Heats of Solution and Derived Thermodynamic Properties of Alkali-Metal Bromates

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THERMAL AND radiolytic stabilities were compared during investigations on the decomposition of crystalline alkali-metal bromates by Co^{60} γ-rays (*1*) Information on only the thermodynamic properties of $KBrO_3$ had been published (*6*), and it was necessary to consider what measurements should be undertaken to give the required heats and free energies of formation for the remaining salts. It became evident that if values for the heats and free energies of solution of the anhydrous compounds were determined, these could be combined with published data on the thermodynamic properties of bromate ion (*7, 10*) and on the alkali-metal cations in aqueous solution to give the desired quantities. Accordingly, in this work calorimetric measurements were made of the heats of solution at high dilution for all the pure alkali-metal bromates. Their free energies of solution using solubility and activity coefficient data also were estimated.

EXPERIMENTAL

Preparation and Purity of the Anhydrous Salts. The lithium, sodium, and potassium bromates were either commercial products shown to be pure by spectrochemical analysis, or were reagent grade (Baker and Adamson) chemicals. These were purified additionally by several recrystallizations from water. Anhydrous $LiBrO_3$ was recrystallized from a hot (>52° C.) solution. A thermogravimetric analysis of the product showed it to be the pure, anhydrous salt.

Rubidium bromate, synthesized from commercial Rb_2CO_3 (A. D. McKay), was shown by flame spectrophotometric analysis to contain negligible amounts of the other alkali metals. The carbonate was converted to $RbHSO_4$ and reacted with pure $Ba(BrO_3)_2 \cdot H_2O$ to give $RbBrO_3$, which was isolated in a yield of ca. 50% from the filtrate after one recrystallization. Flame spectrophotometric analysis gave $<8 \times 10^{-4}\%$ Li, $1.5 \times 10^{-3}\%$ Na, $8 \times 10^{-3}\%$ K, and $<3 \times 10^{-2}\%$ Cs on a weight basis.

Cesium bromate was synthesized from commercial CsCl (A. D. McKay) which was converted to $CsHSO_4$ and reacted with $Ba(BrO_3)_2 \cdot H_2O$. The $CsBrO_3$ formed in ca. 67% yield in the filtrate was isolated and purified from bromide ion by recrystallization. A flame spectrophotometric analysis gave $<3 \times 10^{-4}\%$ Li, $2 \times 10^{-2}\%$ Na, $1.2 \times 10^{-3}\%$ K, and $1.5 \times 10^{-2}\%$ Rb.

All compounds were dried in air at 110° C. and stored away from light in closed vessels.

Apparatus and Procedure. The general details of the calorimeter have been described (*2*). The container was an 800-ml. cylindrical Dewar flask held in a brass jacket. A brass top equipped with O-rings could be bolted to the jacket, to close off the Dewar. The top was perforated by small-diameter brass tubes which carried a stirrer, a thermistor (2000 ohms) for the temperature measurement, a 200-ohm heater for energy calibrations, and the supports for a cylindrical 1 × 2 cm. glass pipet used to hold the crystalline salts prior to initiating their dissolution in the calorimeter liquid. The calorimeter also was fitted with a stirring tube to facilitate mixing and thereby speed the dissolution reaction. Amounts of dry salt weighed to the nearest 0.1 mg. were placed in the pipet, which was sealed by thin gold sheets held by paraffin at the upper and lower ends. In working with the anhydrous lithium bromate, loadings were conducted in a dry box to avoid the formation of $LiBrO_3 \cdot H_2O$. Redistilled water (500 ml.) was placed in the Dewar, and the calorimeter was assembled and submerged so that its top was approximately 1 inch below the surface of a water bath regulated at 25° ± 0.001° C.

