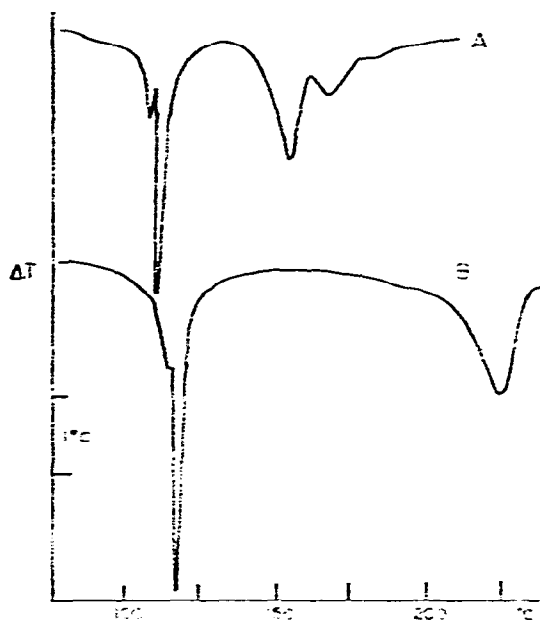
Fig. 3. DTA curves of $BaCl_2 \cdot 2H_2O$ (A) and $BaBr_2 \cdot 2H_2O$ (B).

The DTA curve for $BaCl_2 \cdot 2H_2O$ contains two peaks (or possibly three) for the evolution of the second water of hydration. The exact origin of these peaks is not known because only a single step mass-loss was found in the TG curve. Since $BaCl_2 \cdot H_2O$ may exist in two different crystalline forms[8], perhaps one of the peaks is due to a phase transition, or, since it is known that the 1/2-hydrate exists[9], perhaps the water is lost in two steps which overlap to the extent that they were not distinguishable on the TG curve, but were detected by the highly sensitive DTA measurements.

The heats of the deaquation reactions of $BaCl_2 \cdot 2H_2O$ and $BaBr_2 \cdot 2H_2O$ obtained from quantitative DTA measurements are given in Table I. The ΔH values

TABLE I

QUANTITATIVE DTA DATA FOR $BaCl_2 \cdot 2H_2O$ AND $BaBr_2 \cdot 2H_2O$

Compound	ΔH (open tube), kcal/mole		ΔH (sealed tube), kcal/mole
	First water loss	Second water loss	First water loss
$BaCl_2 \cdot 2H_2O$	14.8	13.5	4.0
$BaBr_2 \cdot 2H_2O$	12.8	14.2	4.0

obtained using an open sample tube are the sum of reactions (1) and (2). Using a sealed sample tube, the vaporization of water is supressed and the ΔH values obtained are therefore those for reaction (1) only. As can be seen, if the ΔH values obtained using sealed sample tubes are subtracted from those for the first water loss obtained using open sample tubes, values close to the expected heat of vaporization of water

(~ 10 kcal/mole) are obtained. The enthalpy of reaction (1) for the chloride compound has previously been estimated[8]. This was done by first estimating the ΔV of the reaction using solubility and X-ray density data and calculating the ΔH value by the use of the Clapyron equation. The value obtained was 4.54 kcal/mole; in reasonable agreement with that of 4.0 kcal/mole determined in this investigation. The enthalpy of the reaction,

$$BaCl_2 \cdot H_2O \rightarrow BaCl_2 + H_2O(l)$$
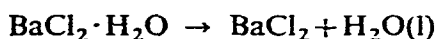
was estimated to be about 4.1 kcal/mole in the same manner[8]. This reaction enthalpy can also be estimated by subtracting the approximate value of the heat of vaporization of water from the reaction enthalpy of the second water loss obtained using an open sample tube. This calculation gave a value of approximately 3.5 kcal/mole and again the agreement is reasonable. Finally, it should be pointed out that the sum of the enthalpies for the deaquation of both water molecules for $BaCl_2 \cdot 2H_2O$ (28.3 kcal/mole) are in good agreement with the value of 28.5 kcal/mole which has previously been obtained[13].

ACKNOWLEDGMENT

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