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THERMOCHEMISTRY OF POLYHALIDES. II*. CAESIUM AND RUBIDIUM DIBROMOIODIDES

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ABSTRACT

Using a solution-reaction calorimeter the standard enthalpies of formation of crystalline caesium and rubidium dibromoiodides have been determined as -445.5 ± 4.1 and -428.3 ± 4.2 kJ mol^{-1}, respectively. Thermodynamic parameters, including lattice energies, are calculated and the thermal stability of polyhalides discussed. Thermometric titrations have been used to investigate the mechanism of reaction of caesium dibromoiodide with aqueous silver nitrate.

INTRODUCTION

Although generally well characterised structurally[1,2] and readily preparable in a pure state[3], thermodynamic measurements on crystalline polyhalides are available only for a small number of triiodides[4–6], a tribromide[7], and two dichloroiodides*. In this communication we report the extension to $CsIBr_2$ and $RbIBr_2$ of a solution-reaction procedure which has been successfully developed and used with the polyhalides MIX_2 (M = Cs, Rb; X = Br, Cl).

The mechanism of the reaction, shown in eqn (1) (mol ratio, $CsIBr_2$:$AgNO_3$ = 1:3) has been investigated using a thermometric titration and also by measuring the enthalpy of reaction of $CsIBr_2$ with silver nitrate under different conditions (mol ratio, $CsIBr_2$:$AgNO_3$ = 1:2, eqn (2)).

$$3MIBr_2+9AgNO_3+3H_2O = 6AgBr+2AgI+AgIO_3+6HNO_3+3MNO_3 \quad (1)$$

$$5MIBr_2+10AgNO_3+3H_2O = 10AgBr+HIO_3+5HNO_3+5MNO_3+2I_2 \quad (2)$$

EXPERIMENTAL

Materials and syntheses

$CsIBr_2$. To aqueous CsBr (10.6 g, 0.05 mol; 100 cm^3 H_2O; B.D.H., reagent grade) powdered I_2 (6.4 g, 0.025 mol; B.D.H. AnalaR-quality reagent) was added, and the mixture warmed to ca. 60 °C with stirring. Bromine (4.0 g, 0.025 mol;

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* Part I, A. Finch, P. N. Gates and S. J. Peake, *J. Chem. Soc. (Dalton)*, in press.

B.D.H., reagent grade) was added and stirred for ca. 15 min. Glistening, orange-red crystals appeared on cooling in ice; these were dried on a sintered glass funnel and stored in a desiccator[3] over P_2O_5.

$RbIBr_2$. This was similarly prepared using RbBr (20.0 g, 0.12 mol; Koch-Light Laboratories Ltd.), iodine (15.3 g) and bromine (9.66 g)[8].

Analyses. Duplicate samples were analysed gravimetrically for Cs (and Rb) as tetraphenylborates. Total halide (I+Br) was measured volumetrically (Volhard procedure) after reduction of each polyhalide with aqueous SO_2. Iodine was measured in separate samples by the palladous iodide gravimetric procedure after reduction of the polyhalide by aqueous SO_2. Bromine was then calculated by difference. Results were: $CsIBr_2$: Cs, 31.82 and 31.80% (calc., 31.67%); I, 30.55% (calc., 30.24%); Br, 37.62% (calc. 38.09%). $RbIBr_2$: I, 34.02% (calc. 34.09%); Br, 42.76% (calc. 42.94%).

Calorimetry

The isoperibol calorimeter used in the ampoule-breaking mode for the reactions with $CsIBr_2$ and $RbIBr_2$ is conventional and has been described elsewhere[9]. Check experiments were made, using the neutralisation of 2-amino-2-hydroxymethylpropane-1,3 diol in aqueous 0.100 mol dm^{-3} hydrochloric acid as a test reaction before and after the dibromoiodide reactions. Results were: $\Delta H° = -29.87 \pm 0.05$ kJ mol^{-1}; $1296 < n < 1780$ (lit.[10] $\Delta H° = -29.790 \pm 0.031$ kJ mol^{-1}, $n = 1345$).

