Thermochemistry of Polyhalides. Part 5.[1] Standard Enthalpies of Formation of Tetramethylammonium and Tetraethylammonium Tetrachloroiodates

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The standard enthalpies of formation of methyl- and ethyl-ammonium tetrachloroiodates $NR_nH_{4-n}ICl_4$ (R = Me or Et, $0 \leqslant n \leqslant 4$), have been determined by a solution reaction method using aqueous silver nitrate. Lattice energies have been estimated from these data and trends in these and in the standard enthalpies of formation as a function of alkyl substitution are discussed.

The thermochemistry of crystalline metal polyhalides, MIX_2 (X = Cl, Br, or I; M = Cs or Rb),[2] $MICl_4$ (M = Cs or Rb),[3] hydrated and anhydrous $KICl_4$,[1] and various alkylammonium halides, $NR_nH_{4-n}X$ ($1 \leqslant n \leqslant 3$; X = Cl, Br, or I; R = Me[4] or Et[5,6]) and $NPr_nH_{4-n}Cl$,[7] has been reported and the results discussed in terms of the chemical stability of the compounds[1-3] and the trends in standard enthalpies of formation and lattice energies as functions of *n* and R.[4-7] As a logical extension of these studies we now report the standard enthalpies of formation of the compounds $NR_nH_{4-n}ICl_4$ ($1 \leqslant n \leqslant 4$; R = Me or Et) and NMe_4ICl_2 together with the calculation of lattice energies *U*; trends in those quantities in terms of various thermodynamic parameters are considered.

Experimental

Preparation of Compounds.—NMe_4ICl_2. To a solution of NMe_4Cl (11.0 g, 0.2 mol) in glacial acetic acid (200 cm^3) was added ICl (16.3 g, 0.2 mol). Yellow crystals of NMe_4ICl_2 were filtered off on a glass sinter, washed with tetrachloromethane, and stored over $CaCl_2$ in a desiccator (Found: Cl, 26.8, I, 46.2. Calc. for $C_4H_{12}Cl_2IN$: Cl, 26.1; I, 46.7%).

Tetrachloroiodate salts. Typically, preparations of the yellow crystalline solids were carried out by passing a current of dry Cl_2 into a solution containing ICl and the appropriate amine (or its hydrochloride). These methods together with analyses (potentiometric titration) for Cl and I are summarised in Table 1. Attempts to prepare pure samples of NMe_3ICl_4 and NEt_2HICl_4 were unsuccessful, the products being contaminated with the parent amine hydrochloride in both cases.

Table 1. Preparation and analysis of tetrachloroiodate salts

Compound	Reactants	Solvent	Analysis (%)*	
			Cl	I
NH_4ICl_4	NH_4Cl, ICl, Cl_2	Conc. HCl (aq)	49.7 (49.5)	43.6 (44.3)
$NMe_2H_2ICl_4$	NMe_2H, ICl, Cl_2	Conc. HCl (aq)	45.1 (45.1)	40.1 (40.3)
NMe_3HICl_4	NMe_3, ICl, Cl_2	Conc. HCl (aq)	42.6 (43.0)	38.5 (38.6)
NMe_4ICl_4	NMe_4ICl_2, Cl_2	Glacial acetic acid	41.1 (41.4)	36.9 (37.0)
$NEtH_3ICl_4$	$NEtH_2$, ICl, Cl_2	Dichloromethane	45.0 (45.1)	39.3 (40.3)
$NEt_2H_2ICl_4$	NEt_2H, ICl, Cl_2	Conc. HCl (aq)	42.0 (41.5)	36.9 (37.0)
NEt_4ICl_4	NEt_4Cl, ICl, Cl_2	Glacial acetic acid	35.2 (35.6)	31.5 (31.8)

* Calculated values are given in parentheses.

Calorimetry.—The established procedure[1] of treating crystalline samples of the relevant alkylammonium polyhalide with excess of aqueous silver nitrate was used. This is based on the reactions (1) and (2) where R = Me or Et and $0 \leqslant n \leqslant 4$.

The isoperibol calorimeter used has been described elsewhere.[1] Satisfactory check experiments using the enthalpy of neutralisation of 2-amino-2-hydroxymethylpropane-1,3-diol in 0.100 mol dm^{-3} aqueous HCl were made before and after each series of runs. Reactions were fairly quick, equilibrium being attained after *ca*. 5 min. Great care was needed to ensure adequate and uniform stirring of the dense precipitates. The calorimetric fluid was pre-saturated with $AgIO_3$ to ensure complete precipitation of this product.

