Pergamon

PII: S0277-5387(97)00114-9

Polyhedron Vol. 16, No. 20, pp. 3571–3575, 1997

0277–5387/97 $17.00+0.00

Standard enthalpy of formation of dichloroiodine(III) tetrachloroaluminium(III), $[ICl_2^+][AlCl_4^-]$ and the thermochemistry and energetics of the gaseous dichloroiodine(III) cation, $[ICl_2^+]$

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(Received 24 February 1997; accepted 20 March 1997)

Abstract—The experimental determination of the standard enthalpy of formation of the crystalline salt, $[ICl_2^+][AlCl_4^-]$, is reported to be $\Delta_fH^0(IAlCl_6,c)/kJ\ mol^{-1} = -836.6 \pm 6.2$ along with the total lattice potential energy, $U_{POT}(IAlCl_6)/kJ\ mol^{-1}$, calculated to be 562.5 ± 5.0 using the program LATEN. The standard enthalpy of formation of the $[ICl_2^+]$ cation, $\Delta_fH^0([ICl_2^+],g)/kJ\ mol^{-1}$ is found to be 926.9 ± 9.0. The electron attachment enthalpies for the ICl_2 (g) and $[ICl_2^+]$ (g) species, are in $kJ\ mol^{-1}$: 533.2 and −999, respectively. © 1997 Elsevier Science Ltd

Keywords: enthalpy of formation; lattice energy; LATEN; thermochemistry; $[ICL_2^+]$.

Exothermic combination of halogens with each other gives rise to interhalogen compounds possessing four different stoichiometries (XY, XY_3, XY_5, XY_7) where X represents the central and heavier halogen. Whilst only even numbers of halogen atoms combine to form these stable neutral compounds, the closely related polyhalide cations XY_{2n}^+ (and also in the anions XY_{2n}^-) each have an odd number of halogen atoms.

We have been concerned recently with the thermochemistry and stabilities of compounds possessing complex inorganic halogen containing cations and anions [1–3] particularly those of phosphorus, as well as with thermodynamic studies on iodine(III) compounds [4]. In this paper our interests combine in the form of the study of the thermochemistry of the interhalogen cation dichloriodine(III) and its salt, dichlorioidine(III) tetrachloroaluminium(III), $IAlCl_6$ formed with the tetrachloroaluminium(III), $[AlCl_4^-]$ anion and containing the complex ions, $[ICl_2^+][AlCl_4^-]$.

The dichloroiodine(III) cation, $[ICl_2^+]$ is formed, *inter alia*, during the ionic self-dissociation [5].

$$I_2Cl_6 \Leftrightarrow [ICl_2^+]+[ICl_4^-] \tag{1}$$

of the bright yellow molten liquid dimer I_2Cl_6. Solid ICl_3 does not exist as a monomer, and the gas decomposes to ICl and Cl_2. I_2Cl_6 is utilised as a nonaqueous ionising solvent and exhibits appreciable electrical conductivity. Thermodynamic data on I_2Cl_6 is well established [5] but data for the interhalogen cation $[ICl_2^+]$ have not previously been studied.

The corresponding electrical conductivity of the salt formed between the $[ICl_2^+]$ cation and $[AlCl_4^-]$ shows it to be typically ionic in nature. It is for this salt, $IAlCl_6$—existing as $[ICl_2^+]$ $[AlCl_4^-]$—that the experimental determination of the standard enthalpy of formation is reported along with calculations of the lattice potential energy and the estimated standard enthalpy of formation of the dichloroiodine(III) cation and related thermochemistry.

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A self-consistent field approach, extended by MP2-correlation energy considerations [6], has recently been applied to study electronic structure, charge distribution, geometry and some energetics of the four trihalogen homoatomic clusters, X_3^+ and six trihalogen heteratomic clusters including $[ICl_2^+]$.

EXPERIMENTAL

Preparation of $[ICl_2^+][AlCl_4^-]$

This was prepared following a method previously described [7]. Equivalent amounts of ICl_3 and $AlCl_3$ were sealed in a glass tube in chloroform and maintained at 100°C for 2 h. After cooling, the red crystals of $IAlCl_6$ were filtered off under suction in a drybox, washed several times with a small quantity of chloroform and dried *in vacuo*. Found: Cl 34.9; I 57.8. Calc. for $IAlCl_6$: Cl 34.6, I 58.0%.

