Thermochemistry of Polyhalides. Part 1. Caesium and Rubidium Dichloroiodates(I)

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The standard enthalpies of formation of crystalline Cs[ICl_2] and Rb[ICl_2] have been determined as −511.1 ± 4.1 and −491.4 ± 4.1 kJ mol^{-1} respectively, based on enthalpies of reaction with aqueous silver(I) nitrate. The results are discussed in relation to various thermodynamic parameters.

A LARGE number of polyhalides is known, and their preparation, structures, and properties are well documented.[1,2] However, thermodynamic data, even for simple systems, are largely restricted to stability-constant measurements in aqueous and in non-aqueous solvents.[1,2] There are no data for crystalline compounds, other than several tri-iodides M[I_3] (M = Cs, Rb, or NH_4) which have been studied using various techniques [3-5] and a single determination for Cs[Br_3].[6] None of these methods seems capable of extension to higher, or non-symmetrical, polyhalides.

This paper describes the evaluation of a much more generally applicable method, *viz.* reaction with aqueous silver(I) nitrate, capable of use with several polyhalide complexes, and reports its use in the determination of the standard enthalpies of formation of caesium and rubidium dichloroiodates(I).

EXPERIMENTAL

Materials.—Commercial samples of caesium chloride and iodide, rubidium chloride, iodine, palladium(II) chloride, and silver(I) nitrate (B.D.H., purest available grade) and chlorine (Matheson Co. Ltd.) were used directly.

Syntheses.—To aqueous CsCl (16.8 g, 0.1 mol; 170 cm^3 of water) or RbCl (15 g, 0.12 mol; saturated solution) in a two-necked flask was added powdered iodine (12.7 g, 0.05 mol; 16 g, 0.07 mol, respectively), with stirring, and the solution was warmed to *ca.* 75 °C. Chlorine was passed into the solution until the iodine just dissolved; excess of Cl_2 was avoided to prevent formation of $[ICl_4]^-$.[7] Golden Cs[ICl_2] (or orange-yellow Rb[ICl_2]) crystals, formed on cooling in ice, were filtered on a glass sinter; Cs[ICl_2] was recrystallised from hot aqueous hydrochloric acid (HCl : water = 1 : 1), Rb[ICl_2] appeared to be too soluble to permit recrystallisation.[8] Samples were dried at room temperature over P_4O_{10}. Caesium tri-iodide was prepared by an established procedure from aqueous CsI (9.6 g, 0.04 mol; 80 cm^3 of water) and saturated alcoholic iodine (30 cm^3).[3] Dark violet crystals of Cs[I_3] were dried over P_4O_{10} and used without further purification.

Analysis.—Solid-state Raman spectra (Coderg PHO Raman spectrometer using 647.1-nm exciting radiation) confirmed the presence of $[ICl_2]^-$ species.[9] Alkali-metal contents were determined gravimetrically using sodium tetraphenylborate as precipitant. Total halide was determined by a titrimetric procedure (Volhard) after reduction to halide ions by boiling with aqueous sulphur dioxide. Iodine was analysed in the presence of chlorine gravimetrically as palladium(II) iodide according to an established procedure; chlorine was calculated by difference

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[1] A. I. Popov, 'Halogen Chemistry,' ed. V. Gutmann, Academic Press, 1967, vol. 1, p. 225.

[2] A. I. Popov, *M.T.P. Internat. Rev. Sci.*, 1972, **3**, 53.

[3] A. V. Babkov and B. D. Stepin, *Russ. J. Inorg. Chem.*, 1968, **13**, 5.

[4] L. E. Topol, *Inorg. Chem.*, 1968, **7**, 451.

[5] L. E. Topol, *Inorg. Chem.*, 1971, **10**, 736.

[6] L. R. Morss, *J. Chem. Thermodynamics*, 1975, **7**, 709.