For thermometric titrations, the calorimeter was equipped with an 8 cm tapered-glass titrant delivery tube sealed into an entry ferrule with epoxy resin. This connected to a polyethylene tube, ca. 1 mm diameter and 12 m in length, coiled round a 5 cm diameter brass tube immersed in the constant-temperature bath (25.00±0.01 °C; Tronac, model 1040) holding the calorimeter; this acted as a reservoir of ca. 13 cm^3 capacity. The titrant was supplied to the reservoir via a hypodermic needle from a 10 cm^3 precision syringe ("Re-pette", Jencons Ltd.) activated by a syring-motor (Razel Scientific Instruments, U.S.A., type A-99). The delivery system was calibrated from the results of eleven replicate measurements of weights of water delivered at measured times.

The a.c. thermistor bridge was adjusted such that each thermometric titration could be recorded within one ten inch potentiometric recorder chart width. The performance of the system was checked before use by titrating 100 cm^3 of carbonate-free aqueous NaOH (0.006 mol dm^{-3}) with aqueous HCl (0.30 mol dm^{-3}), and calculating the enthalpy of neutralisation, ΔH_N°, and also by titrating KBr (0.150 mol dm^{-3}) with $AgNO_3$ (1.00 mol dm^{-3}, B.D.H. volumetric standard solution) and calculating the enthalpy of precipitation ΔH_P°. Results were: $\Delta H_N^\circ = -55.74 \pm 0.36$ kJ mol^{-1} (5 runs); (lit.[11] $\Delta H_N^\circ = -55.80 \pm 0.06$ kJ mol^{-1}); $\Delta H_P^\circ = -84.71$ (single run) (lit.[12] $\Delta H_P^\circ = -84.84$ kJ mol^{-1}).

Since the thermometric apparatus was used to investigate mechanisms of reaction and not to measure precisely enthalpies of reaction no attempts were made to improve further the performance.

RESULTS

Standard enthalpies of formation

Using the ampoule-breaking mode, the standard enthalpies of reaction (Table 1) of $RbIBr_2$ and $CsIBr_2$ with excess $AgNO_3$, aq were measured according to thermochemical eqn (1). Reactions were reasonably fast, being thermally complete in ca. 5 min. Considerable care was needed to ensure adequate and controlled stirring of the dense precipitates of silver halides and iodate. Initial liberation of iodine, followed by its disappearance, was clearly seen. Using the following ancillary data:

$\Delta H_f^\circ[AgI, AgBr, and AgIO_3](c) = [-61.84 \pm 0.1^{13}, -100.37 \pm 0.1^{13},$
and -166.24 ± 0.7^{14}, repectively];
$\Delta H_f^\circ[RbNO_3, (aq)$ and $CsNO_3, (aq)]^{15,16} =$ [i.e. -458.06 ± 0.84
and -465.0 ± 0.84, respectively];
$\Delta H_f^\circ[HNO_3(3.000\ H_2O)]^{16}, = -206.97 \pm 0.46$
$\Delta H_f^\circ\ H_2O(1)^{17} = -285.83 \pm 0.04$.

TABLE 1

ENTHALPY OF REACTION OF $CsIBr_2$(c), AND $RbIBr_2$(c), WITH SILVER NITRATE IN WATER AT 298.15 K[a]

$3MIBr_2(c) + [(p+9)\ AgNO_3]\ mH_2O(l) + (q+3)\ H_2O(l) = 6AgBr(c) + 2AgI(c) + AgIO_3(c) +$
$+ [pAgNO_3 + 6HNO_3 + 3MNO_3](m+q)\ H_2O(l)$

Mass $RbIBr_2$ (g)	n[b]	*$-\Delta H_R$ (kJ mol^{-1})*	*Mass $CsIBr_2$ (g)*	n[b]	*$-\Delta H_R$ (kJ mol^{-1})*
0.29340	7026	149.37	0.31460	7410	139.69
0.28082	7363	150.31	0.29318	7951	140.30
0.26698	7745	151.10	0.32880	7090	139.96
0.30994	6671	150.68	0.29866	7805	140.06
0.32852	6294	149.34	0.34481	6761	139.00
0.35326	5853	150.62	0.31829	7324	139.69
0.34001	6081	150.45	0.22705	10261	140.55
0.33173	6233	149.13	0.33177	7027	139.66
0.32096	6442	149.61	0.31316	7444	139.32
0.31522	6559	149.94	0.30744	7583	139.74

Mean $\Delta H_R = -150.06 \pm 0.48^c$ kJ mol^{-1}; mean $\Delta H_R = -139.80 \pm 0.32^c$ kJ mol^{-1}.