Calorimetry

The calorimetric reaction chosen was aqueous acid hydrolysis in HCl:

$$5[ICl_2^+][AlCl_4^-](c) + 9H_2O(l) \xrightarrow{HCl} 5[AlCl_4^-](aq) + I_2(aq) + 3[IO_3^-](aq) + 10Cl^-(aq) + 18H^+(aq) \quad (2)$$

Under such acid conditions it was assumed that no hydrolysis of the $[AlCl_4^-]$ ion occurred and that the species remained intact [8]. A Raman spectrum of an aqueous solution of $NaAlCl_4$ showed no evidence for species other than $[AlCl_4^-]$.

Enthalpies of aqueous acid hydrolysis were measured by breaking ampoules containing $IAlCl_6$ into 0.1 mol dm^{-3} HCl using an LKB 8700 isoperibol calorimeter, the performance of which was satisfactorily checked using the enthalpy of neutralisation of tris(hydroxymethyl)methylamine in an excess of HCl as a test reaction.

RESULTS AND CALCULATIONS

Enthalpy of formation of $IAlCl_6$

The mean value (9 determinations, in which the molar ratio of $H_2O:IAlCl_6$ was in the range 18,735–31,841) of the enthalpy of hydrolysis, $\Delta_h H^0$/kJ mol^{-1}, was -320.9 ± 2.6.

On the basis of the equation:

$$5\Delta_f H^0([ICl_2^+][AlCl_4^-], c) = 5\Delta_f H^0([AlCl_4^-], aq) + \Delta_f H^0(I_2, aq) + 3\Delta_f H^0([IO_3^-], aq) + 10\Delta_f H^0(Cl^-, aq) + 18\Delta_f H^0(H^+, aq) - 9\Delta_f H^0(H_2O, l) - \Delta_h H^0 \quad (3)$$

A value for $\Delta_f H^0([ICl_2^+][AlCl_4^-], c)$/kJ/$mol^{-1}$ = -833.6 ± 6.2 was calculated using the following ancilliary data [8,9] (all values in kJ mol^{-1}): $\Delta_f H^0([AlCl_4^-], aq) = -1200.53 \pm 4.00$; $\Delta_f H^0(I_2, aq) = -22.59 \pm 0.40$; $\Delta_f H^0([IO_3^-], aq) = -221.33 \pm 4.0$; $\Delta_f H^0(Cl^-, aq) = -167.08 \pm 0.004$; $\Delta_f H^0(H_2O, l) = -285.83 \pm 0.04$.

Lattice potential energy

Figure 1 represents the relationship which exists between the total lattice potential energy of $IAlCl_6$, $U_{POT}(IAlCl_6)$, the internal energy of the salt, $E(IAlCl_6)$, and of the ions, $E([ICl_2^+])$ and $E([AlCl_4^-])$, and acoustic energy of the lattice, U_{ACOU} and rotational and translational contributions to the energy of the gaseous ions, which amount to some 6RT. Accordingly, we can write:

$$\Delta E = 6RT + U_{POT}(IAlCl_6) - U_{ACOU} \quad (4)$$

We can, of course, calculate U_{ACOU} for the crystal lattice either from a knowledge of the heat capacities as a function of temperature and from the zero point energy of the lattice or by means of the Einstein or the Debye theory of heat capacities. At absolute zero:

$$U_{ACOU} \cong 3Nk\Theta_E \quad \text{or } 9/4Nk\Theta_D \quad (5)$$

(where Θ_E and Θ_D are the Einstein and Debye characteristic temperatures, N is Avogadro's number and k is Boltzmann's constant) and at temperatures considerably greater than this $U_{ACOU} \cong 3RT$ per ion. Accordingly:

$$\Delta E = U_{POT}(IAlCl_6) \quad (6)$$

The total lattice potential energy of the crystalline salt, $U_{POT}(IAlCl_6)$ is then related to the lattice enthalpy [10], ΔH^0_{lat}, for the process:

$$IAlCl_6(c) \xrightarrow{\Delta H^0_{lat}} [ICl_2^+](g) + [AlCl_4^-](g) \quad (7)$$

