The Standard Enthalpies of Formation of Aluminium(III) Bromide and Aluminium(III) Iodide

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By use of solution reaction calorimetry, the standard enthalpies of formation of aluminium bromide and aluminium iodide have been determined as: ΔH_f° $AlBr_3$†(cryst.)298·15 K = $-494{\cdot}8 \pm 2{\cdot}7$ kJ mol^{-1} ($-118{\cdot}3 \pm 0{\cdot}6$ kcal mol^{-1}); and ΔH_f° AlI_3†(cryst.)298·15 K = $-280{\cdot}4 \pm 2{\cdot}6$ kJ mol^{-1} ($-67{\cdot}0 \pm 0{\cdot}6$ kcal mol^{-1}). Relevant thermodynamic parameters for the series $(AlX_3)_n$† (X = F, Cl, Br, or I; n = 1 or 2) have been recalculated and are reported.

ALTHOUGH the standard enthalpy of formation of aluminium(III) chloride is well established,[1-7] values for the analogous bromide and iodide are much more divergent, and frequently rely on old data which are not corrigible by use of modern ancillary data. Further, in a recent paper, Webb *et al.*[8] conclude that a precise determination of the standard enthalpy of formation of crystalline aluminium(III) bromide would complete the data needed to characterize thermodynamically the $(AlBr_3)_n$ system. We have therefore determined the enthalpies of aqueous alkaline hydrolysis of both aluminium(III) bromide and aluminium(III) iodide, in order to derive the standard enthalpies of formation.

EXPERIMENTAL

Purification of Compounds.—*Aluminium*(III) *bromide and aluminium*(III) *chloride*. Commercial samples (B.D.H.) were repeatedly vacuum-sublimed, initially from mixtures of the individual halide with finely divided aluminium powder. Purities were confirmed by Volhard's method for halide and precipitation (8-hydroxyquinolinate) for aluminium (Found: Br, 89·8; Al, 10·2. Calc. for $AlBr_3$: Br, 89·9; Al, 10·1%. Found: Cl, 79·1; Al, 20·3. Calc. for $AlCl_3$: Cl, 79·7; Al, 20·3%).

Aluminium(III) *iodide*. Commercial samples (Alfa Inorganics) were used directly after being checked analytically as above. Purification *via* sublimation is not possible owing to decomposition (Found: I, 93·2; Al, 7·0. Calc. for AlI_3: I, 93·4; Al, 6·6%).

Sodium halides. AnalaR samples of sodium chloride, bromide, and iodide were dried at 120 °C.

Sodium hydroxide. Commercial aqueous solutions (B.D.H. volumetric solution, 0·100M) were used directly.

Calorimeter and Procedure.—Experiments were performed with duplicate all-glass calorimeters,[9,10] operated in the isoperibol mode, immersed in a thermostat maintained at $298{\cdot}15 \pm 0{\cdot}01$ K. The performance of both calorimeters was checked by use of the neutralization of 2-amino-2-hydroxy-methylpropane-1,3-diol in excess (200 cm^3) of aqueous 0·100M-hydrochloric acid as a test reaction. Mean results (seven determinations) for each calorimeter (A and B) were as follows: A, ΔH (298·15 K: $1450 > N > 1219$) = $-29{\cdot}75 \pm 0{\cdot}09$ kJ mol^{-1}; and B, ΔH (298·15 K: $1617 > N > 1134$) = $-29{\cdot}79 \pm 0{\cdot}06$ kJ mol^{-1} where N is the mol ratio of water to the diol. For this reaction, Hill *et al.* report[11] ΔH (298·15 K: $1574 > N > 1170$) = $-29{\cdot}744 \pm 0{\cdot}006$ kJ mol^{-1}.