[7] M. Schmeisser, 'Handbook of Preparative Inorganic Chemistry,' ed. G. Brauer, Academic Press, 1965, vol. 1, p. 293.

[8] H. L. Wells, H. L. Wheeler, and S. L. Penfield, *Amer. J. Sci.*, 1892, **43**, 475.

[9] W. Gabes and H. Gerding, *J. Mol. Structure*, 1972, **14**, 267.

from the total halide contents (Found: Cl, 21.4; Cs, 40.3; I, 38.4. Calc. for $Cs[ICl_2]$: Cl, 21.45; Cs, 40.2; I, 38.35. Found: Cl, 25.3; I, 44.45; Rb, 30.2. Calc. for $Rb[ICl_2]$: Cl, 25.05; I, 44.8; Rb, 30.15. Found: I, 74.05. Calc. for $Cs[I_3]$: I, 74.1%).

Calorimetric Reactions.—These were checked by ancillary experiments in which samples of polyhalide (*ca.* 0.3 g) were treated with a known excess of aqueous $Ag[NO_3]$ saturated with silver(I) iodate (*ca.* 25 cm³, 0.100 mol dm⁻³) in conical flasks. The precipitates were collected, washed with minimal amounts of ice-cold saturated aqueous $Ag[IO_3]$, dried at 120 °C, and weighed on sintered-glass crucibles. The ratio, R_1, of the mass of precipitate, calculated according to equations (1) or (2) as appropriate, to the mass of polyhalide was calculated. In addition, the excess of $Ag[NO_3]$ was measured titrimetrically, and the mol ratio, R_2, $Ag[NO_3]$: polyhalide, was calculated for comparison with that required by the appropriate equation (Found: $R_1 = 1.235$; $R_2 = 2.99$. Calc. for $Cs[I_3]$: $R_1 = 1.237$; $R_2 = 3.00$. Found: $R_1 = 1.607$; $R_2 = 2.99$. Calc. for $Cs[ICl_2]$: $R_1 = 1.625$; $R_2 = 3.00$. Found: $R_2 = 2.96$. Calc. for $Rb[ICl_2]$: $R_2 = 3.00$).

Solution Calorimeter.—A twin system was used with identical calorimeters except that no ampoule was included in the reference vessel. The calorimetric vessel, 100-cm³ capacity, was a thin-walled borosilicate Dewar, to the neck of which was bonded an aluminium flange which located an aluminium lid *via* a fine thread. Various inserts, *e.g.* thermometers, stirrer guides, *etc.*, were carried by individually machined aluminium ferrules screwing into the lid. The stirrer was servo-controlled (Electrocraft, type E-150 MGH) and operated at 700 revolutions min⁻¹. The stirrer shaft terminated in a double-bladed glass propeller, and also carried a poly(tetrafluoroethylene) paddle, *ca.* 1 cm below the surface of the calorimetric liquid. This resulted in very efficient stirring, essential since the reactions studied involved precipitation of dense silver compounds. Double-bulb ampoules, blown from B-5 Pyrex sockets, were used as described previously,[10] and the entire assembly was immersed in a water-bath maintained at 25.00 ± 0.005 °C (Tronac proportional controller, model 1 040) set in a room maintained at 25 ± 2 °C. Temperature changes were monitored using thermistors (YSI, 100 KΩ) connected to a commercial a.c. differential bridge (Carwyn Instruments, type 401B). This was modified in order to operate in a 'back-off' mode by additional circuitry, including an operational amplifier and μV source, such that the output could be displayed on a potentiometric recorder with 1 cm of paper equivalent to 4×10^{-4} °C. The resistance of the calibration heater, a Teflon-encased nominal 100-Ω resistor of very low thermal mass, and with double ends (Tronac Inc., Provo, Utah), was measured using a precision potentiometer (Stabaumatic, type 5345, Tinsley Co.). The potential across the heater was measured directly, using a digital voltmeter [SM210, S.E. Labs. (E.M.I.) Ltd.], an electric timer being activated simultaneously when the 6-V constant-voltage supply (Ether, type AA 100) was switched to the heater. The performance of the calorimeter was assessed by determining the enthalpy of reaction, ΔH_R, of 2-amino-2-hydroxymethylpropane-1,3-diol (THAM) with (*a*) excess of aqueous 0.100 mol dm⁻³ HCl and (*b*) excess of aqueous 0.100 mol dm⁻³ Na[OH], for both of which definitive literature values are available.[11] Results were: (*a*) ΔH_R (298.2 K, $1\,296 < n < 1\,780$) = -29.87 ± 0.05 kJ mol⁻¹ (mean of eight determinations); (*b*) ΔH_R (298.2 K, $1\,241 < n < 1\,550$) = 17.18 ± 0.05 kJ mol⁻¹ (mean of eight determinations); n = mol ratio of water to THAM. Accepted values are: (*a*) ΔH_R (298.2 K, n 1 345) = -29.790 ± 0.031 kJ mol⁻¹ and (*b*) ΔH_R (298.2 K, n 1 345) = 17.177 ± 0.023 kJ mol⁻¹. Further details concerning the calorimeter are available on request.