Results

Enthalpies of Formation.—Experimental enthalpies of reaction, $\Delta H_R^{\ominus}$, for reactions (1) and (2) below are collated in Table 2. Calculated standard enthalpies of formation of the dichloroiodate and the tetrachloroiodate salts $\Delta H_f^{\ominus}$, based on equations (3) and (4), are given in Table 3.

$$3NMe_4ICl_2(c) + \{(p + 9)AgNO_3\}mH_2O(l) + (q + 3)H_2O(l) \longrightarrow 6AgCl(c) + 2AgI(c) + AgIO_3(c) + \{3NMe_4NO_3 + 6HNO_3 + pAgNO_3\}(m + q)H_2O(l) \quad (1)$$

$$3NR_nH_{4-n}ICl_4(c) + \{(p + 15)AgNO_3\}mH_2O(l) + (q + 6)H_2O(l) \longrightarrow 12AgCl(c) + AgI(c) + 2AgIO_3(c) + \{pAgNO_3 + 3NR_nH_{4-n}NO_3 + 12HNO_3\}(m + q)H_2O(l) \quad (2)$$

$$3\Delta H_f^{\ominus}(NMe_4ICl_2, c) = 6\Delta H_f^{\ominus}(AgCl, c) + 2\Delta H_f^{\ominus}(AgI, c) + \Delta H_f^{\ominus}(AgIO_3, c) + 3\Delta H_f^{\ominus}(NMe_4^+, aq) + 3\Delta H_f^{\ominus}(NO_3^-, aq) + 6\Delta H_f^{\ominus}[HNO_3(4\,000H_2O)] - 3\Delta H_f^{\ominus}(H_2O, l) - 9\Delta H_f^{\ominus}[AgNO_3(2\,000H_2O)] - 3\Delta H_R^{\ominus} \quad (3)$$

$$3\Delta H_f^{\ominus}(NR_nH_{4-n}ICl_4, c) = 12\Delta H_f^{\ominus}(AgCl, c) + \Delta H_f^{\ominus}(AgI, c) + 2\Delta H_f^{\ominus}(AgIO_3, c) + 3\Delta H_f^{\ominus}(NR_nH_{4-n}^+, aq) + 3\Delta H_f^{\ominus}(NO_3^-, aq) + 12\Delta H_f^{\ominus}[HNO_3(4\,000H_2O)] - 15\Delta H_f^{\ominus}[AgNO_3(2\,000H_2O)] - 6\Delta H_f^{\ominus}(H_2O, l) - 3\Delta H_R^{\ominus} \quad (4)$$

Table 2. Enthalpies of reaction, $\Delta H_R^\ominus$, of NMe_4ICl_2 and tetrachloroiodate salts in excess of aqueous silver nitrate solution (0.025 mol dm^{-3})

Compound	Dilution	No. of values	Mean $-\Delta H_R^\ominus$/ kJ mol^{-1}
NMe_4ICl_2	7 460—14 191	8	126.73 ± 2.70
NH_4ICl_4	9 798—12 000	7	311.82 ± 3.20
$NMe_2H_2ICl_4$	16 978—29 117	5	292.00 ± 1.70
NMe_3HICl_4	10 592—16 960	7	279.74 ± 1.00
NMe_4ICl_4	13 654—15 119	6	272.00 ± 6.1
$NEtH_3ICl_4$	6 909—16 508	7	299.50 ± 3.80
$NEt_2H_2ICl_4$	10 292—21 564	7	302.00 ± 3.30
NEt_4ICl_4	20 738—29 622	7	273.75 ± 3.5

Ancillary Data.—The following data were used (all values in kJ mol^{-1}): $\Delta H_f^\ominus(AgCl, c) = -127.07 \pm 0.1$;[8] $\Delta H_f^\ominus(AgI, c) = -61.84 \pm 0.1$;[8] $\Delta H_f^\ominus(AgIO_3, c) = -166.2 \pm 0.7$;[9] $\Delta H_f^\ominus[AgNO_3(2\,000H_2O), l] = -101.73 \pm 0.1$;[8] $\Delta H_f^\ominus[HNO_3(4\,000H_2O), l] = -207.0 \pm 0.46$;[10] $\Delta H_f^\ominus(H_2O, l) = -285.83$;[11] $\Delta H_f^\ominus(NMeH_3^+, aq) = -124.93$;[12] $\Delta H_f^\ominus(NMe_2H_2^+, aq) = -120.25$;[12] $\Delta H_f^\ominus(NMe_3H^+, aq) = -112.92$;[12] $\Delta H_f^\ominus(NMe_4^+, aq] = -103.34$;[13] $\Delta H_f^\ominus(NEtH_3^+, aq) = -156.06$;[12] $\Delta H_f^\ominus(NEt_2H_2^+, aq) = -188.70$;[12] $\Delta H_f^\ominus(NEt_3H^+, aq) = -216.73$;[12] $\Delta H_f^\ominus(NH_4^+, aq) = 132.51$.[12] A value for $\Delta H_f^\ominus(NEt_4^+, aq) = -248.0$ kJ mol^{-1} may be obtained by extrapolation of data given in ref. 6.

