Thermochimica Acta, 5 (1973) 451–454

DEUTERIUM ISOTOPE EFFECT ON THE HEATS OF HYDRATION OF BARIUM CHLORIDE

LARRY E. SMITH and GARY L. BERTRAND
Department of Chemistry, University of Missouri–Rolla, Rolla, Mo. 65401 (U. S. A.)
(Received 30 June 1972)

ABSTRACT

Heats of solution of barium chloride, its mono- and dihydrates, and the deuterated hydrates at 25°C have been measured and combined to calculate the deuterium isotope effect on the heats of hydration of barium chloride. Substitution of D_2O for H_2O in the hydrates enhances the heats of dehydration by 1–2%.

INTRODUCTION

Previous studies of isotope effects on the heats of hydration of barium chloride[1,2] have involved temperature dependence of the vapor pressure. A combination of effects (narrow ranges of temperature, temperature dependence of the heat of hydration, and non-ideality of the vapor) render these values somewhat questionable. As part of a continuing study of thermochemical isotope effects[3–5], we have measured the heats of solution of barium chloride, its mono- and dihydrates, and the deuterated hydrates at 25°C. These results have been combined to yield heats of hydration and deuteration, and heats of formation (relative to barium chloride) of the hydrates and deuterium substituted hydrates (hereafter referred to as deuterates) of barium chloride.

EXPERIMENTAL SECTION

Materials

Fisher Certified barium chloride was dried at 250°C for 24 hours. Sample bulbs were filled and sealed in a drybox under an argon atmosphere.

Barium chloride dihydrate was prepared by exposing a weighed sample of the anhydrous compound to water vapor until the weight increase showed that more than the stoichiometric amount of water had been acquired by the sample. The sample was then transferred to a desiccator containing anhydrous barium chloride and allowed to come to constant weight. This process was repeated several times until the sample showed a consistent final weight. The sample was then ground and screened to a particle size of 125–250 microns. The degree of hydration was periodically checked by weight loss on dehydration at 250°C, and the composition was consistently found to be $BaCl_2 \cdot 1.99H_2O$.

Barium chloride dideuterate was prepared by a procedure similar to that above, except that deuterium oxide (Stohler Isotope Chemicals, 99.8+ mole %) was used in place of water, and the samples were prepared and handled in the drybox. Dehydration analysis showed the sample to be $BaCl_2 \cdot 2.00D_2O$.

Barium chloride monohydrate and monodeuterate were prepared by partial dehydration of the dihydrate and dideuterate. The samples were kept in closed containers for 1 to 2 weeks prior to use, in order to allow the crystals to become uniform. As a test of possible non-uniformity of the sample, a portion of the monohydrate sample was placed in a sealed tube, held at 250°C for 24 hours, then allowed to return to equilibrium at room temperature. Heats measured with this sample were in excellent agreement with those measured for the untreated sample. Analysis by dehydration showed the compounds to be $BaCl_2 \cdot 1.00H_2O$ and $BaCl_2 \cdot 1.10D_2O$.

Calorimetry

The calorimeter has been described previously[6,7]. Sample bulbs were approximately 2 ml in volume and required a bulb-breaking correction of 0.02 ± 0.02 cal. The electrically determined energy equivalent was generally reproducible to within 0.5%. All measurements were made at 25.0 ± 0.1 °C. The accuracy of the calorimeter was checked by measuring the heat of solution of tris(hydroxymethyl)aminomethane (TRIS) prepared in the manner described by Irving and Wadsö[8] in 0.1012 *M* HCl. Our measurements gave -7120 ± 20 cal/mole under conditions very similar to those for which Irving and Wadsö reported -7102 cal/mole. Other values that have more recently been cited for this test reaction are -7107[9] and -7112[10].

RESULTS AND DISCUSSION

Heats of solution of the solids in 300 ml of distilled water were measured for 3–9 samples of each, containing 2–5 millimoles of barium chloride. These heats were adjusted to standard (infinite dilution) values with heats of dilution calculated from data given by Parker, Wagman, and Evans[11]. In treating our data for heats of solution of the deuterates in water, we have assumed that the partial molar enthalpies of aqueous barium chloride and aqueous D_2O (which probably exists almost entirely as HDO) are each independent of the other at the levels of concentration used in this study. As a check of this assumption, we found the heat of solution of D_2O in 0.02 *M* aqueous barium chloride to be in excellent agreement with that measured in pure water, 31.5 cal/mole[4]. This value was used to remove the contribution of aqueous D_2O to the heats of solution of the deuterates in water. Two of our samples were not of exact stoichiometry with respect to hydration. The heats of solution of these samples were adjusted to the heats that would be observed for hydrates of exact stoichiometry by assuming the sample to be a mixture of two crystalline forms. Our calorimetric results are shown as reactions 1a–1e in Table I.

