Enthalpies of Formation of Alkali-metal Hexabromo-zirconate, -hafnate, and -stannate

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Enthalpies of reaction have been determined by solution calorimetry for the process (i) where M'_2M = K_2Zr, Cs_2Zr, Cs_2Hf, or K_2Sn. The data lead to the following standard enthalpies of formation, $\Delta H_f^\ominus$(298 K): $K_2[ZrBr_6]$,

$$2M'Br(c) + MBr_4(c) \longrightarrow M'_2[MBr_6](c) \qquad (i)$$

−1 603; $Cs_2[ZrBr_6]$, −1 665; $Cs_2[HfBr_6]$, −1 793; and $K_2[SnBr_6]$, −1 214 kJ mol^{-1}. The halide-ion affinities of the gaseous MBr_4 and MCl_4 molecules have been calculated by assuming semi-empirical values for the lattice energies of the complexes. Tin halides show markedly less affinity for halide than zirconium and hafnium halides. Hafnium tetrabromide has an unusually high affinity for bromide. In this respect it differs considerably from the zirconium halides.

THERMOCHEMICAL comparisons which reflect differences in electronic effects are of particular interest in making quantitative studies of bond character. Experiments in which there is little influence from structural factors are of particular value. The metals in a given periodic Group and in the second and third transition series respectively usually form analogous compounds which are isostructural and which have crystal dimensions which differ very little from one to another.

We have previously determined the enthalpy of formation of some alkali-metal hexachloro-zirconates, -hafnates, -niobates, and -tantalates.[1,2] The results suggested that a p_π–d_π dative bond is of considerable importance in the bonding of the halogen to the central atom. A thermochemical study of adduct formation between zirconium and hafnium tetrachlorides and certain organic bases [3,4] indicated that zirconium and especially hafnium show a slight tendency toward class b character.[5] A thermochemical investigation of the process (1) was of interest in order to further our understanding of the bonding of the early transition metals to

$$MBr_4 + 2Br^- \longrightarrow [MBr_6]^{2-} \qquad (1)$$

non-metal atoms. We have therefore examined the enthalpies of formation of alkali-metal hexabromozirconate and -hafnate salts by means of solution calorimetry. Potassium hexabromostannate was included in the study in order to provide a comparison with an element whose valence *d* shell is fully occupied.

RESULTS AND DISCUSSION

Enthalpies of complexing for $M'_2[ZrBr_6]$, $Cs_2[HfBr_6]$, and $K_2[SnBr_6]$, *i.e.* enthalpies of reaction (2), were

$$2M'Br\ (c) + MBr_4\ (c) \longrightarrow M'_2[MBr_6]\ (c) \qquad (2)$$

determined by measuring the heats of solution of each of processes (3)—(5). The braces denote solutions of

$$M'Br\ (c) + \{HCl, MBr_4\} \xrightarrow{\Delta H_1} \text{solution} \qquad (3)$$

$$MBr_4\ (c) + \{HCl, M'Br\} \xrightarrow{\Delta H_2} \text{solution} \qquad (4)$$

$$M'_2[MBr_6]\ (c) + HCl \xrightarrow{\Delta H_3} \text{solution} \qquad (5)$$

the appropriate quantity of solute dissolved in 4.02 mol dm^{-3} hydrochloric acid (200 cm^3). Throughout we assumed that $M'_2[MBr_6]$ dissolved to give the same dissolved species as were formed from M'Br and MBr_4 dissolved in HCl. This is based on an analogy with the chloro-complexes which precipitate immediately when hydrogen chloride gas is passed into solutions containing MCl_4 and CsCl. The bromo-complexes do not precipitate under similar conditions but bromo-salts are usually more soluble than their chloro-analogues. Acid was used as the calorimeter liquid in order to suppress hydrolysis. When distilled water was used instead, the extent of hydrolysis was poorly defined as the heat evolved was dependent on sample size.