Stirring was begun, and after an initial temperature adjustment of the calorimeter contents, 1 hour was allowed for the attainment of a small and linear drift of the temperature with time. Resistance readings (from a Wheatstone bridge) were taken on the thermistor each minute for 10 to 15 minutes, and the pipet was opened by breaking the gold foils with a glass rod. The alkali-metal bromates dissolved completely within 6 minutes, except for the large $RbBrO_3$ crystals which required 10 to 15 minutes before a linear temperature drift was attained. Two energy calibrations were performed following the dissolution. The voltage across the calorimeter heater was read on the P-branch of a White double potentiometer; the heater current was determined from the potential drop across a standard resistance measured with the Q-branch. The length of the heating period was controlled by a tuning fork–exciting clock coupled to the energy switch.

The reaction heats were estimated by linear extrapolation of the thermistor resistances to the mid-point of the reaction period and were expressed as a change in resistance in ohms. The energy input from the heater was divided by the observed thermistor resistance change to give the calorimeter energy equivalent in calories per ohm. The product of the "reaction resistance change" with the energy equivalent divided by the number of moles of bromate dissolved gave the "experimental" heat of solution, $\Delta H_{\text{soln.}}$, in kcalories per mole (Table I). Correction of the "experimental" heats to the desired heats of solution at infinite dilution, $\Delta H^{\circ}_{\text{soln.}}$, was performed following accepted procedures (*3*). Experimental heats of dilution on $NaBrO_3$ (*5*) solutions were employed to make these corrections whose magnitudes were only slightly greater than the uncertainty in the heat of solution measurements themselves.

The value for $KBrO_3$(cryst.), $\Delta H^{\circ}_{\text{soln.}} = 9.70$ kcal. mole^{-1}, found in this work (Table II) agrees with that of 9.76 ± 0.05 kcal. mole^{-1} previously reported (*7*). During this research a value for $NaBrO_3$(cryst.) of 6.43 ± 0.06 kcal. mole^{-1} was published (*10*). This value agrees reasonably well with that found by us (cf. Table II).

RESULTS AND DISCUSSION

Observed and standard heats of solution for the alkali-metal bromates are summarized in Table II, where values are listed also for the standard enthalpies of formation,

Table I. Heats of Solution of Crystalline Alkali-Metal Bromates at 25° C.

Moles × 10^3/500 Ml.	Calorimeter Equivalent, Cal. Ohm^{-1}	Reaction Resistance Change, Ohms	ΔH, Kcal. $Mole^{-1}$
		$LiBrO_3$	
3.232	3.906	0.304	0.367
3.378	3.931	0.317	0.369
3.920	3.916	0.367	0.367
		$NaBrO_3$	
3.350	3.932	5.417	6.36
3.848	3.929	6.250	6.38
5.320	3.924	8.683	6.41
		$KBrO_3$	
1.421	3.931	3.516	9.72
		$RbBrO_3$	
1.488	3.932	4.400	11.63
1.857	3.938	5.562	11.80
1.935	3.934	5.763	11.72
		$CsBrO_3$	
0.640	3.932	1.959	12.04
0.707	3.948	2.145	11.99
1.243	3.934	3.810	12.06
1.535	3.921	4.738	12.10
2.490	3.929	7.745	12.22

Table II. Heats of Solution and Thermodynamic Properties of Crystalline Alkali-Metal Bromates at 298.15° K.

Salt	$\Delta H_{soln.}$	$\Delta H^{\circ}_{soln.}$	$-\Delta H^{\circ}_f$	Satn. Molality	Molal Activity Coeff. at Satn.	$\Delta F^{\circ}_{soln.}$	$-\Delta F^{\circ}_f$	S°
$LiBrO_3$	0.367 ± 0.002	0.337	85.19	...	...	...	...	...
$NaBrO_3$	6.38 ± 0.02	6.35	81.93	2.614	0.418	−0.10	60.38	31.2
$KBrO_3$	9.70	9.70	88.04	0.4878	0.552	1.55	66.91	35.6_5
$RbBrO_3$	11.71 ± 0.08	11.69	88.90	0.1414	0.711	2.72	68.07	37.9
$CsBrO_3$	12.03 ± 0.06	12.01	89.51	0.1456	0.706	2.69	68.00	38.8