[a] The calorimetric liquid was pre-saturated with $AgIO_3$ to ensure complete precipitation of this compound upon reaction. [b] n is the mol ratio, $H_2O:MIBr_2$. [c] Uncertainties are calculated throughout as 95% levels, using a student's t distribution table with the appropriate number of degrees of freedom.

All values are in kJ mol^{-1}; where not stated explicitly in the original references, uncertainties are estimated as ten times the last recorded figure; the following standard enthalpies of formation were calculated: $\Delta H_f^\circ(\mathrm{RbIBr_2}, c) = -428.3 \pm 4.2$ and $\Delta H_f^\circ(\mathrm{CsIBr_2}, c) = -445.5 \pm 4.1$ kJ mol^{-1}.

Mechanism of reaction

(a) Thermometric titrations of aqueous $AgNO_3$ against aqueous $CsIBr_2$ were performed; duplicate experiments gave identical results, shown in Fig. 1. Four distinct changes in slope are apparent, at mol ratios, $CsIBr_2$:$AgNO_3$ of 2.00 to 1; 2.47:1; 2.67:1; and 3.00:1, the last representing complete reaction.

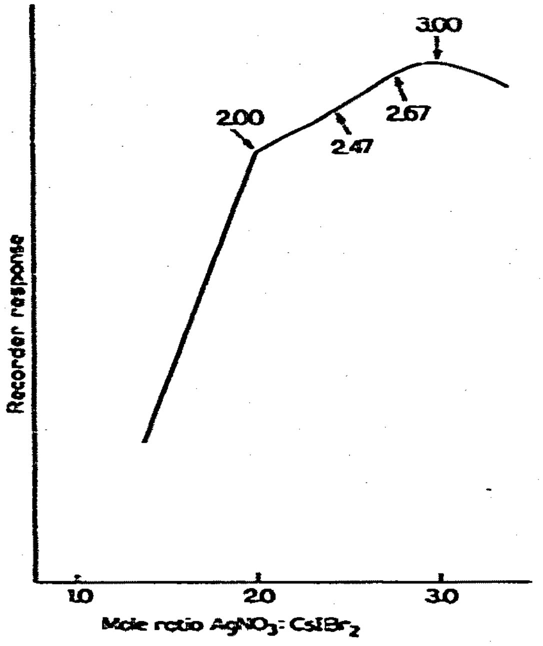

Fig. 1. Thermometric titration of aqueous $AgNO_3$ against aqueous $CsIBr_2$.

Two further experiments were performed, (i) a thermometric titration of KIO_3, 0.0028 mol dm^3, and (ii) a titration of "$CsIBr_2$, aq" over the range specified by the 2.67:1 to 3.00:1 portions of the thermogram. For these appropriate calibrations were made and results for measured enthalpies of reaction were (a) $\Delta H^\circ = -51.2$, and (b) $\Delta H^\circ = -51.9$ kJ mol^{-1}.

(b) Ampoule-breaking experiments: results are collated in Table 2. Using appropriate ancillary data, vide supra, together with ΔH_f° (HIO_3, 23 000 H_2O), $= -221.9 \pm 0.4$[18,19] and ΔH_f° (I_2, aq) $= +22.59 \pm 0.42$ kJ mol^{-1}[20] we calculate, assuming thermochemical eqn (2), $\Delta H_f^\circ(\mathrm{CsIBr_2}, c) = -450.15 \pm 6.41$ kJ mol^{-1}.

TABLE 2

ENTHALPY OF REACTION OF $CsIBr_2$ (1 mol) WITH $AgNO_3$ (2 mol) IN H_2O AT 298.15 K
$5CsIBr_2(c)+[10AgNO_3,\ mH_2O](l)+(q+3)H_2O(l)=10AgBr(c)+$
$[HIO_3+5HNO_3+5CsNO_3](m+q)H_2O(l)+2I_2(c)$

Mass $CsIBr_2$(g)	n[a]	$-\Delta H_R$ *(kJ mol^{-1})*
0.55057	4234	91.89
0.48643	4793	92.25
0.60548	3850	90.90
0.51202	4553	92.69
0.50088	4654	92.43

Mean $\Delta H_R = -92.03 \pm 0.80$ kJ mol^{-1}.
[a] $\langle n \rangle = 4417$.