We have explained previously that, for complexing reactions of the type under consideration, the enthalpy of complexing is very close to $2\Delta H_1 + \Delta H_2 - \Delta H_3$, *i.e.* a combination of the molar heats for processes (3)—(5).[1] Molar heats of solution for the alkali bromides are given in Table 1. A quantity of $ZrBr_4$ was dissolved in the calorimeter liquid before each run in order to give a final solution composition close to that formed by dissolving $M_2[ZrBr_6]$. However, the addition of the $ZrBr_4$ had no discernible effect on the measured values. We assumed that this would have been true also if $HfBr_4$ had been added instead. The limits given throughout this paper refer to 95% confidence. Heats of solution of the tetrabromides are given in Table 2.

TABLE 1

Molar heats of solution, ΔH_1, for KBr and CsBr in 4.02 mol dm^{-3} hydrochloric acid containing $ZrBr_4$

Compound	Weight/g	ΔH_1/kJ mol^{-1}	Mean/kJ mol^{-1}
KBr	0.468 9	19.87	19.87 ± 0.05
	0.492 5	19.87	
	0.495 5	19.92	
	0.570 0	19.83	
CsBr	1.242 9	23.39	
	2.360 2	23.26	
	2.452 7	23.10	23.25 ± 0.17

TABLE 2

Heats of solution of metal tetrabromides, ΔH_2, in 4.02 mol dm^{-3} hydrochloric acid containing alkali bromide

Compound	Weight/g	ΔH_2/kJ mol^{-1}	Mean/kJ mol^{-1}
$ZrBr_4$	0.358 3	−282	−281 ± 1
	0.372 9	−280	
	0.527 0	−280	
	0.769 0	−281	
	0.805 0	−283	
$HfBr_4$	0.437 9	−306	−303 ± 2
	0.457 2	−303	
	0.526 0	−303	
	0.647 6	−301	
	0.841 5	−302	
$SnBr_4$	1.210 8	−72.0	−72.8 ± 0.8
	1.299 3	−72.9	
	1.550 0	−73.4	

Equivalent amounts of alkali bromide were added to the calorimeter liquid in most of the runs. There was no evidence that such additions had any influence on the measured values. The results appeared to be independent of the weight of sample; therefore the solutes behaved as though they were at infinite dilution. Halide mixing according to equation (6) was apparently of

$$MBr_4 + (6 - x)Cl^- \longrightarrow [MBr_xCl_{6-x}]^{2-} + (4 - x)Br^- \qquad (6)$$

little significance for the measurements. Presumably there was negligible complexed bromide in the system owing to the large ratio of chloride to bromide in solution. In addition, the halogeno-species were partially hydrolysed to a mixture of hydroxo- and aqua-species. The validity of the calorimetric measurements depends on the ready attainment of the same equilibrium state in each case. Fortunately, compounds of the elements concerned in their quadrivalent state are highly labile.

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[1] P. Gelbman and A. D. Westland, *J.C.S. Dalton*, 1975, 1598.

[2] D. Lal and A. D. Westland, *J.C.S. Dalton*, 1974, 2505.

[3] F. M. Chung and A. D. Westland, *Canad. J. Chem.*, 1969, **47**, 195.

[4] A. D. Westland and V. Uzelac, *Canad. J. Chem.*, 1970, **48**, 2871.

[5] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.

Data for the ternary salts are given in Table 3. The data for the complexes of Zr and Hf are less precise than those obtained for the chloro-complexes.[1] This may be due in part to a greater tendency to hydrolyze during handling. We noticed that $ZrBr_4$, $HfBr_4$, and their salts fume strongly in moist air. Abnormally large and variable heats of solution were found with preparations having the composition $K_2[HfBr_6]$. We assume that we were unable fully to form $K_2[HfBr_6]$ from its components even though *X*-ray diffraction gave no indication of the presence of the starting materials. The salts $Cs_2[SnBr_6]$ and $Sr_2[SnBr_6]$ were insufficiently soluble in 4 mol dm^{-3} HCl for solution calorimetry to be carried out. This observation could be predicted by extrapolating from the value of ΔH_3 for $K_2[SnBr_6]$ on the basis of the data in Table 3.