RESULTS

TABLE 1

Enthalpies of reaction of caesium tri-iodide with aqueous silver(I) nitrate

m/g	n[a]	$-\Delta H_R$/kJ mol⁻¹
0.412 61	6 916	149.12
0.275 84	10 344	148.56
0.397 08	7 186	147.80
0.378 40	7 541	148.67
0.370 12	7 709	149.85
0.345 83	8 250	151.59
	Mean	−149.27 ± 1.39[b]

[a] The mol ratio of the compound to water. [b] Uncertainties are 95% confidence limits, calculated using the student's *t* distribution with the appropriate number of degrees of freedom.

The reaction of caesium tri-iodide, and of caesium and rubidium dichloroiodates, with aqueous silver(I) nitrate saturated with silver(I) iodate were rapid and quantitative, according to equations (1) and (2) (M = Cs or Rb). The

$$3Cs[I_3](c) + \{(p + 9)\ Ag[NO_3]\}\cdot mH_2O(l) + (q + 3)H_2O(l) \longrightarrow 8AgI(c) + Ag[IO_3](c) + \{pAg[NO_3] + 3Cs[NO_3] + 6HNO_3\}\cdot(m + q)H_2O(l) \quad (1)$$

$$3M[ICl_2](c) + \{(p + 9)Ag[NO_3]\}\cdot mH_2O(l) + (q + 3)H_2O(l) \longrightarrow 6AgCl(c) + 2AgI(c) + Ag[IO_3](c) + \{pAg[NO_3] + 6HNO_3 + 3M[NO_3]\}\cdot(m + q)H_2O(l) \quad (2)$$

observed enthalpies of reaction are collected in Tables 1 and 2. Standard enthalpies of formation were calculated from equations (3) and (4) (M = Cs or Rb), respectively, which assume that the enthalpies of mixing of the products are

$$3\Delta H_f^{\ominus}(CsI_3,c) = 8\Delta H_f^{\ominus}(AgI,c) + \Delta H_f^{\ominus}(AgIO_3,c) + 6\Delta H_f^{\ominus}(HNO_3,\ 3\,000\ H_2O) + 3\Delta H_f^{\ominus}(CsNO_3,aq) - 9\Delta H_f^{\ominus}(AgNO_3,\ 2\,000\ H_2O) - 3\Delta H_f^{\ominus}(H_2O,l) - 3\Delta H_R \quad (3)$$

