Synthesis and Thermodynamic Functions of Rubidium and Caesium Tetrachloroborates

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Pure rubidium and caesium tetrachloroborates have been prepared by a modification of an established method. Their standard heats of formation at 298·15 K are −220·7 ± 0·4 and −225·0 ± 0·3 kcal mol^{-1} respectively as obtained from a thermochemical study of their hydrolyses. Dissociation pressures of caesium tetrachloroborate have been determined over the range 55—80 °C, from which the equilibrium constant for the dissociation at 25 °C has been estimated as 8×10^{-5}.

In contrast to the ready preparation of tetrafluoroborates, corresponding tetrachloroborates have proved difficult to isolate and were not characterised until 1957 [1] when pyridinium tetrachloroborate was prepared. Subsequently Muetterties [2] reported autoclave syntheses at 500 °C of $M^{I}[BCl_4]$ (M = Cs, Rb, and K) from $M^{I}Cl$ and BCl_3 (under these conditions $Na[BCl_4]$ was not formed). This synthetic route was modified later [3] by inclusion of a nitrobenzene solvent when smooth reaction proceeded at *ca.* 100 °C. Approximate measurements by Muetterties revealed that the alkali-metal tetrachloroborates are thermodynamically less stable than the corresponding tetrafluoroborates in terms of both lower enthalpies of dissociation and higher dissociation pressures.

This paper describes a modification of Muetterties' synthetic procedure for rubidium and caesium tetrachloroborates and the aqueous-solution thermochemistry of these compounds; dissociation pressures and derived thermodynamic functions are reported for $Cs[BCl_4]$.

EXPERIMENTAL

Materials.—Rubidium and caesium chlorides (B.D.H.) were dried at 110 °C. Chloroform (ethanol removed by water extraction), nitrobenzene, and carbon tetrachloride were dried over type 4A molecular sieves (B.D.H.).

Syntheses.—Caesium chloride [6·0 g or rubidium chloride (4·0 g)] was added to nitrobenzene (50 cm^3) in a Pyrex glass ampoule (a spherical bulb with an 8 cm neck and volume of *ca.* 80 cm^3) in a nitrogen-filled dry-box. The ampoule contents were cooled to *ca.* −80 °C and boron trichloride (20 cm^3) was added after which the ampoule was sealed. The autoclave (series 4652, internal volume 500 cm^3, Parr Instrument Co., Moline, Illinois) was charged with the ampoule and isopentane (100 cm^3) to act as a pressure equaliser (rough calculation indicates the pressure differential across the ampoule wall at 90 °C was 0·9 atm and the total autoclave internal pressure was 7 atm).‡ The autoclave was maintained at 90 °C for 4 h when the ampoule was removed and opened at −80 °C. The following operations were carried out in a nitrogen-filled dry-box. The ampoule contents were washed into a conical flask with nitrobenzene (50 cm^3), allowed to settle, and the supernatant liquid decanted into chloroform (500 cm^3) when the tetrachloroborate precipitated. The impure product was collected on a glass sinter (No. 3) and vacuum-dried, followed by redissolution in nitrobenzene–boron trichloride (100 cm^3; 15 cm^3) and reprecipitation with chloroform. The white precipitate was filtered off, washed with chloroform, and dried at room temperature for 2 h at 0·001 Torr.

Analysis.—Raman spectra (Coderg PHO, 6 471 Å exciting line) were compared with literature spectra [4] of other tetrachloroborates and the presence of $[BCl_4]^-$ and the absence of BCl_3 confirmed. Alkali-metal contents were determined gravimetrically [5] using a sodium tetraphenylborate precipitant and total chloride contents were obtained from a Volhard titration [6] on the hydrolysate. The liberated hydrochloric and boric acids in the hydrolysate were determined *via* potentiometric titration {Found: B, 4·55; Cl^-, 59·5; Cl^- (equivalent to liberated HCl), 44·6; Rb, 36·0. Calc. for $Rb[BCl_4]$: B, 4·55; Cl, 59·55; Rb, 35·9. Found: B, 3·80; Cl^-, 49·5; Cl^- (equivalent to liberated HCl), 37·2; Cs, 46·6. Calc. for $Cs[BCl_4]$: B, 3·80; Cl, 49·65; Cs, 46·55%}. Densities at 25 °C were measured under carbon tetrachloride as 2·40 and 2·68 g cm^{-3} for $Rb[BCl_4]$ and $Cs[BCl_4]$ respectively.