The calorimetric procedure was to measure the heat of hydrolysis of aluminium bromide (or iodide) in aqueous alkali in which had been dissolved the requisite amount of sodium chloride, such that the chemical composition of the post-calorimetric solution was identical to that formed (in separate runs) from aluminium chloride and sodium bromide (or iodide). In effect, this enables the standard enthalpies of formation of the aluminium bromide (and iodide) to be calculated by use of the well established value for the standard enthalpy of formation of aluminium chloride as an ancillary datum. The relevant equations are as (1) and (2), whence, ignoring contributions from

$$\begin{aligned}AlX_3(\text{cryst.}) + [n\text{NaOH} + 3\text{NaCl}](556n\text{H}_2\text{O}) \\ = [\text{NaAl(OH)}_4 + 3\text{NaX} + 3\text{NaCl} + \\ (n-4)\text{NaOH}](556n\text{H}_2\text{O}) \quad \Delta H_{\text{obs}} \quad (1)\end{aligned}$$

$$\begin{aligned}AlCl_3(\text{cryst.}) + [n\text{NaOH} + 3\text{NaX}](556n\text{H}_2\text{O}) \\ = [\text{NaAl(OH)}_4 + 3\text{NaX} + 3\text{NaCl} + \\ (n-4)\text{NaOH}](556n\text{H}_2\text{O}) \quad \Delta H_{\text{obs}} \quad (2)\end{aligned}$$

(a) enthalpies of dilution arising from slight differences in concentration between the final solutions of (1) and (2), and (b) enthalpies of mixing of aqueous sodium halide and sodium hydroxide, we obtain equation (3).

$$\begin{aligned}\Delta H_f^\circ AlX_3(\text{cryst.}) = \Delta H_{\text{obs}}(2) - \Delta H_{\text{obs}}(1) + \\ 3\Delta H_f^\circ \text{NaX}(185n\text{H}_2\text{O}) - 3\Delta H_f^\circ \text{NaCl}(185n\text{H}_2\text{O}) + \\ \Delta H_f^\circ AlCl_3(\text{cryst.}) \quad (3)\end{aligned}$$

Samples of aluminium halide were loaded in a dry-box into glass ampoules, each with two fragile bulbs, and transferred to the calorimeters which were charged with aqueous 0·100M-sodium hydroxide (200 cm^3) containing dissolved sodium halide.

Units and Errors.—Enthalpies are expressed throughout in kJ mol^{-1}; for comparison, relevant literature values have been recalculated by use of 1 calorie = 4·184 J. Uncertainties are expressed as ± two standard deviations of the mean.

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† Throughout this paper AlX_3 (X = halogen) is used to symbolise conveniently one mole of aluminium(III) halide, without prejudice as to structure or molecular formulation.

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RESULTS

All calorimetric reactions proceeded rapidly, quantitative reaction being attained within *ca.* 0·5 min. Acid mist was observed over the surface of the calorimetric liquid immediately after ampoule fracture, but disappeared rapidly and had no apparent effect on the reaction time–resistance trace. Post-calorimetric halide analyses were consistent with quantitative reaction according to equations (1) and (2). The calorimetric results are in Table 1.

TABLE 1

Enthalpies of hydrolysis of aluminium halides at 298·15 K

(1) $AlBr_3(cryst.) + [nNaOH + 3NaCl](556nH_2O) =$
$[NaAl(OH)_4 + 3NaBr + 3NaCl + (n - 4)NaOH](556nH_2O)$

w/g	n	$-\Delta_{obs}$/kJ mol^{-1}
0·1386	38·5	424·6
0·1756	30·4	422·0
0·1728	30·9	430·0
0·0907	58·8	424·6
0·0886	60·2	428·1
0·1308	40·8	425·0
0·0758	70·4	424·5
0·1481	36·0	424·7
0·1472	36·2	421·8
0·1639	32·5	422·5
0·1219	43·8	428·0
0·1445	36·9	418·2
	Mean 43·0	Mean 424·5 ± 1·8

(2) $AlCl_3(cryst.) + [nNaOH + 3NaBr](556nH_2O) =$
$[NaAl(OH)_4 + 3NaBr + 3NaCl + (n - 4)NaOH](556nH_2O)$

w/g	n	$-\Delta H_{obs}$/kJ mol^{-1}
0·1175	22·7	350·7
0·1090	24·5	357·1
0·0916	29·1	350·2
0·0602	44·3	355·1
0·0831	32·1	349·5
0·0478	55·8	359·0
0·0605	44·1	349·3
0·1202	22·2	353·9
0·0929	28·7	354·4
0·0799	33·4	354·0
0·1108	24·1	351·3
	Mean 32·8	Mean 353·1 ± 1·9