$$3\Delta H_f^{\ominus}(MICl_2,c) = 6\Delta H_f^{\ominus}(AgCl,c) + 2\Delta H_f^{\ominus}(AgI,c) + \Delta H_f^{\ominus}(AgIO_3,c) + 3\Delta H_f^{\ominus}(MNO_3,aq) + 6\Delta H_f^{\ominus}(HNO_3,\ 2\,000\ H_2O) - 9\Delta H_f^{\ominus}(AgNO_3,\ 2\,000\ H_2O) - 3\Delta H_f^{\ominus}(H_2O,l) - 3\Delta H_R \quad (4)$$

zero, and from the following ancillary data: $\Delta H_f^{\ominus}(AgI,c) = -61.84 \pm 0.1$;[12] $\Delta H_f^{\ominus}(AgCl,c) = -127.07 \pm 0.1$;[12] $\Delta H_f^{\ominus}(AgIO_3,c) = -166.24 \pm 0.72$;[13] $\Delta H_f^{\ominus}(AgNO_3,\ 2\,000\ H_2O) = -101.73 \pm 0.1$;[12] $\Delta H_f^{\ominus}(CsNO_3,aq) = -465.01 \pm$

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[10] N. Hill, Ph.D. Thesis, University of London, 1976.

[11] E. J. Prosen and M. V. Kilday, *J. Res. Nat. Bur. Stand.*, 1973, **A77**, 581.

[12] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, 'Selected Values of Chemical Thermodynamic Properties,' Nat. Bur. Stand., Technical Note 270-4, U.S. Government Printing Office, Washington D.C., 1969.

[13] A. Finch, P. N. Gates, and S. J. Peake, *J. Chem. and Eng. Data*, in the press.

0.84;[14,15] $\Delta H_f^{\ominus}(RbNO_3,aq) = -458.06 + 0.84$;[14,15] and $\Delta H_f^{\ominus}(HNO_3, 3\,000\ H_2O) = -206.97 \pm 0.46$ kJ mol^{-1}.[15] Where not explicitly stated in the original references, confidence limits have been assigned as ten times the last reported figure. Hence $\Delta H_f^{\ominus}(CsI_3,c) = -359.0 \pm 5.8$, $\Delta H_f^{\ominus}(CsICl_2,c) = -511.1 \pm 4.1$, and $\Delta H_f^{\ominus}(RbICl_2,c) = -491.4 \pm 4.1$ kJ mol^{-1}.

DISCUSSION

Calorimetric Reaction.—Early, but meticulous, work by Cremer and Duncan[16] suggests that reaction of dichloroiodates with aqueous Ag[NO$_3$] is quantitatively described by the sequential processes (5) and (6), and this

$$5[ICl_2]^- + 3H_2O \rightleftharpoons 2I_2 + [IO_3]^- + 10Cl^- + 6H^+ \quad (5)$$

$$3I_2 + 6Ag^+ + 3H_2O \longrightarrow 5AgI + 6H^+ + Ag[IO_3] \quad (6)$$

is fully consistent with the present results. During reaction of dichloroiodates with Ag[NO$_3$], initial formation of iodine was clearly seen; further precipitation accompanied the discharge of the iodine colour, and the reaction was complete within *ca.* 5 min. That precipitation of (silver) chloride precedes that of iodate is plausible because of their relative solubilities (K_{sp}[AgCl] : K_{sp}[AgIO$_3$] $\simeq$ 1 : 200), the final precipitation of AgI ensuring displacement of equilibrium (5) and hence completion of the overall reaction. More certainly, the quantitative precipitation of mixed halide and iodate, and the experimental dichloroidate : silver nitrate ratios, fully substantiate the stoicheiometries of reactions (1) and (2). The definitive measurements of Wagman and Kilday[17] suggest that precipitated silver halides are in their thermodynamic standard states. However, a final check of the suitability of this reaction is the test experiment with caesium tri-iodide, for the standard enthalpy of formation of which two independent values are available. These derive respectively from (*a*) e.m.f. measurements over the range 25—113.5 °C and (*b*) dissociation-pressure measurements over the range 140—270 °C. Comparison of these values, *viz.* $-\Delta H_f^{\ominus}$(CsI$_3$,c,298)/kJ mol^{-1} = 357.69 * (*a*), 363.63 * (*b*), and 359.0 ± 5.8 (this work), gives the strongest support to the proposed solution reaction. The caesium tri-iodide reaction is more difficult experimentally than analogous reactions with lower polyhalides, *e.g*, dichloroiodates, due to the massive precipitation of dense AgI, which makes uniform stirring difficult. This is reflected in the much greater precision of the experimental results for [ICl$_2$]$^-$ compounds, the relative standard deviations for the calorimetric reactions with Cs[I$_3$], and either Cs[ICl$_2$] or Rb[ICl$_2$], being respectively 0.9 and 0.1%, *i.e.* a difference of almost one order of magnitude.

