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THE ENTHALPY OF PRECIPITATION OF UNIVALENT CATIONS WITH TETRAPHENYLBORATE BY TITRATION CALORIMETRY

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ABSTRACT

The enthalpy of precipitation of six common univalent cations with the tetraphenylborate anion has been measured at 25.0°C. Reaction entropies range from −8.24 kcal/mole for ammonium to −19.7 kcal/mole for silver(I). The entropy of reaction was computed from the above measurements and the corresponding Gibbs free energy changes. A linear relationship exists between $\Delta F^{\circ\prime}$ and $\Delta H^{\circ\prime}$. The entropy of precipitation of ammonium ions was +5.0 e.u., an unusually large positive value.

INTRODUCTION

The precipitation of univalent cations with tetraphenylborate as indicated by reaction 1 is a significant process since it is the basis of a number of gravimetric and volumetric methods for some of the alkali metals[1-4]. Tetraphenylborate also reacts with silver(I), ammonium(I), thallium(I), quaternary ammonium salts and protonated amines to form sparingly soluble salts.

$$M^+ + \Phi_4B^- \leftrightarrow M\Phi_4B \qquad (1)$$

Tetraphenylborate and analogous compounds such as the toluyl derivative are of theoretical interest since these anions are quite large and therefore may be useful in establishing a scale of partial molar ionic free energies[5]. Rubidium[6], ferrocenium[7], and cobaltocenium[7], due to their large size, have been examined as reference cations. The Stokes or hydrodynamic radius of tetraphenylborate may be estimated from the aqueous ionic conductivity of its sodium salt. The equivalent ionic conductivity of this anion[8] is 21 ohm^{-1}/cm at 25°C indicating a Stokes radius of 4.36 Å. This is in reasonable agreement with the *a priori* calculation of the harmonic radius according to Ref. 6. The solubility of tetraphenylborate salts has been studied by several groups[9-11], by different methods and the heat of solution of several alkali tetraphenylborates have been determined[12]. Since very few anions react extensively with the alkali metals, tetraphenylborate and its analogs are virtually unique species for the investigation of relative differences in the solution chemistry of the alkali metals. McClure and Rechnitz[10] reported a correlation between the rates of formation and free energies of precipitation of ammonium, potassium, cesium, rubidium, thallium(I) and silver(I) tetraphenylborate. In light of the above results the enthalpy of precipitation of these six common cations was obtained by titration calorimetry.

EXPERIMENTAL

Reagents

Solutions of potassium chloride, ammonium chloride, cesium bromide, rubidium chloride, thallium nitrate, and silver nitrate were prepared from dried commercially available salts. In all cases the materials were analytical reagent grade and assayed better than 99.8% pure. A 0.5 M stock solution of sodium tetraphenylborate was prepared from reagent grade material (Fisher Scientific Co.) after purification by absorption on freshly precipitated aluminum hydroxide.

Apparatus

All reaction enthalpies reported in this work were measured by titration calorimetry. The dewar was a 40 ml version of the design of Hansen, Izatt, and Christensen[12]. The measurement head, which contained a 2000 Ω thermistor (VECO, 41A7), a stirrer, a calibration heater and a tube for admitting titrant was inserted into the dewar. The entire assembly was thermostatted to ±0.02°C in a large plexiglass box. This thermostating was accomplished by means of an on–off controller (Yellow Springs Instruments, Model-71), a 300-W incandescent lamp, a reclaimed air conditioner heat transfer element, and a large (35 cm) fan. The titrant was thermostatted to ±0.01°C by circulating water from an external water bath. A syringe pump (Sage, Model 234-3) and syringe (Hamiton, 5 ml) were used to transfer the titrant to the dewar. The calibration heater and its power supply were similar to a design of Stern, Withnell, and Raffa[13].

Temperature changes during both dewar calibration experiments and actual experimental runs were recorded as the "unbalance" potential of a d.c. Wheatstone bridge on a 1 mV full scale recorder (Sargent, Model-SR).

Procedure

All reaction enthalpies were measured by transferring a known amount of sample into the dewar via calibrated glassware. The temperature of the sample was brought to 24.7°C by preheating with a heater. Three replicate heater calibrations were obtained prior to an actual reaction run. After the reaction-temperature–time curve was measured, three additional heat capacity measurements were obtained. Heats of reaction were measured by the technique illustrated in Fig. 1. The accuracy of the entire calorimetric system was checked by measuring the heat of neutralization of hydrochloric acid with sodium hydroxide under conditions where CO_2 was rigorously excluded from all solutions. For five replicate runs at an initial ionic strength of 5.1 m*M*, a heat of neutralization of -13.39 ± 0.05 was obtained in comparison with $-13.37 \pm .03$ kcal/mole at an ionic strength of 0.0047 obtained from the data of Hale, Izatt, and Christensen[14].

