HEAT OF FORMATION OF CO-ORDINATION COMPLEXES OF BORON, ALUMINIUM AND GALLIUM

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One of the prerequisites to a full understanding of the nature of co-ordination compounds is a knowledge of the strength of the donor–acceptor bonds which hold them together. In many complexes the situation is complicated by the presence of several such bonds; for example the compound may be 4-, or 6-co-ordinate so that several terms go to make up the total heat of formation of the complex. For this reason it was decided to study simple 1 : 1 and 1 : 2 addition compounds rather than the usual octahedral, square, or tetrahedral complexes. In this way we hoped to be able to interpret the various energy terms more satisfactorily and so arrive at a sequence of strengths of donor–acceptor bonds between a given ligand and a series of electron acceptors, or between a given acceptor and a series of ligands. The systems we have been most interested in are those in which the electron acceptor is an element of Group III and this paper reviews the results obtained on the 1 : 1 complexes of boron trichloride and tribromide and the 1 : 1 and 1 : 2 complexes of gallium trichloride and tribromide.

Two methods have been used to determine the heat of formation of a crystalline complex: equilibrium vapour pressure measurements and direct reaction calorimetry. These give the heat of formation of the solid complex and from these, the heats of formation in the gas phase can be obtained in those cases where the relevant heats of sublimation and vaporization are known.

The equilibrium vapour pressure method is normally restricted to those cases where a solid complex dissociates either into a solid and a gas or into two gases. Experimentally the method simply involves synthesizing the complex in a vacuum line and then measuring its vapour pressure directly or on a spiral gauge. In this work it has been used mainly to cross-check the calorimetric measurements. As an example of its independent use, the dissociation pressure of triphenylmethyl tetrachloroborate was determined:

$$\mathrm{Ph_3C^+BCl_4^-{}_{(c.)}} \rightleftharpoons \mathrm{Ph_3CCl_{(c.)}} + \mathrm{BCl_{3(g.)}}$$

The vapour pressure followed the relation log $P(\mathrm{atm}) = 4{\cdot}069 - 2077/T$. Hence the heat of the reaction is 9·51 kcal mole^{-1} and the entropy of formation $-18{\cdot}6$ cal mole^{-1} deg^{-1}.

The direct calorimetric method is more involved experimentally but is much more versatile. Many of the compounds studied were volatile, hygroscopic, or readily oxidized and it was necessary to design a calorimeter to work in an inert atmosphere and over a range of temperature. In the final design[1] the mixing vessel was made from a B55 ground-glass cone and was 18 cm deep and 4 cm in diameter. It had a vacuum jacket to reduce heat losses. The calorimeter head was made from a B55 socket and carried six attachments; the stirrer and breaker rod had mercury seals and guide tubes; the thermocouple well and electrical heater for internal calibration during each experiment were of specially thinned glass; there was a drip feed for distilling or pouring in a known weight of ligand (which also served as the calorimetric liquid or " solvent "); and finally there was an inlet for dried nitrogen. The ground-glass joints carried sleeves of poly-(tetrafluoroethylene)—no grease was used.

Temperature changes were measured by a 15-junction copper–constantan thermocouple (0·0008°). The heater circuit for electrical calibration was of standard design; current from large-capacity storage batteries was stabilized by passage through a matched dummy heater for three hours before being switched through the true heater for a timed two minutes. The stirrer ran at 160 rev/min and gave no detectable heat of stirring. A formal assessment of the errors involved in timing, thermometry, and weighing shows that the expected precision is about 5 parts per thousand; in practice a reproducibility of 1–2 parts per thousand was frequently obtained.

The first complex studied was $GaCl_3.POCl_3$ (m.p. 118·5°)[1].

$$GaCl_{3(c.)} + (n+1)POCl_{3(l.)} = GaCl_3.POCl_3 \text{ (in n } POCl_3); \quad -\Delta H = 11{\cdot}00 \pm 0{\cdot}01 \text{ kcal mole}^{-1}$$

$$GaCl_3.POCl_{3(c.)} + nPOCl_{3(l.)} = GaCl_3.POCl_3 \text{ (in n } POCl_3); \quad -\Delta H = 0{\cdot}83 \pm 0{\cdot}01 \text{ kcal mole}^{-1}$$