Heats of solution were combined to yield the heats of stepwise dehydration, listed as reactions 2a–2d in Table I. These heats were combined with tabulated data

TABLE I

STANDARD HEATS OF REACTION AT 298.15°K

Reaction	*No.*	*n*	*X*	*ΔH°(cal/mole)*	*Stand. dev.*
$BaCl_2 \cdot nX_2O(s) \rightarrow BaCl_2(aq) + nX_2O(l)$	1a	0	—	−3,260	15
	1b	1	H	400	20
	1c	1	D	220	50
	1d	2	H	3,890	20
	1e	2	D	3,630	15
$BaCl_2 \cdot nX_2O(s) \rightarrow BaCl_2 \cdot (n-1)X_2O(s) + X_2O(l)$	2a	1	H	3,660	25
	2b	1	D	3,480	55
	2c	2	H	3,490	30
	2d	2	D	3,410	55
$BaCl_2 \cdot nX_2O(s) \rightarrow BaCl_2 \cdot (n-1)X_2O(s) + X_2O(g)$	3a	1	H	14,180	30
	3b	1	D	14,330	55
	3c	2	H	14,010	30
	3d	2	D	14,260	55
$BaCl_2 \cdot nH_2O(s) + nD_2O(g) \rightarrow BaCl_2 \cdot nD_2O(s) + nH_2O(g)$	4a	1	—	−150	55
	4b	2	—	−400	30

for the heats of formation of liquid and gaseous H_2O and D_2O[12] to obtain the heats of vapor phase dehydration (reactions 3a–3d), and the isotope effects on the heats of hydration (reactions 4a, 4b). In Table II, we report standard heats of formation of the hydrates and deuterates calculated by combination of our results with the heats of formation of anhydrous barium chloride[11], water, and deuterium oxide[12].

TABLE II

STANDARD HEATS OF FORMATION AT 298.15°K

Compound	*ΔH°f (kcal/mole)*	
	This work	*NBS Tech. Note 270-6* (ref. 11)
$BaCl_2(s)$	(−205.20)	−205.2
$BaCl_2(aq)$	−208.46	−208.40
$BaCl_2 \cdot H_2O(s)$	−277.18	−277.4
$BaCl_2 \cdot 2H_2O(s)$	−348.98	−348.98
$BaCl_2 \cdot D_2O(s)$	−279.09	
$BaCl_2 \cdot 2D_2O(s)$	−353.27	

The heats of formation of aqueous barium chloride and the crystalline hydrates are in excellent agreement with recently tabulated values[11], as shown in Table II. The only values available for comparison of our calculated isotope effects on heats of hydration are based on temperature dependence of the vapor pressure of water above mixtures of hydrates. The difficulties of obtaining reliable heats of dehydration for the Clausius–Clapeyron equation are well known. However, it is reasonable to assume that many of the complicating factors will be almost identical for isotopic isomers, and that the difference in heats of hydration obtained by one operator on a single apparatus by this method might be considerably more accurate than either of the individual values. From the vapor pressure data of Homma and Takai[1], we calculate that the loss of one mole of $D_2O(g)$ from $BaCl_2 \cdot 2D_2O$ is 490 cal more endothermic than the loss of one mole of $H_2O(g)$ from $BaCl_2 \cdot 2H_2O$. The data of Bell[2] gives 420 cal for this difference, while his individual heats of dehydration differ from our values by almost 2000 cal. In view of the inaccuracy of the vapor pressure method, we regard these values for the isotope effect for the loss of the first molecule of water in reasonable agreement with our value of 250 ± 60 cal, calculated by combination of our values for the heats of reactions 3c and 3d (Table I).

The uncertainties in our results preclude any differentiation of the isotope effects on the enthalpy changes accompanying the loss of the first and second waters of hydration. Our results show that there is a 1–2% enhancement of the heats of hydration of barium chloride by the substitution of D_2O for water. It is impossible to determine whether this is a primary isotope effect resulting from changes in the strengths of the interactions of hydrogen atoms with neighboring atoms, or a secondary effect involving the interaction of the oxygen atoms. It may be of some interest to note that there is also an enhancement of approximately 1% in the strength of the hydrogen bonds of chloroform with acetone and dioxane (in solution) due to the substitution of deuterium for hydrogen in chloroform[5].

ACKNOWLEDGEMENT

This work was supported by a grant from Research Corporation.

REFERENCES

1 M. Homma and T. Takai, *Bull. Inst. Phys. Chem. Res., Tokyo*, 17 (1938) 331; *Chem. Abstr.*, 33 (1939) 3238^8.
2 J. Bell, *J. Chem. Soc.*, (1940) 72.
3 J. O. Stoffer, W. C. Duer and G. L. Bertrand, *Chem. Commun.*, (1969) 1188.
4 W. C. Duer and G. L. Bertrand, *J. Chem. Phys.*, 53 (1970) 3020.
5 W. C. Duer, *Ph.D. Dissertation*, University of Missouri–Rolla, 1970.
6 G. L. Bertrand, R. D. Beaty and H. A. Burns, *J. Chem. Eng. Data*, 13 (1968) 436.
7 E. L. Taylor, *M.Sc. Thesis*, University of Missouri–Rolla, 1969.
8 R. J. Irving and I. Wadsö, *Acta Chem. Scand.*, 18 (1964) 195.
9 J. O. Hill, G. Öjelund and I. Wadsö, *J. Chem. Thermodynamics*, 1 (1969) 111.
10 S. R. Gunn, *J. Chem. Thermodynamics*, 2 (1970) 535.
11 V. B. Parker, D. D. Wagman and W. H. Evans, *Nat. Bur. Stand. Tech. Note 270-6*, U.S. Government Printing Office, Washington, D.C., 1971.
12 D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Baily and R. H. Schumm, *Nat. Bur. Stand. Tech. Note 270-3*, 1968.