Each enthalpy reported here represents the average of at least four replicate measurements at an initial cation concentration of 5.7 m*M*. No attempt was made to determine the effect of concentration on the reaction enthalpy since detailed studies of the corresponding free energy as a function of ionic strength are not available and since our main interest was to measure under a constant set of conditions the effect of cations on the heat of reaction.

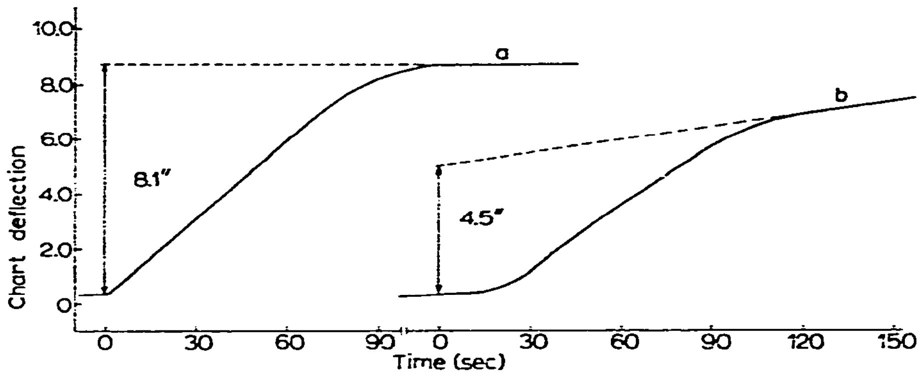

Fig. 1. Curve a: Plot of recorder deflection *vs.* time during the titration of 199.5 μmoles of silver(I) nitrate. Cation concentration 5.7 m*M*, rate of titrant addition 2×10^{-6} moles/sec. Sensitivity 0.38 cal/inch. Curve b: Plot of recorder deflection *vs.* time during the titration of 201.6 μmoles of ammonium chloride. Cation concentration 5.7 m*M*, rate of titrant addition 2×10^{-6} moles/sec. Sensitivity 0.34 cal/inch.

RESULTS AND DISCUSSION

Two types of temperature-time curves were observed. Both are illustrated in Fig. 1. Ammonium, potassium, and to a very much lesser extent, rubidium have titration curves (Fig. 1b) which are initially quite non-linear and ultimately become straight. All other species have rectilinear titration curves (Fig. 1a) with little or no initial curvature.

Rechnitz and McClure[10] have measured the rates of precipitation of univalent cations and have found that in the absence of seed crystals the order of precipitation rates is: $NH_4^+ < K^+ < Rb^+ \ll Cs^+ < Tl^+ < Ag^+$. At extremely low concentration of cation and tetraphenylborate they observed significant induction periods before the onset of precipitation. The observed rate law was consistent with a slow reaction on the surface of the precipitate. We attribute the initial curvature in the titration of ammonium, potassium, and rubidium to this slow reaction. No equilibria would induce an initial curvature of the peculiar type shown in Figure 1b. The high initial slope is probably due to a nucleation process which is more exothermic than the overall precipitation. This seems reasonable if in forming the essential nuclei, the component ions do not completely shed the attached water of solvation.

Because heats of reaction were measured by extrapolation of the enthalpograms from regions where the reaction is essentially complete they should be free of errors due to slow reaction and finite solubility. It is for this reason the extrapolation method of Jordan[15], rather than the initial slope method of Keilly and Hume[16], or the mathematical technique of Christensen *et al.*[17] was employed. The experimental results on the enthalpy of ionization of water, indicate that the technique used in this work is reasonably accurate with our calorimetric system.

The heats of precipitation, measured at an ionic strength of 0.0057, are presented in Table I. There is a discrepancy between those enthalpy values determined in this work and that of Wu and Freidman[20] (see Table I). This difference may be outside the range of the experimental precision reported in both studies. Part of the difference may be related to the ionic strength since the data of Wu and Friedman have been corrected to infinite dilution. Since some of their results were obtained by precipitation (potassium, rubidium), some by dissolution (sodium), and one by reaction of a solution of tetraphenylborate with the crystalline chloride (cesium), our results may be more consistent because all were determined in the same fashion at a constant ionic strength.