Hence

$$GaCl_{3(c.)} + POCl_{3(l.)} = GaCl_3.POCl_{3(c.)}; \quad -\Delta H_f = 10{\cdot}17 \pm 0{\cdot}02 \text{ kcal mole}^{-1}$$

To calculate the heat of reaction in the gas phase, heats of sublimation are needed. A value of 15 kcal $mole^{-1}$ for the complex was obtained manometrically. Other values are 8·5 kcal for $GaCl_{3(c.)}$ and 8·4 kcal for $POCl_{3(l.)}$. Thus

$$\tfrac{1}{2}Ga_2Cl_{6(g.)} + POCl_{3(g.)} = GaCl_3.POCl_{3(g.)}; \quad -\Delta H = 12{\cdot}1 \text{ kcal mole}^{-1}$$

and

$$GaCl_{3(g.)} + POCl_{3(g.)} = GaCl_3.POCl_{3(g.)}; \quad -\Delta H = 22{\cdot}6 \text{ kcal mole}^{-1}$$

The results indicate that the oxygen atom in phosphorus oxychloride is a better donor to gallium trichloride by 12 kcal than is the chlorine atom in dimeric gallium trichloride. The heat of the gas phase reaction between monomeric gallium trichloride and phosphorus oxychloride is 22·6 kcal $mole^{-1}$, but not all of this energy resides in the O—Ga bond, since the other bonds in the complex are modified during the process of donor–acceptor bonding.

Similar results for $GaCl_3.Et_2O$, m.p. 16°, and $GaCl_3.2Et_2O$, m.p. 9·0° are shown in the following equations:

$$GaCl_{3(c.)} + n\,Et_2O_{(l.)} = GaCl_3.2Et_2O \text{ (in excess ether)};$$
$$-\Delta H = 21{\cdot}46 \pm 0{\cdot}06 \text{ kcal mole}^{-1}$$

$$GaCl_3.Et_2O_{(l.)} + n\,Et_2O_{(l.)} = GaCl_3.2Et_2O \text{ (in excess ether)};$$
$$-\Delta H = 12{\cdot}12 \pm 0{\cdot}02 \text{ kcal mole}^{-1}$$

$$GaCl_3.2Et_2O_{(l.)} + n\,Et_2O_{(l.)} = GaCl_3.2Et_2O \text{ (in excess ether)};$$
$$-\Delta H = 5{\cdot}98 \pm 0{\cdot}03 \text{ kcal mole}^{-1}$$

Hence

$$GaCl_{3(c.)} + Et_2O_{(l.)} = GaCl_3.Et_2O_{(l.)};$$
$$-\Delta H_f = 9{\cdot}34 \pm 0{\cdot}08 \text{ kcal mole}^{-1}$$

$$GaCl_{3(c.)} + 2Et_2O_{(l.)} = GaCl_3.2Et_2O_{(l.)};$$
$$-\Delta H_f = 15{\cdot}48 \pm 0{\cdot}09 \text{ kcal mole}^{-1}$$

$$GaCl_3.Et_2O_{(l.)} + Et_2O_{(l.)} = GaCl_3.2Et_2O_{(l.)};$$
$$-\Delta H = 6{\cdot}14 \pm 0{\cdot}05 \text{ kcal mole}^{-1}$$

Addition of the first mole of ether evolves 9·34 kcal mole, whereas the second mole evolves only a further 6·14 kcal $mole^{-1}$. The heat of vaporization of the 1 : 1 complex was found to be 12·7 kcal $mole^{-1}$, which leads to the following data for the gas phase reactions:

$$\tfrac{1}{2}Ga_2Cl_{6(g.)} + Et_2O_{(g.)} = GaCl_3.Et_2O_{(g.)}; \quad -\Delta H = 11{\cdot}8 \text{ kcal mole}^{-1}$$
$$GaCl_{3(g.)} + Et_2O_{(g.)} = GaCl_3.Et_2O_{(g.)}; \quad -\Delta H = 22{\cdot}3 \text{ kcal mole}^{-1}$$

This last equation indicates that the heat of interaction of ethyl ether with monomeric gallium trichloride (22·3 kcal $mole^{-1}$) is more than twice its heat of reaction with boron trifluoride under the same conditions (10·9 kcal $mole^{-1}$).