ΔH°_f, for the crystalline solids. These latter quantities were derived from the $\Delta H^{\circ}_{soln.}$ values in column 3 taken together with the value of −18.3 kcal. $mole^{-1}$ for the heat of formation of bromate ion in aqueous solution (*7*) and the appropriate values for ΔH°_f for the alkali-metal cations (*6*). The pattern of the enthalpy of formation values in Table II is typical of that for the salts formed when the alkali-metal cations are combined with large anions—e.g., the cesium salt shows the largest formation enthalpy. Furthermore, the ΔH°_f values are consistent with those reported (*6*) for the alkali-metal chlorates and iodates in so far as these are known.

Standard free energies of solution were computed from available solubility (*9*) and activity coefficient data (*8*). Activity coefficients for the saturated solutions of $RbBrO_3$ and $CsBrO_3$ were estimated using the values for $KBrO_3$, KNO_3, $RbNO_3$ and $KBrO_3$, KNO_3 $CsNO_3$, respectively. The activity coefficient value for a saturated $LiBrO_3$ solution was derived by comparison with LiCl at the same concentration using Åkerlöf's relation (*4*). The required constant, $B = 0.0345$, was based on $\gamma_{LiBrO_3} = 0.786$ found using activity coefficient values for $NaBrO_3$, $NaNO_3$, and $LiNO_3$ at $m = 2.0$. Standard free energies of formation of the crystalline salts (Table II, column 8) were derived from the estimated $\Delta F^{\circ}_{soln.}$ taken together with the value 2.1 ± 2 kcal. $mole^{-1}$ for the free energy of formation of bromate ion in aqueous solution (*7*), and the appropriate values for ΔF°_f for the alkali metal cations (*6*).

The standard entropies for the crystalline compounds at 298.15° K. may be derived from the entropies of formation, ΔS°_f (cryst.), of the salts and the entropies (*6*) of their constituent elements, or from the entropies of solution of the compounds, $\Delta S^{\circ}_{soln.}$, and the standard partial molal entropy of aqueous BrO_3^- (*10*) and of the alkali-metal cations (*6*). The latter procedure was followed to give the entropies in the last column of Table II. The magnitudes and the differences between the entropy values for the potassium, rubidum, and cesium salts are comparable with those reported for the corresponding alkali-metal nitrates and chlorates. The entropies of the three heaviest members of the series which are isostructural (*1*) could be correlated by the formula:

$$S_{MBrO_3} = S_{M'BrO_3} + \tfrac{3}{2} R \ln (M/M').$$

The observed entropy for $NaBrO_3$(cryst.), however, was significantly lower than the value estimated from the entropy of $KBrO_3$(cryst.). A difference in the force constant for the binding of sodium ion from those for the heavier alkali-metal cations could be a cause for the discrepancy.

LITERATURE CITED

(1) Boyd, G.E., Graham, E.W., Larson, Q.V., *J. Phys. Chem.* **66**, (1962).

(2) Boyd, G.E., Harkins, W.D., *J. Am. Chem. Soc.* **64**, 1190 (1942).

(3) Harned, H.S., Owen, B.B., "Physical Chemistry of Electrolyte Solutions," 3rd ed., pp. 331 ff., Reinhold, New York, 1958.

(4) *Ibid.*, p. 617.

(5) Lange, E., Robinson, A.L., *Z. physik. Chem.* **148A**, 97 (1930).

(6) Latimer, W.M., "Oxidation Potentials," 2nd ed., pp. 329–35, Prentice-Hall, New York, 1952.

(7) Mel, H.C., Jolly, W.L., Latimer, W.M., *J. Am. Chem. Soc.* **75**, 3827 (1953).

(8) Robinson, R.A., Stokes, R.H., "Electrolyte Solutions," Butterworth's, London, 1955.

(9) Seidell, A., "Solubilities of Inorganic and Metal Organic Compounds," Van Nostrand, New York, 1940.

(10) Spencer, J.G., Jr., Hepler, L.G., *J. Phys. Chem.* **64**, 499 (1960).

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