TABLE 3

Heats of solution of alkali-metal hexabromometallates, ΔH_3, in 4.02 mol dm^{-3} hydrochloric acid

Complex	Weight/g	ΔH_3/kJ mol^{-1}	Mean/kJ mol^{-1}
$K_2[ZrBr_6]$	0.319 9	−176	−182 ± 5
	0.387 2	−188	
	0.423 9	−177	
	0.476 9	−182	
	0.761 7	−188	
$Cs_2[ZrBr_6]$	0.690 8	−119	−199 ± 1
	0.732 8	−117	
	0.794 0	−119	
	1.108 7	−120	
$Cs_2[HfBr_6]$	0.601 8	−89	−90 ± 4
	0.764 5	−91	
	0.837 7	−87	
	0.858 4	−96	
	1.119 8	−86	
$K_2[SnBr_6]$	0.606 5	19.0	19.4 ± 0.5
	0.828 4	19.8	
	1.500 8	19.4	

The heats of the complexing reactions are given in Table 4 together with enthalpies of formation $\Delta H_f^\ominus$ (298 K). The enthalpies of formation of KBr, CsBr, and $SnBr_4$ (393.2, 394.6, and 377.4 kJ mol^{-1} respectively) were taken from National Bureau of Standards compilations.[6] For $\Delta H_f^\ominus$ of $ZrBr_4$ and $HfBr_4$ we used the literature values (−759.8 and −837 kJ mol^{-1} respectively [7,8]). We see from the enthalpies of complexing that $Cs_2[HfBr_6]$ is more stable than its zirconium analogue by *ca.* 50 kJ mol^{-1}. In the case of the chloro-complexes, $Na_2[MCl_6]$ and $K_2[MCl_6]$, the hafnium complexes are more stable by only 14—17 kJ mol^{-1}. This illustrates the enhanced class b character of Hf^{IV}. It is likely that p_π–d_π bonding is an important factor here and that there is a better overlap of bromine *p* orbitals with the 5*d* orbitals of hafnium than with the 4*d* orbitals of zirconium.

TABLE 4

Heats of complexing, $\Delta H_{comp.}$, and heats of formation, $\Delta H_f^\ominus$, at 298 K for some alkali-metal hexabromometallates

Complex	$\Delta H_{comp.}$/kJ mol^{-1}	$\Delta H_f^\ominus$/kJ mol^{-1}
$Ks_2[ZrBr_6]$	−59 ± 5	−1 603 ± 6
$Cs_2[ZrBr_6]$	−116 ± 2	−1 665 ± 3
$Cs_2[HfBr_6]$	−167 ± 4	−1 793 *
$K_2[SnBr_6]$	−52.5 ± 0.6	−1 214 ± 8 *

* The confidence limits associated with $\Delta H_f^\ominus$ for $HfBr_4$ are not quoted in the literature. According to ref. 6 the confidence limits for $\Delta H_f^\ominus$ of $SnBr_4$ must lie between ±0.8 and ±8 kJ mol^{-1}. We have chosen the wider limits.

The self-consistency of the $\Delta H_{comp.}$ values for $K_2[ZrBr_6]$ and $Cs_2[ZrBr_6]$ was checked by means of a calculation described by Tsintsius and Smirnova.[9] We have also outlined the method previously.[2] In this calculation, the enthalpy of formation of $Cs_2[ZrBr_6]$ was calculated from that of $K_2[ZrBr_6]$ by making use of Yatsimirskii's expression for lattice energy and heats of formation of $K^+(g)$ and $Cs^+(g)$.[6] We used the lattice constants listed in Table 5 which were obtained by the Debye–Scherrer technique. Our calculated value for $\Delta H_f^\ominus$ of $Cs_2[ZrBr_6]$ was −1 672 kJ mol^{-1}, which differs by 7 kJ from our experimental value.