by the equation:

$$\Delta H^0_{lat} = U_{POT}(IAlCl_6) + 2RT \quad (8)$$

The salt $IAlCl_6$ crystallizes in the monoclinic space group $P2_1$ with two molecules per unit cell. The cell parameters are: $a_0/Å = 6.92 \pm 0.03$, $b_0/Å = 11.02 \pm 0.05$, $c_0/Å = 6.11 \pm 0.03$ with $\beta = 99.1°$ taken from Vonk and Wiebenga [7]. We have computed the total lattice potential energy of $IAlCl_6$ using the program LATEN [11–13], developed in this laboratory. The modelling of the 'V' shaped $[ICl_2^+]$ cation is that of a three sphere model having assigned basic radii and bearing a charge distribution found for this cation from the spin restricted Hartree–Fock (RHF) [14] and correlated MP2 calculations [15,16] made using the Gaussian 92/DFT program package [17] by Li, Irle and Schwarz [6]. The model employed for the tetrahedral $[AlCl_4^-]$ anion is identical to that used in our previous study of the tetrachloroaluminate salts [18].

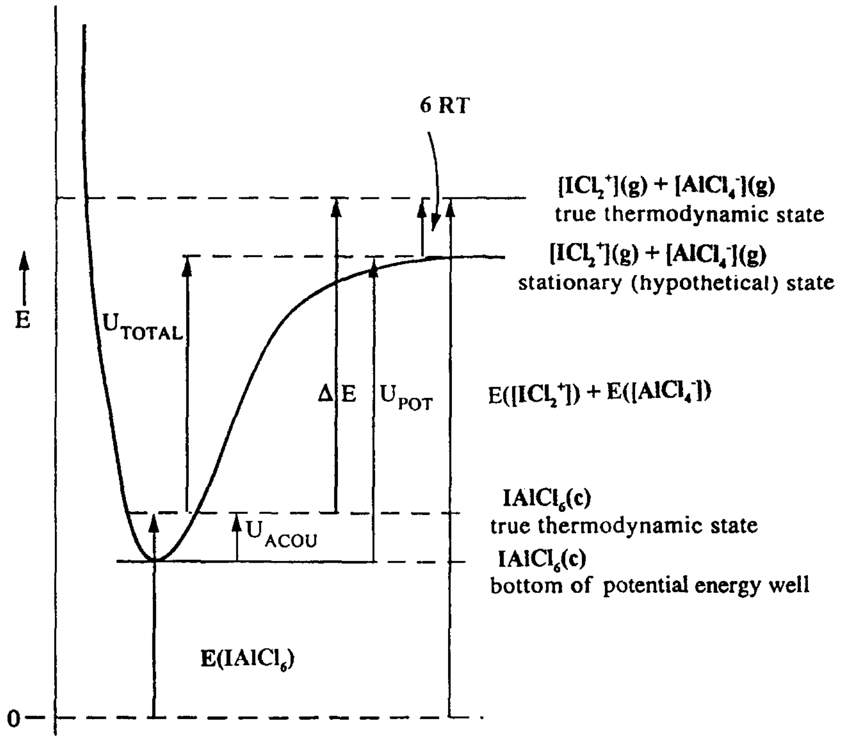

Fig. 1. Relationship between the total lattice potential energy of $IAlCl_6$, U_{POT}, and the internal energy change, ΔE, giving rise to the relationships: $\Delta E = E_{ICl_2^+} + E_{AlCl_4^-} - E_{IAlCl_6}$; $U_{POT} = U_{TOTAL} + U_{ACOU}$; $\Delta E = 6RT + U_{TOTAL}$; $\Delta E = 6RT + U_{POT} - U_{ACOU}$.

The total lattice potential energy of $IAlCl_6$ was found to be:

$$U_{POT}(IAlCl_6)/kJ\,mol^{-1} = 562.5 \pm 5.0 \qquad (9)$$

comprising an electrostatic energy, $U_{ELEC}/(kJ\ mol^{-1}$ $= 531.4$, a repulsion energy, $U_R/kJ\ mol^{-1} = 230.9$ and a dipole–dipole dispersion energy, $U_{dd}/kJ\ mol^{-1}$ $= 232.4$ and quadrupole–dipole dispersion energy, $U_{qd}/kJ\ mol^{-1} = 29.6$.