TABLE I

THERMODYNAMIC PARAMETERS FOR THE REACTION: $M^+ + \Phi_4B^- \rightleftharpoons M\Phi_4B(\downarrow)$

Cation	ΔF° (*kcal/mole*)[a]	$\Delta F^{\circ\prime}$ (*kcal/mole*)[b]	ΔH° (*kcal/mole*)[c]	$\Delta H^{\circ\prime}$ (*kcal/mole*)[d]	$\Delta S^{\circ\prime}$ (*cal·mole^{-1}·deg^{-1}*)[e]
NH_4^+	−9.74[f]	−9.47		−8.24±0.09	+5.0±0.9
K^+	−10.16	−9.93	−9.41	−10.05±0.10	+0.4±1.0
Rb^+	−11.69	−11.39	−11.73	−12.34±0.12	−2.2±1.2
Cs^+	−11.92	−11.64	−12.40	−12.67±0.19	−2.5±1.4
Tl^+	−13.80[f]	−13.53		−17.28±0.28	−11.6±1.9
Ag^+	−14.24[f]	−13.97		−19.69±0.17	−18.3±1.5

[a] From the solubility data of B. Hays taken from Ref. 18 at most the ionic strength was 4×10^{-4}. [b] From the solubility data of Ref. 10 $\mu = 0.10$. [c] From the results of Ref. 20. [d] Experimental results obtained in this work. [e] Computed from column 2 and 5. Precision estimate by assuming a 2% uncertainty in ΔF° and indicated uncertainty in ΔH°. [f] Estimated by subtracting +0.27 kcal/mole from the results of Ref. 10.

Also presented in this table are the best available Gibbs free energy changes at $\mu = 0$ (18) and at $\mu = 0.1$ in a pH 5.1 buffer[10]. We chose to use the solubility of McClure and Rechnitz because it is the most complete single set of data and therefore experimental errors would tend to be more consistent than a collection of solubility data from several groups. The maximum difference in free energies between the work of McClure and Rechnitz[10], and the solubility study of Hays[18] for $K\Phi_4B$, $Rb\Phi_4B$, and $Cs\Phi_4B$ is 0.30 kcal/mole or about three percent. The additional ΔF° data for $NH_4\Phi_4B$, $Tl\Phi_4B$, and $Ag\Phi_4B$ were computed from the data of McClure and Rechnitz by subtracting the mean difference in the free energies at $\mu = 0$ and $\mu = 0.1$. Reaction enthalpies were not corrected to infinite dilution since the required correction (<0.1 kcal/mole) would be smaller than the experimental precision. Entropies of precipitation were computed from the data of columns 2 and 5 in Table I. The precision of the entropy change was computed from the measured reaction enthalpy precision and an assumed two percent precision in the free energy change. The experimental data show two interesting results, first the entropy of precipitation of ammonium ion is significantly positive, and second there is a strong correlation between the free energy and enthalpy of precipitation. The free energies (ΔF°) and enthalpy ($\Delta H^{\circ\prime}$) were fitted to a straight line by an unweighted least squares program. The relationship (Eqn. 2 below) is linear with a correlation coefficient of 0.987 at >99.9% confidence level. One would expect a correlation with unity slope if the entropy change were constant. However the slope differs significantly from unity and the entropy contribution to the free energy varies from 4% for potassium to 38% for silver(I). Consequently the linear relationship expressed in Eqn. 2 is non-trivial.

$$\Delta F^\circ_{\text{ppt}} = +0.417\,\Delta H^{\circ\prime}_{\text{ppt}} - 6.34 \tag{2}$$

Since the overall precipitation process can be viewed as the sum of the individual reactions given below:

$$\begin{tikzcd}
M^+(\text{aq}) + \Phi_4B^-(\text{aq}) \arrow[d, "\Delta H_{\text{ppt}}"] & M^+(\text{g}) + \Phi_4B^-(\text{g}) \arrow[l, "\Delta H_{\text{solv}}"'] \arrow[dl, "E_{\text{lattice}}"] \\
M\Phi_4B &
\end{tikzcd} \tag{3}$$

where

$$\Delta H^\circ_{\text{ppt}} = E_{\text{lattice}} - \Delta H^\circ_{\text{solv}}(M^+) - \Delta H^\circ_{\text{solv}}(\Phi_4B^-) \tag{4}$$

similarly

$$\Delta F^\circ_{\text{ppt}} = F_{\text{lattice}} - \Delta F^\circ_{\text{solv}}(M^+) - \Delta F^\circ_{\text{solv}}(\Phi_4B^-) \tag{5}$$