TABLE 5

Lattice constants of alkali-metal hexabromometallates *

Complex	*a*/Å
$K_2[ZrBr_6]$	10.62 ± 0.01
$Cs_2[ZrBr_6]$	10.91 ± 0.01
$K_2[HfBr_6]$	10.58 ± 0.01
$Cs_2[HfBr_6]$	10.91 ± 0.01
$K_2[SnBr_6]$	10.59 ± 0.02

* All the salts possess the $K_2[PtCl_6]$ structure.

In order to compare halide-ion affinities, it is essential to consider the reaction when all the participants are in the gaseous state. This has the advantage of eliminating the effect of crystal forces but has the disadvantage that it introduces a reorganization energy in going from tetrahedral MX_4 molecules to octahedral $[MX_6]^{2-}$ ions. Process (7) can be described with the aid of the following

$$MBr_4(g) + 2Br^-(g) \longrightarrow [MBr_6]^{2-}(g) \qquad (7)$$

cycle:

$$\begin{tikzcd}
2M'^{+}(g) + 2Br^{-}(g) + & MBr_4(g) \arrow[r, "\Delta H_g"] & 2M'^{+}(g) + [MBr_6]^{2-}(g) \\
2M'Br(c) \arrow[u, "U(M'Br)"] & MBr_4(c) \arrow[u, "\Delta H_{subl.}"] \arrow[r, "\Delta H_c"] & M'_2[MBr_6](c) \arrow[u, "U(M'_2MBr_6)"]
\end{tikzcd}$$

Admittedly the lattice energy of a ternary salt is given only approximately by an equation such as that used by Yatsimirskii and ourselves because the anion is treated as a point charge. However, differences in $U(M'_2MBr_6)$ for various M may be fairly accurate as a comparable error is made in each calculation of lattice energy. In fact, there must be various charge distributions in $[ZrBr_6]^{2-}$, $[HfBr_6]^{2-}$, and $[SnBr_6]^{2-}$ but we had no way of allowing for this.

From a Born–Haber cycle we obtain 672.0 and 621.1

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[6] 'Selected Values of Chemical Thermodynamic Properties,' Nat. Bur. Standards, Washington, Circular 500, 1952; Technical Note 270–3, 1968.

[7] A. G. Turnbull, *J. Phys. Chem.*, 1961, **65**, 1652.

[8] S. N. Lungu, *Acad. Rep. Populare Romini, Sudii Cercetari Fiz*, 1962, **13**, 29.

[9] V. M. Tsintsius and E. K. Smirnova, *Russ. J. Inorg. Chem.*, 1969, **14**, 1729.

kJ mol^{-1} for the lattice energies of KBr and CsBr respectively. The sublimation energies and ionization potentials of potassium and caesium were taken from recent literature.[10,11] Normanton and Shelton[12] gave 106.62 ± 3.55 kJ mol^{-1} as the heat of sublimation of $ZrBr_4$, and the vapour-pressure data of Berdonosov *et al.*[13] yield 101.0 kJ mol^{-1} as the heat of sublimation of $HfBr_4$.

The data lead to the following comparison for reaction (7): $M = Zr$, $\Delta H_g = -1\,465$ kJ $+ U(Cs_2ZrBr_6)$; $M = Hf$, $\Delta H_g = -1\,510$ kJ $+ U(Cs_2HfBr_6)$. As the lattice constants of $Cs_2[ZrBr_6]$ and $Cs_2[HfBr_6]$ are identical, we may conclude that very nearly $U(Cs_2ZrBr_6) = U(Cs_2HfBr_6)$. Thus the bromide-ion affinity of $HfBr_4$ is *ca.* 45 kJ mol^{-1} greater than that of $ZrBr_4$. However, from reaction (7), $\Delta H = -1\,459$ kJ $+ U(K_2SnBr_6)$ ($M = Sn$) and $\Delta H = -1\,510$ kJ $+ U(K_2ZnBr_6)$ ($M = Zr$), we find that tin exhibits considerably less bromide affinity. A main-group element ion cannot accept p_π–d_π bonding owing to the fact that its *d* shell is full. We used the following data (kJ mol^{-1}) for the reaction of $SnBr_4$: $\Delta H_{vap.}(SnBr_4) = 51.0$;[14] $\Delta H_{fusion}(SnBr_4) = 11.92$;[15] $\Delta H_{subl.}(SnBr_4) = 62.9$.