Solution Calorimeter.—This was of all-glass construction, operated in the isoperibol mode at 25 °C and has been previously described [7] except for the following modifications. The calorimeter (of round-bottomed design) contained liquid (200 cm^3) and additional stirrer blades [fabricated in poly(tetrafluoroethylene) (ptfe)] were fixed to the stirrer shaft *ca.* 1 cm below the surface of the liquid. The calibration heater was replaced by a nominal 100 Ω ptfe-encapsulated resistor (Tronac Inc., Provo, Utah) of low thermal capacity, and the platinum-resistance thermometer for ancillary temperature monitoring has been abandoned. The out-of-balance bridge signal was displayed directly on a 1 mV pen recorder so that the sensitivity was *ca.* 1 Ω cm^{-1} pen displacement with a thermistor of *ca.* 150 Ω K^{-1}. The reaction resistance change was obtained by back extrapolation to a point corresponding to 63% of the total change and the calibration resistance change obtained similarly to a point corresponding to 50% of the total change. The ampoules had two fracture bulbs [8] and reaction was initiated by breaking the bulbs with the stirrer blades. The theoretical precision of this system has been discussed briefly in

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‡ 1 cal = 4·184 J, 1 atm = 101·325 kPa, 1 Torr = (101·325/760) kPa, and 1 Å = 10^{-10} m.

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refs. 9 and 10 and the experimental precision and accuracy were checked by measuring the enthalpy of neutralisation of tris[(hydroxymethyl)amino]methane (thm) in excess of 0·1 mol dm^{-3} aqueous hydrochloric acid. The mean of 10 runs was ΔH(298·15 K, 1 200 < N < 1 364) = −(7·12 ± 0·02) kcal mol^{-1}. Hill *et al.*[11] obtained ΔH (298·15 K, 1 170 < N < 1 574) = −(7·109 ± 0·003) kcal mol^{-1}, where N is the mol ratio of water to thm. The uncertainties in the solution calorimetric results are quoted as ±2σ, σ being the standard deviation of the mean.

Dissociation Pressures.—These were measured with a strain-gauge pressure transducer (Bell and Howell, type 4-366) fused to a glass U tube. The sensitivity of this transducer is low (≈0·08 mV Torr^{-1}) so the output was amplified using a chopper-stabilised amplifier (Ancom, type 15C-3) and displayed on a 3½-digit digital voltmeter. This combination gave a sensitivity of ≈12 mV Torr^{-1}, giving a theoretical resolution of ≈ ±0·08 Torr, but thermal zero and sensitivity shift combine to give an operating resolution of ≈ ±0·3 Torr. The gauge was tested using water and the gradient of a graph of log$_e$(output voltage) against T^{-1} gave ΔH (vaporization, 316 K) = 10·4 kcal mol^{-1} (lit.[12] 10·52 kcal mol^{-1} at 298·15 K). The results from this experiment were also used to calibrate the gauge. Temperature measurement was accurate to ±0·05 K.

RESULTS

The tetrachloroborates hydrolysed rapidly and quantitatively[2] according to equation (1). The observed

$$\mathrm{M[BCl_4](c)} + (n+3)\mathrm{H_2O(l)} = (\mathrm{MCl} + \mathrm{H_3BO_3} + 3\mathrm{HCl}), n\mathrm{H_2O(soln.)} \quad (1)$$

enthalpies of reaction are collected in Table 1. Standard enthalpies of formation were calculated from equation (2), which assumes the enthalpies of mixing of the products are zero, and the following ancillary data: $\Delta H_\mathrm{f}^{\ominus}$(RbCl, 10 000 H_2O) = −99·923 ± 0·037;[13,14] $\Delta H_\mathrm{f}^{\ominus}$(CsCl, 10 000 H_2O) = −101·606 ± 0·037;[13,14] $\Delta H_\mathrm{f}^{\ominus}$(HCl, 3 300 H_2O) = 39·875 ± 0·021;[12,15] $\Delta H_\mathrm{f}^{\ominus}$($H_3BO_3$, 10 000 H_2O) = −256·34 ± 0·31;[13,16,17] and $\Delta H_\mathrm{f}^{\ominus}$($H_2O$, l) = −68·315 ± 0·010[15] kcal