The heats of formation of a series of complexes of gallium trichloride are compared in *Table 1.*

Table 1. Heat of formation of crystalline addition complexes from $GaCl_{3(c.)}$ and Ligand (l.)

Complex	$-\Delta H$(kcal $mole^{-1}$)	*Complex*	$-\Delta H$(kcal $mole^{-1}$)	
$GaCl_3.AsCl_{3(l.+c.)}$	1·4	$GaCl_3.Et_2O_{(c.)}$	9·3	6·2
$GaCl_3.PCl_{3(l.+c.)}$	3·4	$GaCl_3.2Et_2O_{(c.)}$	15·5	
$GaCl_3.POCl_{3(c.)}$	10·2	$GaCl_3.Py_{(c.)}$	29·8	11·7
$GaCl_3.MeCOCl_{(c.)}$	4·1	$GaCl_3.2Py_{(c.)}$	41·5	
$GaCl_3.Me_2CO_{(c)}$	15·3	$GaCl_3.Pip_{(c.)}$	33·7	18·4
		$GaCl_3.2Pip_{(c.)}$	52·1	

The values range from 1 to 52 kcal $mole^{-1}$. The low values for phosphorus trichloride, arsenic trichloride, and acetyl chloride correlate with the observed instability of these compounds[2,3]. The heat of formation[4] of $GaCl_3.Me_2CO$(m.p.42·2°) is 15·3 kcal mole^{-1}, similar to the values found for the other oxygen-containing ligands mentioned above. The strongest donors investigated were pyridine and piperidine[5]. It is seen that for these the second mole of ligand is added with considerably less evolution of energy than the first and that piperidine is a stronger donor than pyridine. Equilibrium vapour pressure measurements afford a useful check on the calorimetric data here, for the solid 1 : 2 pyridine complex dissociates on heating to the solid 1 : 1 complex and pyridine vapour. From the temperature variation of the dissociation pressure and the vapour pressure of pyridine (Py) the heat of the reaction

$$GaCl_3.Py_{(c.)} + Py_{(l.)} = GaCl_3.2Py_{(c.)}$$

is 11·6 kcal, compared with the calorimetric value of 11·7 kcal.

The heat of formation of complexes of boron trichloride with nitrogen donors[6] is even greater than the energy of interaction of these ligands with gallium trichloride. Thus the heat of formation of $BCl_3.Py_{(c.)}$ is 40·7 kcal mole^{-1} and the heat of formation of the piperidine (Pip) complex $BCl_3.Pip_{(c.)}$ is 84·4 kcal mole^{-1}. At the other end of the scale is the very unstable compound between boron trichloride and acetyl chloride which only exists in the solid state[3]; above the m.p., —54°, it is completely dissociated and the heat of interaction of donor and acceptor to give the 1 : 1 liquid mixture is only 0·67 kcal mole^{-1}. When the entropy of complex formation is subtracted, the free energy of formation is substantially negative.

One of the most interesting observations made during this work was that, for a given ligand, the heat of formation of complexes of the tribromides was consistently greater than that for the corresponding trichlorides.

Table 2. Comparison of heats of formation of chloride and bromide complexes

Complex	$-\Delta H_f$ (kcal mole^{-1})	*Complex*	$-\Delta H_f$ (kcal mole^{-1})
$BCl_3.Py$	40·7	$BCl_3.Pip$	84·4
$BBr_3.Py$	45·6	$BBr_3.Pip$	114·5
$GaCl_3.Py$	29·8	$BCl_3.Me_2CO$	44·9*
$GaBr_3.Py$	34·5	$BBr_3.Me_2CO$	68·4*

* Heats of solution of halide in excess of ligand.

Some comparative data are set out in *Table 2.* They confirm the observations of Brown and Holmes on the sequence of acceptor strengths[7]: $BF_3 < BCl_3 < BBr_3$. Likewise the heat of formation of $GaCl_3.Py$ is significantly less than that of $GaBr_3.Py$ and the effect appears to persist even in the gas phase, when allowance has been made for the heats of sublimation and dimerization[5]. The most plausible explanation of the reversed sequence is that back donation of $p\pi$ electrons from the halogen into the vacant $p\pi$ orbital of the acceptor atom is greater for BCl_3 than for BBr_3, and hence the latter is a better acceptor of electrons from an external ligand because less reorganization energy from a planar to a tetrahedral configuration is required[8].

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