(1) $AlI_3(cryst.) + [nNaOH + 3NaCl](556nH_2O) =$
$[NaAl(OH)_4 + 3NaCl + 3NaI + (n - 4)NaOH](556nH_2O)$

w/g	n	$-\Delta H_{obs}$/kJ mol^{-1}
0·0753	108·3	444·8
0·2527	32·3	444·1
0·2735	29·8	445·6
0·2351	34·7	442·1
0·2340	34·8	444·3
0·1680	48·5	443·0
0·3047	26·8	441·0
0·3124	26·1	440·4
0·1824	44·7	444·0
0·2484	32·8	441·7
0·1950	41·8	442·5
	Mean 41·9	Mean 443·0 ± 1·0

(2) $AlCl_3(cryst.) + [nNaOH + 3NaI](556nH_2O) =$
$[NaAl(OH)_4 + 3NaCl + 3NaI + (n - 4)NaOH](556nH_2O)$

w/g	n	$-\Delta H_{obs}$/kJ mol^{-1}
0·0868	30·7	353·7
0·0919	29·3	354·3
0·0765	34·9	345·4
0·1433	18·6	355·7
0·1081	24·7	350·6
0·1202	22·2	354·1
0·0533	50·0	345·5
0·0743	35·9	356·7
0·0958	27·8	347·4
0·1164	22·9	352·6
0·1295	20·6	355·3
0·1139	23·4	355·4
	Mean 28·4	Mean 352·2 ± 2·3

From equation (3), and using the following ancillary data: $\Delta H_f^\circ NaCl(7963H_2O) = -406{\cdot}963$ kJ mol^{-1},[12,*] $\Delta H_f^\circ NaBr(6072H_2O) = -360{\cdot}411$ kJ mol^{-1},[12,*] $\Delta H_f^\circ NaCl(7759H_2O) = -406{\cdot}961$ kJ mol^{-1},[12,*] $\Delta H_f^\circ NaI(5259H_2O) = -295{\cdot}426$ kJ mol^{-1},[12,*] and $\Delta H_f^\circ AlCl_3(cryst.) = -705{\cdot}84 \pm 0{\cdot}67$ kJ mol^{-1} [7] we obtain $\Delta H_f^\circ AlBr_3(cryst.) = -494{\cdot}8 \pm 2{\cdot}7$ kJ mol^{-1} and $\Delta H_f^\circ AlI_3(cryst.) = -280{\cdot}4 \pm 2{\cdot}6$ kJ mol^{-1}.

DISCUSSION

Literature values for the standard enthalpies of formation of aluminium bromide and aluminium iodide differ considerably from those reported above, as shown in Table 2.[13–16] Previous determinations involving neutral or acid aqueous hydrolysis are suspect since (*a*) preliminary experiments showed the formation of acid mist above the solutions to be considerably greater than in alkaline solution; (*b*) the hydrolyses are known to be relatively slow [17] in non-alkaline conditions, while all the calculations assume almost instantaneous reaction; and (*c*) owing to hydrolysis, the enthalpies of solution of aluminium halides in neutral or acid solution are highly dependent on dilution [18] and pH,[19] as are the nature of the ions formed (see, *e.g.*, Grunwald and Dodd [20]). Most calculations involve the assumption that the reaction proceeds quantitatively to $Al^{3+}(aq)$ and $X^-(aq)$ ions. This is only true at low pH ($\leqslant 2$),[21]

TABLE 2

Values of the standard enthalpies of formation of aluminium bromide (cryst.) and aluminium iodide (cryst.)

$\Delta H_f^\circ(298{\cdot}15\ K)$/kJ mol^{-1}

$AlBr_3$	−527 [1,2]	−514·6 [13]	−506 [3,4,*]	−494·8 ±2·7 †	
AlI_3	−318 [1,2]		−297 [3,4,*]	−314·6 [14,15] −280·4 ±2·6 †	−308·4 [15,16]

* At 293·15 K. † This work.

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* No error limits are included owing to the impossibility of assigning meaningful values.