Enthalpy of formation of $[ICl_2^+]$ *gaseous cation*, $\Delta_f H^0([ICl_2^+], g)$

The thermochemical radius [19,20] λ/nm of the tetrachloroaluminium(III) anion, $[AlCl_4^-]$ was previously [17] estimated to be 0.295 ± 0.084 and based on this value the thermochemical radius/nm of the dichloroiodonium ion, $[ICl_2^+]$, is found to be 0.099 as derived from the Kapustinskii equation [20] or its more modern counterpart the Glasser equation [21].

Using the thermochemical cycle of Fig. 2:

$$\Delta_f H^0([ICl_2^+], g) = U_{POT}(IAlCl_6) + 2RT + \Delta_f H^0(IAlCl_6, c) - \Delta_f H^0([AlCl_4^-], g) \qquad (10)$$

and the values of $\Delta_f H^0(IAlCl_6, c)/kJ\ mol^{-1} = -836.6 \pm 6.2$ and $\Delta_f H^0([AlCl_4^-], g)/kJ\ mol^{-1} = -1196 \pm 5.0$ [18], we assign:

$$\Delta_f H^0([ICl_2^+], g/kJ\,mol^{-1} = 926.9 \pm 9.0 \qquad (11)$$

It is of interest to use this value to obtain an independent estimate for the exothermic energy change, ΔE/kJ mol^{-1} (equal to ΔH) for the reaction:

$$[ICl_2]^+(g) + I^-(g) \rightarrow I_2(g) + Cl_2(g) \qquad (12)$$

which has been estimated to be in the range 6–7 eV (579–675 kJ mol^{-1}) by MP2 calculations [6] of Li, Irle and Eugen Schwarz.

Using eq. (13):

$$\Delta H = \Delta E = \Delta_f H^0(I_2, g) + \Delta_f H^0(Cl_2, g) - \Delta_f H^0(I^-, g) - \Delta_f H^0([ICl_2^+], g) \qquad (13)$$

and the values [22,23]: $\Delta_f H^0(I_2, g)/kJ\ mol^{-1} = 62.438$, $\Delta_f H^0(I^-, g)/kJ\ mol^{-1} = -197.0$ together with our value (above) of $\Delta_f H^0([ICl_2^+], g)/kJ\ mol^{-1} = 926.9$, we calculate a value of ΔH/kJ mol^{-1} for reaction (12) of −667.5, near to the upper estimate of the range 579–675 kJ mol^{-1} in the MP2 calculations [6].

DISCUSSION

Previous thermodynamic studies on the iodine(III) tetrachloride anion [24], $[ICl_4^-]$ and the iodine(I) dichloride anion [25], $[ICl_2^-]$ and their salts led to the assignments:

$$\Delta_f H^0([ICl_4^-], g)/kJ\,mol^{-1} = -631 \qquad (14)$$

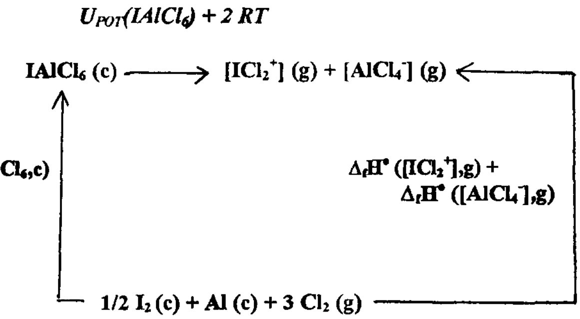

Fig. 2. Thermochemical cycle for dichloroiodine(III) tetrachloroaluminium(III) $IAlCl_6$.

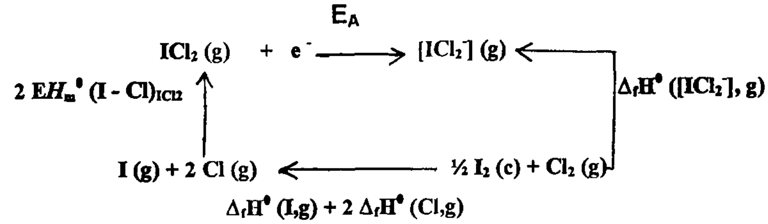

Fig. 3. Electron attachment enthalpy of $ICl_2(g)$.