The data in ref. 1 may be compared with that obtained in the present work. In each case the affinity for chloride in the crystalline state is greater than that for bromide, but the difference in the halide affinities of ZrX_4 and HfX_4 is much greater for $X = Br$ than for Cl. The data are summarized in Table 6. The lattice energy, *U*, is in each case the value for the particular salt, $M'_2[MX_6]$. Within the group of bromides (or chlorides) with a given alkali-metal ion, there is presumably very little difference between the various values of *U*. As there is a significant difference in unit-cell size between the chloride and bromide salts (Table 5), the data in Table 6 do not afford a direct comparison of two systems if the halogen is different in each. However, if we insert the values for the various lattice energies given by the Yatsimirskii equation, we obtain the data in Table 7 which, although not very accurate, probably give a correct picture of the relative halide affinities. All of the values are probably incorrect by a nearly constant amount. The two values for Zr and Br correspond to the independent calculations which are afforded by the $K_2[ZrBr_6]$ and $Cs_2[ZrBr_6]$ systems. Only for hafnium halide is the affinity for bromide greater than that for chloride.

TABLE 6

Comparison of ΔH_g for addition of $2Cl^-$ and $2Br^-$ to MCl_4 and MBr_4 respectively. All the values are in kJ mol^{-1} of MX_4

	$K_2[MCl_6]$	$K_2[MBr_6]$	$Cs_2[MBr_6]$
Zr	$-1\,597 + U$	$-1\,510 + U$	$-1\,465 + U$
Hf	$-1\,611 + U$		$-1\,510 + U$
Sn	$-1\,547 + U$	$-1\,459 + U$	

TABLE 7

Approximate halide affinities (kJ mol^{-1}), *i.e.* ΔH for the process $MX_4(g) + 2X^-(g) \longrightarrow [MX_6]^{2-}(g)$

	Cl	Br
Zr	-26	$-9, -1$
Hf	-37	-46
Sn	$+39$	$+46$

We may conclude that the chief difference in the behaviour of Zr^{IV} and Hf^{IV} is observed when they are bonded to larger or more polarizable atoms. If these metal ions are typical of transition-metal ions of noble-gas type, we might expect that separation techniques for pairs of elements such as Zr^{IV}–Hf^{IV} and Nb^{V}–Ta^{V} might be profitably based on the use of ligands which are highly polarizable. Thus we have found that $HfBr_4$ maintained at 300 °C in a sealed evacuated tube vaporizes and reacts essentially quantitatively with NaBr held at 400 °C at the remote end of the tube. On the other hand, $ZrBr_4$ does not react with NaBr under such conditions and the $ZrBr_4$ remains at the cooler end of the tube. We are pursuing the study of this technique for the purification of $HfBr_4$. The widely used solvent-extraction technique which utilizes thiocyanate seems to depend on the polarizability of that ligand.

EXPERIMENTAL

Preparation of Compounds.—$ZrBr_4$ *and* $HfBr_4$. Crystal-bar zirconium (Ventron 99.95%) or hafnium (Ventron 99.97%) was placed in a Pyrex tube which was evacuated and sealed. A supply of purified bromine was attached to this tube *via* a break-seal. After breaking the seal, the metal was heated to 400 °C while the bromine supply remained at room temperature. Reaction was complete after 5—7 d (Found: Br, 77.85. Calc. for $ZrBr_4$: Br, 77.8. Found: Br, 64.35. Calc. for $HfBr_4$: Br, 64.15%).