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and at low aluminium concentrations. It is significant that for both the bromide and iodide, the literature value that approaches most closely to that in the present work was obtained by a method involving solution in very strong acid.[3,4]

In the present work, the use of alkaline hydrolysis ensured fast reaction. The precise nature of the dissolved aluminium is irrelevant in the use of the calorimetric data to derive standard enthalpies of formation of $AlBr_3$(cryst.) or AlI_3(cryst.). The essential assumption is the identity of the solutions resulting from hydrolysis of the aluminium halides. Since all hydrolyses were carried out in the same apparatus, by identical procedures, and under closely similar conditions of ionic strength, temperature, pH, and dilution, this assumption is reasonable.

$NaAl(OH)_4$(aq).—The nature of aluminium-containing species in aqueous media comparable with those employed in the calorimetric hydrolysis has recently been discussed.[22,23] It is concluded that, under these conditions, $Al(OH)_4^-$ is the predominant species at concentrations less than 1M. From equation (2) and appropriate values of ancillary data given above, together with $\Delta H_f^\circ NaOH(556H_2O) = -469{\cdot}11$ kJ mol^{-1},[12] a value for the standard enthalpy of formation of aqueous sodium tetrahydroxoaluminate can be calculated as $\Delta H_f^\circ NaAl(OH)_4$ (298·15 K, 17,000H_2O) $= -1715{\cdot}0 \pm 1{\cdot}7$ kJ mol^{-1}.

The values reported above for the standard enthalpies of formation of aluminium bromide and aluminium iodide can be used to recalculate the thermodynamic parameters reported by Webb *et al.*[8] for the $(AlBr_3)_n$ system, and by N.B.S. Technical Note 270–3 [2] for the $(AlI_3)_n$ system. The new values are in Table 3, together with the values for the fluoride [2] and chloride [2] [also recalculated, based upon Gross and Hayman's recommended figure for $\Delta H_f^\circ AlCl_3$(cryst.)].*

TABLE 3

Thermodynamic parameters of the $(AlX_3)_n$ system (values taken directly from, or derived using data from, reference 2 unless otherwise stated)

Compound	$-\Delta H_f^\circ$ kJ mol^{-1}	$-\Delta S_f^\circ$ J K^{-1} mol^{-1}	$-\Delta G_f^\circ$ kJ mol^{-1}
AlF_3(cryst)	1504·1	265·9 [e]	1425·1
$AlCl_3$(cryst)	705·8 [d]	252·1 [e]	630·7 [d]
$AlBr_3$(cryst)	494·8 [b]	76·4 [c,e] (216·1 [c,e])	472·0 [c]
AlI_3(cryst)	280·4 [b]	43·5 [e] (260·2 [e])	267·4
AlF_3(liq)	—	—	—
$AlCl_3$(liq)	672·3 [a]	181·0 [a,e]	618·3 [a]
$AlBr_3$(liq)	483·8 [c]	[67·1 [a,e] (206·8 [a,e])]	[463·8] [a]
AlI_3(liq)	267·2 [a]	[−16·9 [a,e] (199·7 [a,e])]	[272·2] [a]
Monomer			
AlF_3(g)	1204·6	55·2 [e]	1188·1
$AlCl_3$(g)	584·8	[50·6] [a,e]	[569·7] [a]
$AlBr_3$(g)	390·8 [c]	[−96·9 [c,e] (42·7 [c,e])]	[429·7] [c]
AlI_3(g)	174·1	[−160·5 [a,e] (56·1 [a,e])]	[221·9] [a]
Dimer			
$\frac{1}{2}Al_2F_6$(g)	1313·8	—	—
$\frac{1}{2}Al_2Cl_6$(g)	647·0	118·0 [e]	611·8
$\frac{1}{2}Al_2Br_6$(g)	452·1 [c]	−17·0 [c,e] (122·6 [c,e])	457·2 [c]
$\frac{1}{2}Al_2I_6$(g)	225·0	[−89·5 [a,e] (127·1 [a,e])]	[251·7] [a]

[ ] Figures in square brackets are estimates. ( ) Values in parentheses calculated by assuming the standard state of the elemental halogen to be gaseous.

[a] Value calculated by use of S° or ΔH_f° values from ref. 15. [b] Present work. [c] Values taken from ref. 8. [d] By use of ΔH_f° from ref. 7. [e] ΔS_f° values calculated from S° data only.

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