DISCUSSION

(a) Lattice energies and thermal stability

Using the well-known Yatsimirskii–Kapustinskii procedure, values of lattice energies and of standard enthalpies of formation of Group IA and Group IIA dibromoiodides have been computed. Results are as follows, and in Table 3: thermochemical radius, $r_{th}(IBr_2^-) = 404$ pm; $\Delta H_f^\circ(IBr_2^-,\ g) = -502$ kJ mol^{-1}. Input data required are: crystal radii, $r(Cs^+)$ and $r(Rb^+) = 168$ and 147 pm[21], respectively, ΔH_f°(Cs^+ and Rb^+)$=459.8$ and 491.2 kJ mol^{-1}, respectively[21], and ΔH_f°[$CsIBr_2$ and $RbIBr_2$], (c), from above (Results section). Computer programmes* were written for solution of the quartic equation for the value of r_{th} (Fortran IV; also for the Hewlett-Packard, Model 65, calculator).

TABLE 3

LATTICE ENERGIES, *U*, AND STANDARD ENTHALPIES OF FORMATION OF $MIBr_2$ AND $M'(IBr_2)$ CRYSTALS (kJ mol^{-1})

M	*U*	$-\Delta H_f^\circ(MIBr_2,\ c)$	*M'*	*U*	$-\Delta H_f^\circ[M'(IBr_2)_2,\ c]$
Li	484	304	Mg	1430	94
Na	449	346	Ca	1349	437
K	423	416	Sr	1308	531
Rb	413	428.3[a]	Ba	1267	621
Cs	399	445.5[a]			
NH_4	415	303			

[a] Experimental values.

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*Available on request.

An interesting use of these data is the prediction and rationalisation of thermal stability. Values of $\Delta H_f^\circ(\mathrm{MIBr_2, c})$ are all substantially negative. However, for alkali-metal salts thermal decomposition to the appropriate interhalogen and binary halide, viz., $\mathrm{MIBr_2 \rightarrow MBr + IBr}$, is the preferred mode, a dissociative process which has also been documented in non-aqueous solvents[22]. For this, the dissociation enthalpy, $\Delta H_\mathrm{D}^\circ = U(\mathrm{MIBr_2}) - U(\mathrm{MBr}) + \Delta H_f^\circ(\mathrm{IBr, c}) + \Delta H^\circ(\mathrm{Br^-, g}) - \Delta H_f^\circ(\mathrm{IBr_2^-, g})$. Substituting accepted data for $\Delta H_f^\circ(\mathrm{Br^-, g}) = -234\ \mathrm{kJ\ mol^{-1}}$, $\Delta_f^\circ H(\mathrm{IBr, c}) = -10.5\ \mathrm{kJ\ mol^{-1}}$ and $\Delta H_f^\circ(\mathrm{IBr_2^-, g}) = -502\ \mathrm{kJ\ mol^{-1}}$ (above), we derive $\Delta H_\mathrm{D}^\circ = \Delta U(\mathrm{MIBr_2 - MBr}) + 258\ \mathrm{kJ\ mol^{-1}}$. For dissociative stability $\Delta H_\mathrm{D}^\circ > 0$, and hence the stability condition is $\Delta U > -258$. For the alkali metal series $-232 > \Delta U > -324$, and only $\mathrm{CsIBr_2}$ and $\mathrm{RbIBr_2}$ are predicted to be thermodynamically stable with respect to dissociation products with $\Delta H_\mathrm{D}^\circ \simeq -1$ for $\mathrm{KIBr_2}$. If, however, the product IBr is written in its gas state, then $\Delta H_\mathrm{D}^\circ = \{-232 \text{ to } -324\} + 309$, and thermodynamic stability is predicted for all except $\mathrm{LiIBr_2}$. In general, for solid phase products, the entropy contribution is quite unlikely to make any significant change, i.e., $\Delta H_\mathrm{D}^\circ \simeq \Delta G_\mathrm{D}^\circ$. At elevated temperatures this will not be so, since both factors in the $(T\Delta S_\mathrm{D}^\circ)$ contribution will increase. $\Delta S_\mathrm{D}^\circ$ will be positive, and $\Delta G_\mathrm{D}^\circ$ will decrease correspondingly.