$SnBr_4$. Purified bromine was dropped on to an excess of granulated tin (Fisher; 30 mesh, 0.02% foreign metals). The product was heated under reflux until the bromine had all reacted. The $SnBr_4$ was distilled with the aid of a Vigreux column at atmospheric pressure to give a straw-coloured product. Partial freezing of the product gave colourless ice-like needles.[16] Tin was determined by reduction with powdered lead and titration with standard iodine solution[17] (Found: Br, 71.6; Sn, 26.95. Calc. for $SnBr_4$: Br, 72.9; Sn, 27.1%).

$M'_2[ZrBr_6]$ *and* $M'_2[HfBr_6]$. Alkali-metal chloride (*ca.* 2 g) was dried *in vacuo*. A stoicheiometric quantity of zirconium or hafnium tetrabromide was added and the two compounds were sealed *in vacuo* in a quartz tube and melted or sintered at 550 °C in a tube furnace. The mass was ground in an inert atmosphere and reheated at 450 °C for 20 h in an evacuated Pyrex tube. The products were reground and stored under nitrogen in ampoules.

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[10] H. A. Skinner and G. Pilcher, *Quart. Rev.*, 1963, **17**, 264.

[11] C. E. Moore, ' Selected Tables of Atomic Spectra,' *Nat. Bur. Standards Ref. Data Ser.*, Nat. Bur. Standards, Washington, NSRDS-NBS, Sect. 3, 1970.

[12] A. S. Normanton and R. A. J. Shelton, *Trans. Faraday Soc.*, 1970, **66**, 33.

[13] S. S. Berdonosov, V. I. Tsirel'nikov, and A. V. Lapitskii, *Vestnik Moskov. Univ., Ser. II, Khim.*, 1965, **20**, 26.

[14] A. Kabesh and R. S. Nyholm, *J. Chem. Soc.*, 1951, 3245.

[15] S. Seki, *J. Chem. Soc. Japan*, 1941, **62**, 789.

[16] G. Brauer, ' Handbook of Preparative Inorganic Chemistry,' Academic Press, New York, 1965, p. 733.

[17] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, ' Applied Inorganic Analysis,' Wiley, New York, 1953, p. 293.

$K_2[SnBr_6]$. Potassium bromide (5.65 g) and $SnBr_4$ (10.4 g) were dissolved in 12% hydrobromic acid. The solution was filtered and allowed to crystallize in a vacuum desiccator which contained concentrated H_2SO_4. The yellow crystals were separated and washed with 48% HBr and dried *in vacuo*. The product was ground and sealed under nitrogen in ampoules (Found: Br, 69.7; Sn, 17.5. Calc. for $K_2[SnBr_6]$: Br, 70.9; Sn, 17.55%).

X-Ray powder-diffraction patterns showed only the lines belonging to the $K_2[PtCl_6]$-type structure in each case. The quantitative measurements were made on patterns obtained with the aid of an internal standard. The lattice constants were obtained from extrapolated Nelson–Riley plots.

Calorimetric Measurements.—The calorimeter has been described previously.[1] In the present study it contained 4.02 mol dm^{-3} HCl (200 cm^3) and was operated at 25 °C. The sample to be dissolved was contained in a thin-walled glass bulb which was crushed under the acid. In the runs in which $SnBr_4$ was being dissolved, the sample was vacuum distilled directly into the bulbs in an all-glass apparatus free from joints. Dissolution was complete in $\leqslant 6$ min in each case. The calorimeter was calibrated electrically before and after each sample run and the mean of the two calibrations was used. The temperature data were treated by the numerical method of Kubaschewski *et al.*[18] in order to correct for heat loss or gain. The calibration of the apparatus was verified by measuring the heat of neutralization of a sample of tris(hydroxymethyl)methylamine with excess of 0.1 mol dm^{-3} HCl at 26 °C (Found: 29.6 kJ mol^{-1}. Lit.,[19] 29.56 kJ mol^{-1}).

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[18] O. Kubaschewski, E. Ll. Evans, and C. B. Alcock, 'Metallurgical Thermochemistry,' 4th edn., Pergamon, Oxford, 1967, p. 90.

[19] R. J. Irving and I. Wadsoe, *Acta Chem. Scand.*, 1964, **18**, 195.