TABLE 2

Enthalpies of reaction of caesium and rubidium dichloroiodates with aqueous silver(I) nitrate[c]

M = Cs			M = Rb		
m/g	n[a]	$-\Delta H_R$/kJ mol^{-1}	m/g	n[a]	$-\Delta H_R$/kJ mol^{-1}
0.351 54	5 226	127.67	0.275 06	5 721	140.39
0.355 30	5 171	126.39	0.232 55	6 767	140.60
0.365 60	5 025	127.19	0.333 61	4 717	140.21
0.356 20	5 158	127.37	0.307 63	5 115	140.27
0.361 58	5 081	127.51	0.290 39	5 419	139.50
0.341 16	5 385	128.37	0.351 33	4 479	140.23
0.301 02	6 104	127.95	0.395 48	3 979	139.59
0.357 08	5 145	127.19	0.361 98	4 347	141.10
0.364 37	5 042	128.11	0.329 49	4 776	140.42
0.346 18	5 307	127.36			
	Mean −127.51 ± 0.40[b]			Mean −140.26 ± 0.37[b]	

[a,b] As in Table 1. [c] Saturated with Ag[IO$_3$].

Gas-phase Measurements.—Pressure-dissociation equilibria, of the type shown in (7) (M = K, Rb, or Cs; X = I$_2$, Cl$_2$, Br$_2$, or IBr), have been studied extensively for more than 50 years.[18] Since ' van't Hoff ' values of

$$M[IX](c) \rightleftharpoons MX(c) + IX(g) \qquad (7)$$

$\Delta H_f^{\ominus}$[MIX(c)] may be calculated from these data, further comment is required. Values for the standard enthalpies of formation (in kJ mol^{-1}) of various polyhalides derived from a least-squares treatment of reported pressure data are compared with values derived from other methods (in parentheses): Cs[I$_3$] −357.7,[a] −306.2[b] (−363.6,[c] −359.0[d]); Rb[I$_3$] −335.5[a] (−341.4[c]); K[ICl$_2$] −454.2,[b] −458.6,[3,e] −469.9;[f] Rb[ICl$_2$] −471.8[b] (−491.4[d]); Cs[ICl$_2$] −478[b] (−511.1[d]) [*a*, ref. 3; *b*, ref. 18; *c*, e.m.f. method, ref. 4; *d*, solution calorimetry, this work; *e*, ref. 19; *f*, ref. 20]. In general, the agreement for tri-iodides is good, whilst that for dichloroiodates is poor, dissociation values being apparently *ca.* 20 kJ mol^{-1} too low. Considerable criticism of early pressure studies on mixed-halogen polyhalides has been

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* Updated values from refs. 3 and 4 using more recent ancillary data.

[14] A. F. Vorob'ev and A. S. Monaenkova, Vestnik Moskov. Univ. Khim., 1972, **27**, 182.

[15] G. Pilcher, ' Nitrogen Compounds,' CATCH Tables, University of Sussex, 1972.

[16] H. W. Cremer and D. R. Duncan, *J. Chem. Soc.*, 1932, 2031.