Discussion

Thermal Stabilities.—The thermal stability of NMe_4ICl_4 compared with $MICl_4$ (M = K, Rb, or Cs) with respect to the dissociation process $NMe_4ICl_4 \rightleftharpoons NMe_4ICl_2 + Cl_2$ can be assessed using thermodynamic values obtained in these experiments. The standard enthalpy for this dissociation, $\Delta H_D^\ominus$, is given by $\Delta H_f^\ominus(NMe_4ICl_2, c) - \Delta H_f^\ominus(NMe_4ICl_4, c) = 68.3$ kJ mol^{-1}, using the values in Table 3. Making the assumption[3] that entropy contributions from the crystalline tetrachloro- and dichloro-iodate will largely cancel and that the $T\Delta S^\ominus$ term for Cl_2(g) is *ca.* 67 kJ mol^{-1} at 298 K, then the standard free energy of dissociation, $\Delta G_D^\ominus \approx 1$ kJ mol^{-1}, reflecting a marginally increased stability of NMe_4ICl_4 relative to $MICl_4$ (M = Rb or Cs), for which $\Delta G_D^\ominus \approx -6$ and -8 kJ mol^{-1} respectively.

Standard Enthalpies of Formation.—The values of the standard enthalpy of formation of ammonium and of all four methylammonium tetrachloroiodate salts are, within experimental error, invariant, all values lying within the range 415.1—427.6 kJ mol^{-1}. A similar effect has been observed for the corresponding iodide series.[4] No very satisfactory rationalisation of this in terms of relevant thermodynamic parameters, such as proton affinities, lattice energies, *etc.* has been made, but the previous suggestion[6] that this follows from the very small and relatively constant values of the standard enthalpies of formation of the relevant parent methyl-substituted amines is reasonable. In the ethylammonium tetrachloroiodate salts there is a smooth increase in the values, roughly paralleling the corresponding values in the $NEt_nH_{4-n}X$ (X = Cl, Br, or I) series.

Table 3. Standard enthalpies of formation, $\Delta H_f^\ominus$ (c), and lattice energies, *U*, of $NR_nH_{4-n}ICl_4$ (R = Me or Et; $0 \leqslant n \leqslant 4$), NH_4ICl_4, and NMe_4ICl_2

Compound	$-\Delta H_f^\ominus$/kJ mol^{-1}	U^a/kJ mol^{-1}
NH_4ICl_4	415.1 ± 3.6	427
$NMeH_3ICl_4$	420.0[b]	392
$NMe_2H_2ICl_4$	422.6 ± 2.0	375
NMe_3HICl_4	427.6 ± 1.6	357
NMe_4ICl_4	425.7 ± 6.2	
$NEtH_3ICl_4$	450.9 ± 4.5	396
$NEt_2H_2ICl_4$	481.1 ± 4.1	362
NEt_3HICl_4	525.0[b]	360
NEt_4ICl_4	569.4 ± 4.1	
NMe_4ICl_2	357.4 ± 3.0	

[a] Calculated from equation (5). [b] Interpolated value.

Lattice Energies.—Values of the lattice energies, *U*, may be calculated from the values of $\Delta H_f^\ominus$ (alkylammonium salt, c) in Table 3 using the expression (5) and the following ancillary data (all values in kJ mol^{-1}): $-\Delta H_f^\ominus(NH_3, g) = 45.48$;[10] $-\Delta H_f^\ominus$(amine, g) = 47.15, 71.42, and 95.81 for $NEtH_2$, NEt_2H, and NEt_3 respectively and 22.97, 18.45, and 24.31 for $NMeH_2$, NMe_2H, and NMe_3 respectively;[12] $\Delta H_f^\ominus(H^+, g) = 1\,539.9$;[14] $\Delta H_f^\ominus(ICl_4^-, g) = -631$;[3] *P*(amine) = 912, 951.4, and 973 (mean values for $NEtH_2$, NEt_2H, and NEt_3 respectively) and 908.8, 932.9, and 950.6 (mean values for $NMeH_2$, NMe_2H, and NMe_3 respectively);[15] $P(NH_3) = 846.6$.[16]

$$U = \Delta H_f^\ominus(\text{amine, g}) + \Delta H_f^\ominus(H^+, g) + \Delta H_f^\ominus(ICl_4^-, g) - \Delta H_f^\ominus(\text{alkylammonium salt, c}) - P(\text{amine}) - 2RT \quad (5)$$

Values of *P*, the proton affinity of the relevant amine, are derived from experimental measurements. Although the value of $\Delta H_f^\ominus(ICl_4^-, g)$ depends on computations[3] using the semiempirical Kapustinskii–Yatsimirskii procedure, the extremely close agreement[1] between the experimental value of $\Delta H_f^\ominus(KICl_4, c)$ and that calculated using the computed $\Delta H_f^\ominus(ICl_4^-, g)$ value, *viz.* 545.2 and 538 kJ mol^{-1} respectively, gives confidence in its adoption here. It is usually accepted that, while such computed values of *U* may contain systematic errors, these will largely cancel when considering *differences*; hence trends may reasonably be inferred. We note that values of *U* for the ethyl-substituted series are, within reasonable confidence limits, very close to those of the methyl series, notwithstanding the (presumed) disparity in cation sizes. This may not be surprising in view of the asymmetric charge distribution expected over such cations and may reflect a similar localised charge distribution around the nitrogen in the corresponding homologues.

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