$$\Delta H_\mathrm{f}^{\ominus}(\mathrm{M[BCl_4],c}) = \Delta(H_\mathrm{f}^{\ominus}\mathrm{MCl},\ 10\,000\ \mathrm{H_2O}) + \Delta H_\mathrm{f}^{\ominus}(\mathrm{H_3BO_3},\ 10\,000\ \mathrm{H_2O}) + 3\Delta H_\mathrm{f}^{\ominus}(\mathrm{HCl},\ 3\,330\ \mathrm{H_2O} - 3\Delta H_\mathrm{f}^{\ominus}(\mathrm{H_2O,l}) - \Delta H(\mathrm{M} = \mathrm{Rb\ or\ Cs}) \quad (2)$$

mol^{-1} (ignoring the thermal effect of the different extent of dilution of the products introduces a maximum error of 0·025 kcal mol^{-1}). Hence $\Delta H_\mathrm{f}^{\ominus}$(Rb[$BCl_4$],c, 298·15 K) = −220·7 ± 0·4 kcal mol^{-1} and $\Delta H_\mathrm{f}^{\ominus}$(Cs[$BCl_4$],c, 298·15 K) = −225·0 ± 0·3 kcal mol^{-1}. The dissociation-pressure measurements for Cs[BCl_4] are given in Table 2. A least-squares fit of the results in Table 2 gives equation (3).

$$\log_e p = -[(11\,790 \pm 360)/T] + (36{\cdot}7 \pm 10 \pm 1) \quad (3)$$

TABLE 1

Heats of hydrolysis of rubidium and caesium tetrachloroborates

n *	$-\Delta H$(M = Rb)/ kcal mol^{-1}	n *	$-\Delta H$(M = Cs)/ kcal mol^{-1}
14 411	50·15	10 725	47·56
14 374	50·82	10 394	47·55
12 237	50·43	9 815	47·57
11 167	50·53	9 721	47·31
10 203	50·24	9 004	47·72
9 842	49·89	7 754	47·53
9 747	50·00	7 068	47·79
9 078	50·19	Mean (±2σ)	47·5 ± 0·1
9 004	49·99		
7 559	49·92		
Mean (±2σ)	50·2 ± 0·2		

* These mol ratios from equation (1) include a buoyancy correction for sample mass.

TABLE 2

Dissociation pressures for Cs[BCl_4]

θ$_c$/°C	55	60	65	70	75	80
p/Torr	2·0	4·0	6·7	10·5	16·7	27·2

DISCUSSION

Assuming the dissociation of Cs[BCl_4] is given by equation (4), we may write $K_p = p_{\mathrm{BCl_3}}$ Torr and $K_{p/p^{\ominus}}$ =

$$\mathrm{Cs[BCl_4](c)} \rightleftharpoons \mathrm{CsCl(c)} + \mathrm{BCl_3(g)} \quad (4)$$

0·001316 $p_{\mathrm{BCl_3}}$ taking the activities of the crystalline phases as unity. Hence equation (5) applies over the

$$\ln K_{p/p^{\ominus}} = -[(11\,790 \pm 360)/T] + (30{\cdot}1 \pm 1{\cdot}1) \quad (5)$$

range 55—80 °C. From equation (5) we obtain $\Delta H_4^{\ominus}$ at the mid-point of the temperature range, *i.e.* $\Delta H_4^{\ominus}$ (341 K) = 23·4 ± 0·7 kcal mol^{-1}. Using $\Delta H_\mathrm{f}^{\ominus}$($BCl_3$, g) = −96·15 ± 0·30 kcal mol^{-1},[18] $\Delta H_\mathrm{f}^{\ominus}$(CsCl,c) = −103·5 ± 0·3 kcal mol^{-1},[14] and the calorimetric results described above, $\Delta H_4^{\ominus}$ may be obtained directly, *i.e.* $\Delta H_4^{\ominus}$(298·15 K) = 25·3 ± 0·5 kcal mol^{-1}. Using heat capacities of similar substances, $\Delta C_p^{\ominus}(4) \approx -3$ cal K^{-1} mol^{-1}, gives a correction of ≈0·12 kcal mol^{-1} for the temperature difference in two measurements of $\Delta H_4^{\ominus}$. Thus the agreement is only fair, although more confidence should be attached to the calorimetric result. Extrapolating equation (5) to 298·15 K we obtain the following estimates at 298·15 K: $K_{p/p^{\ominus}} \approx 8 \times 10^{-5}$; $\Delta G_4^{\ominus} \approx 6$ kcal mol^{-1}; and $\Delta S_4^{\ominus} \approx 60$ cal K^{-1} mol^{-1}.