Estimates for all thermodynamic quantities are available for the three series $\mathrm{MIX_2}$ (X = I, Br, Cl; M = Li, Na, K, Rb, Cs) and, hence, it is instructive to attempt to assess the relative importance of such parameters, especially since as differences are considered, uncertainties introduced by calculations based on approximations such as the Kapustinskii procedure should largely cancel. Somewhat surprisingly, when considering lattice energy values, $U(\mathrm{MIBr_2}) > U(\mathrm{MICl_2}) > U(\mathrm{MII_2})$, over all metals, Li to Cs. The inequalities, however, are relatively small, from ca. 40 to 60 kJ mol^{-1}. For the gas ions, $-\Delta H_f^\circ(\mathrm{ICl_2^-, g}) > -\Delta H_f^\circ(\mathrm{IBr_2^-, g}) \simeq -\Delta H_f^\circ(\mathrm{II_2^-, g})$ with the first number ca. 100 kJ more negative than the second. This parallels in order, but not in magnitudes, the single-halogen ions for which: $-\Delta H_f^\circ(\mathrm{Cl^-, g}) \simeq -\Delta H_f^\circ(\mathrm{Br^-, g}) > -\Delta H_f^\circ(\mathrm{I^-, g})$. Thus it seems that no single parameter predominates, and hence in isolation is likely to be unhelpful. Experimental polyhalide stability studies are neither comprehensive nor in agreement[4,5,23–27], though a concensus view is probably $\mathrm{I_3^- < IBr_2^- < ICl_2^-}$. Thus a general conclusion might be that while a rank order is satisfactorily given by inspection of values of $\Delta H_f^\circ(\mathrm{MIX_2, c})$, the thermodynamic stability of an individual compound is best predicted by a calculation based on the dissociation process.

(b) Mechanism of reaction

Detailed early work[23] has strongly indicated that in the reaction of $\mathrm{CsIBr_2}$ with aqueous $\mathrm{AgNO_3}$ a transient reversible hydrolytic equilibrium is established:

$$5\mathrm{IBr_2^-} + 3\mathrm{H_2O} \rightleftharpoons 2\mathrm{I_2} + \mathrm{IO_3^-} + 10\mathrm{Br^-} + 6\mathrm{H^+} \tag{3}$$

A reasonable sequence of secondary, irreversible, processes which follow is: (a) quantitative precipitation of AgBr only, (b) simultaneous precipitation of $\mathrm{I_2}$, reaching a maximum concentration at a mol ratio, $Ag^+:IBr_2^- = 2:1$, (c) reaction of I_2 with Ag^+, and precipitation of $AgIO_3$ according to $3\,I_2+6\,Ag^+ +3\,H_2O \rightarrow 5\,AgI+6\,H^+ +AgIO_3$. The overall process is hence that given as thermochemical eqn (1), and for which there is abundant chemical evidence.

The above sequence is fully consistent with the results of the thermometric titrations. The first portion of the reaction trace in Fig. 1 clearly represents process (a) since the stoichiometry at the end-point is as expected, $IBr_2^-:Ag^+ = 1:2.00$. In addition, from the results collected in Table 2, a value of $\Delta H_f^\circ(CsIBr_2, c) = -450.2 \pm 6.4$ kJ mol^{-1}, is calculated in good agreement with that derived from the overall reaction, of established stoichiometry, viz., $\Delta H_f^\circ(CsIBr_2, c) = 445.5 \pm 4$ kJ mol^{-1}. The second and third portions of the curve from the 2.00 to the 2.67 mol point, presumably reflects process (b), together with simultaneous precipitation of AgI. Precipitation of $AgIO_3$ is not expected until removal of all Br^- is complete, since the ratio of solubilities of $AgIO_3$ and AgI is 1:10. This implies that the final portion of the curve, from the mol point 2.67 to 3.00, represents precipitation of all IO_3^-. This was confirmed by the close agreement of the enthalpy change measured over this range, (51.9 kJ mol^{-1}) to that obtained from a separate experiment in which aqueous $AgNO_3$ was titrated against aqueous KIO_3, (51.2 kJ mol^{-1}).

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