[17] D. D. Wagman and M. V. Kilday, *J. Res. Nat. Bur. Stand.*, 1973, **A77**, 569.

[18] F. Ephraim, *Chem. Ber.*, 1917, **50**, 1069.

[19] H. W. Cremer and D. R. Duncan, *J. Chem. Soc.*, 1931, 2243.

[20] J. Cornog and E. E. Bauer, *J. Amer. Chem. Soc.*, 1942, **64**, 2620.

made [19,20] and it seems unlikely that the method is of general application, due to side reactions, the necessity to extrapolate from relatively high temperatures, and severe experimental difficulties.

Lattice Energies and Stabilities of Polyhalides.—For ionic crystals for which detailed structural information is lacking, and where the anion is complex, use of the Yatsimirskii modification of the Kapustinskii equation [21] represents the best available method for estimating lattice energies. This procedure was used to calculate lattice energies, U, for the two series $\mathrm{M[IX_2](c)}$ ($\mathrm{X = I}$ or Cl; M = Li, Na, K, Rb, or Cs) using the Newton–Raphson iterative method, for which appropriate computer programs * were written (Fortran IV, and also for the Hewlett–Packard 65 programmable calculator) to derive values of the thermochemical radii, $r_{\mathrm{th}}\ (\mathrm{I_3^-})$ and $r_{\mathrm{th}}\ (\mathrm{ICl_2^-})$. Six input data are required for each series: values of (*a*) $\Delta H_f^\ominus(\mathrm{Cs^+,g})$ and $\Delta H_f^\ominus\ (\mathrm{Rb^+,g}) = 459.8$ and 491.2 kJ mol^{-1},[22] respectively; (*b*) crystal metal cation radii, $r[\mathrm{Cs^+(c)}]$ and $r[\mathrm{Rb^+(c)}] = 168$ and 147 pm,[22] respectively; and (*c*) $\Delta H_f^\ominus(\mathrm{CsI_3,c})$ and $\Delta H_f^\ominus\ (\mathrm{RbI_3,c})$ and $\Delta H_f^\ominus(\mathrm{CsICl_2,c})$ and $\Delta H_f^\ominus(\mathrm{RbICl_2,c})$; $\Delta H_f^\ominus\ (\mathrm{RbI_3,c}) = -335.5$ kJ mol^{-1}. Other values are those derived above. Substitution of the output r_{th} values into the Kapustinskii equation gives values of lattice enthalpies from which U values are readily calculable. Using a simple thermodynamic cycle, estimates of standard enthalpies of formation of the gaseous ions, $\Delta H_f^\ominus\ (\mathrm{I_3^-,g})$ and $\Delta H_f^\ominus(\mathrm{ICl_2^-,\ g})$, were made, and these were employed, with calculated values of U, to generate values of $\Delta H_f^\ominus(\mathrm{MIX_2,c})$ for the two series. The results are as follows, and in Table 3: $r_{\mathrm{th}}(\mathrm{I_3^-}) = 601$, r_{th}-$(\mathrm{ICl_2^-}) = 466$ pm; $\Delta H_f^\ominus(\mathrm{ICl_2^-,\ g}) = -605$ kJ mol^{-1}, $\Delta H_f^\ominus(\mathrm{I_3^-,\ g}) = -491$ kJ mol^{-1}. Values of the lattice energies and standard enthalpies of formation of other tri-iodide and dichloroiodate species, *e.g.* Group 2A or ammonium compounds, are similarly calculable.