Heats of formation of two salts with a common anion

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may be used,[19] in combination with readily available ancillary data, to determine a ' thermochemical radius ' for that anion. This permits estimation of the lattice energies of salts containing that anion *via* Kapustinskii's equation.[19,20] This method of estimation is only useful when crystallographic dimensions are not available and hence a more refined calculation [19] of lattice energy is not possible. The equation for ' thermochemical radius ' is a quartic whose coefficients include the differences between the heats of formation of the salts and the cation gases. Unfortunately the heats of sublimation [21,22] of Rb and Cs, and hence the heats of formation of the ion gases, are not known to high accuracy. Hence the derived thermochemical radius for $[BCl_4]^-$ (4·48 ± 1·45 Å) has a large uncertainty. The ancillary data for this calculation were: $r(Rb^+) = 1{\cdot}48$;[23] $r(Cs^+) = 1{\cdot}69$ Å;[23] $\Delta H_f^\ominus(Rb^+,g) = 116{\cdot}78 \pm 1{\cdot}00$;[21,24] and $\Delta H_f^\ominus(Cs^+,g) = 109{\cdot}58 \pm 1{\cdot}00$ kcal mol^{-1}.[22,24] From covalent bond lengths and van der Waals radii, the radii of circumscribing spheres for $[BCl_4]^-$ and $[BF_4]^-$ may be estimated as 3·5 and 2·9 Å respectively. The ' thermochemical radius ' of $[BF_4]^-$ is 2·4 Å (calculated using recent heats of formation [25] for the Group 1 tetrafluoroborates) and this figure in comparison with the radii derived above leads us to prefer the lower limit of 3·0 Å for the ' thermochemical radius ' of $[BCl_4]^-$.

Using this value in the Kapustinskii equation we obtain the lattice-energy estimates $\Delta H_L(Rb[BCl_4]) = 119$ and $\Delta H_L(Cs[BCl_4]) = 114$ kcal mol^{-1}, from which $\Delta H_f^\ominus([BCl_4]^-,g) \approx -220$ kcal mol^{-1} {*cf.* $\Delta H_f^\ominus([BF_4]^-,g) \approx -432$ kcal mol^{-1}, calculated using 2·4 Å for the thermochemical radius of $[BF_4]^-$ in Kapustinskii's equation and recent heat of formation [25] data for $Li[BF_4]$, $Na[BF_4]$, and $K[BF_4]$}. The sensitivity of these lattice enthalpies to choice of anion radius is *ca.* 20 kcal mol^{-1} Å^{-1}. The enthalpy change in the gas-phase formation of $[BCl_4]^-$ [equation (6)] is −65 kcal mol^{-1} compared with −79 [19] for $[BH_4]^-$ and −96 for $[BF_4]^-$.

$$BCl_3(g) + Cl^-(g) \longrightarrow [BCl_4]^-(g) \qquad (6)$$

Thus the thermodynamic instability of the tetrachloroborates compared with tetrafluoroborates may not be readily deduced from the relative magnitudes of the lattice energies $\{\Delta H_L(Rb[BF_4]) \approx 135$, $\Delta H_L(Cs[BF_4]) \approx 129$ kcal mol^{-1} *via* Kapustinskii's equation}, although the difference in the gas-phase heats of formation of the complex ions is significant. The relative stability is clearly demonstrated in the dissociation pressures and enthalpies given in Table 3.

TABLE 3

Enthalpy changes and dissociation pressures for the reaction $M^I[BX_4](c) \longrightarrow M^IX(c) + BX_3(g, p_{BX_3})$ (M = Rb or Cs; X = F or Cl)

Compound	$\Delta H^\ominus$ (25 °C)/ kcal mol^{-1}	p_{BX_3} (60 °C)/ Torr
$Rb[BCl_4]$	21·7	≈20 *
$Rb[BF_4]$	>44 †	5×10^{-11} ‡
$Cs[BCl_4]$	25·3	4·0
$Cs[BF_4]$	>44 †	5×10^{-11} ‡

* Unpublished results. † Based on $\Delta H^\ominus(Li[BF_4]) < \Delta H^\ominus(Na[BF_4]) < \Delta H^\ominus(K[BF_4]) = 44$ kcal mol^{-1}.[25] ‡ Extrapolated (J. H. de Boer and J. A. M. van Liempt, *Rec. Trav. chim.*, 1927, **46**, 317).

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