The linear relationship between $\Delta F^\circ_{\text{ppt}}$ and $\Delta H^\circ_{\text{ppt}}$ requires that a linear relationship exist between E_{lattice} and F_{lattice}, and between $\Delta H^\circ_{\text{solv}}$ (M^+) and $\Delta F^\circ_{\text{solv}}(M^+)$ or that non linearities exactly cancel. It should be noted that E_{lattice} and $\Delta H^\circ_{\text{solv}}(M^+)$ are quite large compared to $\Delta H^{\circ\prime}_{\text{ppt}}$ and similarly F_{lattice} and $\Delta F^\circ_{\text{solv}}$ are large compared to $\Delta F^\circ_{\text{ppt}}$. It is well known that $\Delta F^\circ_{\text{solv}}$ and $\Delta H^\circ_{\text{solv}}$ are linearly related. Latimer, Pitzer, and Slansky[19] have shown that the free energy of solvation of gaseous ions is well represented by a modified Born equation:

$$\Delta F^\circ_{\text{solv}} = \frac{-e_i^2(1-1/D)}{2(r_i+\delta)} \tag{6}$$

where D is the dielectric constant, e_i the charge on the ion, r_i the Pauling radius, and δ an adjustable parameter which for water at 25°C is taken as 0.85 Å for cations and 0.10 Å for anions. Wu and Friedman[20] have shown that the enthalpy of solvation is well represented as:

$$\Delta H^\circ_{\text{solv}} = \Delta F^\circ_{\text{solv}}\left[\frac{1-T\,\partial D/\partial T}{D(D-1)} + \frac{T}{r_i+\delta}\,\frac{\partial\delta}{\partial T}\right] \tag{7}$$

where the temperature coefficient of δ is small, thus a linear relationship between $\Delta H^\circ_{\mathrm{solv}}$ and $\Delta F^\circ_{\mathrm{solv}}$ exists. The data of Table II (columns 2 and 3) support the result. Consequently in view of the linear relationship between $\Delta H^{\circ\prime}_{\mathrm{ppt}}$ and $\Delta F^\circ_{\mathrm{ppt}}$, E_{lattice} and F_{lattice} are related linearly as one might expect if the change in entropy contribution to the lattice free energy upon change in cation is zero or proportional to the free energy change. If the entropy change is zero then the slope of the relationship between F_{lattice} and E_{lattice} should be unity. From a least squares data analysis one finds that:

TABLE II

CONVENTIONAL THERMODYNAMIC HYDRATION ENERGIES AND COMPUTED LATTICE PARAMETERS[a]

Species	$\Delta F^\circ_{\mathrm{solv}}$[b]	$\Delta H^\circ_{\mathrm{solv}}$[b]	$F_{\mathrm{lattice}}-\Delta F^\circ_{\mathrm{solv}}(\Phi_4B^-)$[d]	$E_{\mathrm{lattice}}-\Delta H^\circ_{\mathrm{solv}}(\Phi_4B^-)$[d]	$\Delta S_{\mathrm{lattice}}-\Delta S^\circ_{\mathrm{solv}}(\Phi_4B^-)$[d]
NH_4^+	+182.7[c]	+185	+173.0	+176.8	−1.3
K^+	+179.92	+183.98	+169.8	+174.0	−1.4
Rb^+	+185.0	+189.9	+173.3	+177.6	−1.4
Cs^+	+192.7	+197.8	+180.8	+185.1	−1.4
Tl^+	+178.48	+182.83	+164.7	+165.5	−0.3
Ag^+	+146.02	+147.12	+131.8	+127.4	+1.5

[a] All energies are in kcal/mole, entropy in cal·mole^{-1}·deg^{-1}. [b] These are conventional hydration energies with respect to the hydrations of H^+ and are taken from Ref. 25. [c] This result was computed from the enthalpy of hydration and an estimate of $\Delta S^\circ_{\mathrm{solv}}$ by interpolating the entropy data for potassium and rubidium against the Pauling radii. [d] Computed from the experiment results and Eqns. 5 and 6.

$$\frac{d(F-\Delta F^\circ_{\mathrm{solv}}(\Phi_4B^-))}{d(E-\Delta H^\circ_{\mathrm{solv}}(\Phi_4B^-))} = 0.832\pm0.02 \tag{8}$$

Although the data is weighted heavily by the results for silver(I) and thallium(I), it appears that changes in $\Delta S_{\mathrm{lattice}}$ contribute significantly to the change in $\Delta F_{\mathrm{lattice}}$.

As Table II indicates $\Delta S_{\mathrm{lattice}}$ is constant or approximately so, for ammonium, potassium, cesium, and rubidium as might be the case if the entropy of the gaseous ions were constant and the crystals isomorphic. X-ray crystallagraphic studies[21–24] have shown this to be so. The lattice entropies of the silver(I) and thallium(I) salts are considerably different and this *may* imply that these crystals are not isomorphic with the alkali metal salts.

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