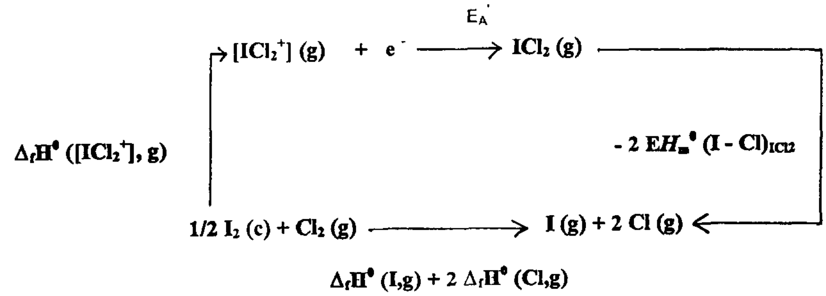

Fig. 4. Electron attachment enthalpy of $[ICl_2^+](g)$.

$$\Delta_f H^0([ICl_2^-],g)/\mathrm{kJ\,mol^{-1}} = -605 \qquad (15)$$

Using the data for the standard enthalpy of formation of the $[ICl_2^+]$ (g) cation

$$[ICl_2^+](g)+2Cl^-(g)\xrightarrow{A_{2Cl}}[ICl_4^-](g) \qquad (16)$$

derived in this paper we can estimate the, strongly exothermic, double chloride ion affinity of the dichloriodine(III) cation, $A_{2Cl}/\mathrm{kJ\,mol^{-1}}$, to be:

$$A_{2Cl}/\mathrm{kJ\,mol^{-1}} = -1092 \pm 10 \qquad (17)$$

Using the standard enthalpies of formation/kJ mol^{-1} [22,23] of I(g) (= 106.8), Cl(g) (= 121.679) and ICl(g) (= 17.506), the bond enthalpy of the I—Cl bond, EH^0_m (I—Cl)$_{ICl}$ in the compound ICl(g) may be calculated to be:

$$EH^0_m(I\text{—}Cl)_{ICl}/\mathrm{kJ\,mol^{-1}} = \Delta_f H^0(I,g) + \Delta_f H^0(Cl,g) - \Delta_f H^0(ICl,g) = 211 \qquad (18)$$

Incorporation of this value in the cycle shown in Fig. 3 leads to a value for the electron attachment energy for gaseous ICl_2, E_A/kJ mol^{-1} for the process:

$$ICl_2(g)+e^-\xrightarrow{E_A}[ICl_2^-](g) \qquad (19)$$

given by:

$$E_A/\mathrm{kJ\,mol^{-1}} = 2EH^0_m(I\text{—}Cl)_{ICl} - \Delta_f H^0(I,g) - 2\Delta_f H^0(Cl,g) + \Delta_f H^0([ICl_2^-],g) = 533.2 \qquad (20)$$

The corresponding electron attachment energy for the gaseous cation $[ICl_2^+]$, E'_A/kJ mol^{-1} for the process:

$$[ICl_2^+](g)+e^-\xrightarrow{E'_A}ICl_2(g) \qquad (21)$$

is given by the equation:

$$E'_A/\mathrm{kJ\,mol^{-1}} = \Delta_f H^0(I,g) + 2\Delta_f H^0(Cl,g) - \Delta_f H^0([ICl_2^+],g) - 2EH^0_m(I\text{—}Cl)_{ICl} = -999 \qquad (22)$$

Bonds in $[ICl_2^+]$ would be expected to be slightly shorter and stronger than in ICl so we would expect that $EH^0_m(I\text{—}Cl)_{[ICl_2]^+}$ derived from the former to be greater than that calculated in eq. (18). The value from $[ICl_2^+]$ considerations (Fig. 4):

$$EH^0_m(I\text{—}Cl)_{[ICl_2]^+}/\mathrm{kJ\,mol^{-1}} = \{\Delta_f H^0([ICl_2]^+,g)$$

$$-\Delta_f H^0(\mathrm{I}, g) - 2\Delta_f H^0(\mathrm{Cl}_2, g)\}/2 = 292.9 \qquad (23)$$

is consistent with these expectations.

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