TABLE 3

Lattice energies and standard enthalpies (in kJ mol^{-1}) of formation of $\mathrm{M[I_3]}$ and $\mathrm{M[ICl_2]}$ compounds

	$\mathrm{M[I_3]}$		$\mathrm{M[ICl_2]}$	
M	U	$-\Delta H_f^\ominus$	U	$-\Delta H_f^\ominus$
Li	344	174	425	348
Na	329	235	403	402
K	315	317	382	477
Rb	310	336	374	492
Cs	302	359	362	512

The stabilities of metal tri-iodides and dichloroidates, with respect to dissociation, or to other products, may now be discussed in terms of the derived quantities in Table 3. Both species are known to dissociate, *e.g.* $\mathrm{M[I_3](c)} \rightleftharpoons \mathrm{MI(c)} + \mathrm{I_2(c)}$. The enthalpy of this reaction, $\Delta H_D^\ominus$, may be shown to be given by $\Delta H_D^\ominus = U(\mathrm{MI_3}) - U(\mathrm{MI}) + \Delta H_f^\ominus(\mathrm{I},^-\ \mathrm{g}) - \Delta H_f^\ominus\ (\mathrm{I_3^-,\ g})$ whence, substituting appropriately, $\Delta H_D^\ominus = \Delta U(\mathrm{MI_3} - \mathrm{MI}) + 315$ kJ mol^{-1}. Entropy changes for the dissociation reaction as written are clearly negligible at ambient temperatures and hence, within the limits of the available data, $\Delta G_D^\ominus \simeq \Delta H_D^\ominus$. Hence, for stability $\Delta H_D^\ominus > 0$ and $\Delta U \geqslant -315$ kJ. Using Table 3, and accepted values [23] for $U(\mathrm{MI})$, the range for ΔU for the alkali metals is $-409 \gtrsim \Delta U \gtrsim -296$. Thus only for $\mathrm{Cs[I_3]}$ and $\mathrm{Rb[I_3]}$ is stability predicted; for $\mathrm{K[I_3]}$, $\Delta H_D^\ominus \simeq -11$ kJ mol^{-1}, while, for $\mathrm{Na[I_3]}$ and $\mathrm{Li[I_3]}$, $\Delta H_D^\ominus$ would be substantially exothermic. This appears to be entirely consistent with information from synthesis, with no apparent reports of solid-phase alkali-metal tri-iodides other than for rubidium or caesium. With increasing temperature, when gaseous iodine equilibria would result, the $T\Delta S_D^\ominus$ term would increasingly reduce the limit of stability.

An exactly similar treatment for dichloroiodates {*viz.* $\mathrm{M[ICl_2](c)} \rightleftharpoons \mathrm{MCl(c)} + \mathrm{ICl(l)}$} leads to the expression $\Delta H_D^\ominus = \Delta U(\mathrm{MICl_2} - \mathrm{MCl}) - \Delta H_f^\ominus(\mathrm{ICl_2^-,\ g}) + \Delta H_f^\ominus$-$(\mathrm{Cl^-,\ g}) + \Delta H_f^\ominus(\mathrm{ICl,\ l})$, whence the stability condition is $\Delta U \geqslant -335$ kJ mol^{-1}. From Table 3 and accepted sources of ancillary data, $-416 \gtrsim \Delta U \gtrsim -287$. This leads to the prediction that only $\mathrm{Li[ICl_2]}$ and $\mathrm{Na[ICl_2]}$ would be clearly unstable at ambient temperatures. Similar stability calculations, based on $\Delta H_f^\ominus(\mathrm{MI_3,c})$ and $\Delta H_f^\ominus(\mathrm{MICl_2,c})$ values, are possible, but are unrealistic in view of the experimentally observed dissociation reaction in which a binary compound between the more electronegative element and the metal, together with interhalogen, forms. Similar reactions have been demonstrated in non-aqueous solutions. The stability of complex ions as crystals is generally enhanced by increasing the size of the counter cation; however, when dissociation mechanisms prevail the determining factor is the difference in the lattice energies of the halide or polyhalide.

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* Available on request.

[21] T. C. Waddington, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 157.

[22] D. A. Johnson, 'Some Thermodynamic Aspects of Inorganic Chemistry,' Cambridge University Press, 1968.

[23] D. F. C. Morris, *Acta Cryst.*, 1956, **9**, 197.