234. *The Relative Acceptor Strength of Gallium Trichloride and Tribromide towards Pyridine as a Reference Ligand, and the Thermochemistry of Complexes of Gallium Trichloride with Piperidine.*

By N. N. Greenwood and P. G. Perkins.

The heats of formation of the 1 : 1 and 1 : 2 complexes of gallium trichloride with pyridine and piperidine have been determined calorimetrically, and the value for gallium trichloride–di(pyridine) has been checked by measurement of its dissociation pressure as a function of temperature. For both sets of complex, addition of the first mole of ligand liberates more heat than does that of the second, and the heats of formation of the piperidine complexes are greater than those of pyridine. The heat of formation of crystalline gallium tribromide–pyridine is greater than that of gallium trichloride–pyridine and estimates of the heats of sublimation of these complexes suggest that the same order also holds for the gas-phase reactions. The results are compared with analogous data for complexes of the boron and aluminium trihalides.

It has been recognized for some time that the heat of formation of an addition compound in the gas phase involves, not only the heat of formation of the new donor–acceptor bond, but also the energy of reorganization of the donor and acceptor moieties.[1] In the case of the boron trihalides, where there is partial double-bonding due to the π-overlap of filled p-orbitals on the halogen atoms with the empty p-orbital on the boron atom, the energy difference between the planar and tetrahedral configurations [2] is a dominant factor in determining the overall heat of reaction.[3,4] The situation is more complicated with the aluminium halides because they are dimeric, and, in the absence of values for the heats of sublimation of the complexes themselves, it is difficult to assess the magnitude of the reorganization energy.[2,5] No comparable study has been made of the gallium halides, though information on such complexes would undoubtedly help to elucidate the relative importance of the various factors involved. The present work establishes that the heat of formation of the crystalline complex of gallium tribromide with pyridine is greater than that of the corresponding gallium trichloride complex and suggests that the effect persists for the gas-phase reaction of this ligand with either the dimeric or monomeric forms of the acceptor molecules. In addition, the heats of formation of the complexes $GaCl_3,2C_5H_5N$, $GaCl_3,C_5H_{11}N$, and $GaCl_3,2C_5H_{11}N$ are reported and discussed.

The experimental techniques for handling these highly reactive compounds and for measuring their heats of formation have been described previously.[4,6]

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[1] Bauer, Finlay, and Laubengayer, *J. Amer. Chem. Soc.*, 1943, **65**, 889.

[2] Cotton and Leto, *J. Chem. Phys.*, 1959, **30**, 993.

[3] Brown and Holmes, *J. Amer. Chem. Soc.*, 1956, **78**, 2173.

[4] Greenwood and Perkins, preceding paper.

[5] Eley and Watts, *J.*, 1954, 1319; Dear and Eley, *J.*, 1954, 4684.

[6] Greenwood and Perkins, *J. Inorg. Nuclear Chem.*, 1957, **4**, 291.

RESULTS

The heats of solution of crystalline gallium trichloride, gallium trichloride–pyridine, and gallium trichloride–di(pyridine) in excess of pyridine are given in equations 1, 2, and 3. These are based on the thermochemical data in Table 1, the serial numbers in the Table referring to the corresponding heat of solution equations. The weight (in g.) of ligands and of acceptor or complex are shown, and also the mole ratio; the temperature rise, ΔT, is expressed in microvolts, and the electrical calibration in terms of the thermochemical calorie (4·1840 abs. joules). All results refer to 25·0°.

(1) $\mathrm{GaCl_3(c)} + x\mathrm{C_5H_5N(l)} = \mathrm{GaCl_3,2C_5H_5N(in\ soln.)}$; $-\Delta H = 40\cdot5 \pm 0\cdot1$ kcal. mole^{-1}

(2) $\mathrm{GaCl_3,C_5H_5N(c)} + x\mathrm{C_5H_5N(l)} = \mathrm{GaCl_3,2C_5H_5N(in\ soln.)}$; $-\Delta H = 10\cdot7 \pm 0\cdot1$ kcal. mole^{-1}

(3) $\mathrm{GaCl_3,2C_5H_5N(c)} + x\mathrm{C_5H_5N(l)} = \mathrm{GaCl_3,2C_5H_5N(in\ soln.)}$;
$-\Delta H = -1\cdot0 \pm 0\cdot1$ kcal. mole^{-1}

These results lead to the following heats of formation of the crystalline 1 : 1 and 1 : 2 complexes from crystalline gallium trichloride and liquid pyridine:

(4) $\mathrm{GaCl_3(c)} + \mathrm{C_5H_5N(l)} = \mathrm{GaCl_3,C_5H_5N(c)}$; $-\Delta H_f = 29\cdot8 \pm 0\cdot1$ kcal. mole^{-1}

(5) $\mathrm{GaCl_3(c)} + 2\mathrm{C_5H_5N(l)} = \mathrm{GaCl_3,2C_5H_5N(c)}$; $-\Delta H_f = 41\cdot5 \pm 0\cdot1$ kcal. mole^{-1}

It is seen that addition of the first mole of pyridine is more than $2\frac{1}{2}$ times as exothermic as the addition of the second mole. By subtraction of eqn. (4) from eqn. (5), the heat of formation of the 1 : 2 complex from the 1 : 1 adduct is:

(6) $\mathrm{GaCl_3,C_5H_5N(c)} + \mathrm{C_5H_5N(l)} = \mathrm{GaCl_3,2C_5H_5N(c)}$; $-\Delta H = 11\cdot7 \pm 0\cdot2$ kcal. mole^{-1}

This calorimetric value can be checked independently by measurement of the dissociation pressure of the 1 : 2 complex since this is a reaction of the type solid $\rightarrow$ solid + gas. The equilibrium constant K_p is then just the pressure (in atm.), and the heat and entropy of dissociation can be obtained directly from the vapour-pressure equation. Dissociation pressures

TABLE 1. *Heats of solution of acceptors and complexes in excess of ligands.*

No.	Ligand (g.)	Acceptor or complex (g.)	Mole ratio	$\Delta T(\mu\text{v})$	Calibration (cal. per μv)	$-\Delta H$ (kcal. mole^{-1})
1	105	0·0550	4260 : 1	112·5	0·1128	40·6
	105	0·0566	4130 : 1	117·5	0·1108	40·5
2	105	0·0690	4910 : 1	26·5	0·1080	10·6
	85	0·0505	5430 : 1	22·0	0·0975	10·8
3	85	0·2436	1480 : 1	−9·0	0·0853	−1·1
	85	0·2261	1590 : 1	−6·5	0·0886	−0·9
7	90	0·1720	2050 : 1	356·5	0·0858	55·1
	110	0·1922	2250 : 1	314·5	0·1079	54·7
	122	0·1531	3120 : 1	247·0	0·1108	54·6
8	119	0·1101	5310 : 1	54·5	0·1060	20·4
	123	0·1623	3720 : 1	61·5	0·1370	20·2
10	86	0·1052	1700 : 1	372·5	0·1035	64·5
	86	0·0853	2100 : 1	338·0	0·0904	63·1
	86	0·0599	2980 : 1	193·0	0·1138	64·6
	99	0·1064	1930 : 1	356·5	0·1152	67·9
	47	0·0501	1940 : 1	334·0	0·0542	63·6
11	92	0·1457	1930 : 1	190	0·089	~32
	61	0·0967	1930 : 1	150	0·073	~30
12	79	0·1675	1920 : 1	46·5	0·1287	12·4
	57	0·1515	1530 : 1	60·5	0·0931	12·9
	77	0·1620	1930 : 1	46·0	0·1280	12·6

TABLE 2. *Dissociation pressure of solid* $\mathrm{GaCl_3,2C_5H_5N}$.

Temp.	24·5°	26·3°	29·0°	32·4°	34·2°	39·2°	42·0°	45·7°	48·2°
p (mm.)	1·60	2·82	3·85	4·79	6·09	10·00	14·49	21·38	25·12

were measured between 25° and 50° (Table 2) and can be represented with a mean deviation of 0·5 mm. by the equation

$$\log p \text{ (mm.)} = 15{\cdot}973 - 4670/T$$

From this, $-\Delta H_{\text{dissoc.}} = -21{\cdot}3$ kcal. mole^{-1} and $\Delta S = 59{\cdot}9$ cal. deg.$^{-1}$ mole^{-1}. The heat of vaporization of pyridine at 25° is 9·7 kcal. mole^{-1},[7] so the heat involved in the dissociation reaction (which is the reverse of eqn. 6) is $-11{\cdot}6$ kcal. mole^{-1}, in excellent agreement with the calorimetric value for the forward reaction, $+11{\cdot}7$ kcal. mole^{-1}.

The entropy of dissociation of gallium trichloride–di(pyridine) seems, at first sight, to be unusually large. However, the value is reasonable, as can be seen by considering the three main terms which comprise the overall entropy change: (i) entropy of dissociation of the solid 1 : 2 complex into solid 1 : 1 complex and solid pyridine; (ii) entropy of sublimation of solid pyridine into pyridine vapour at 760 mm.; (iii) entropy of expansion of pyridine vapour from 760 mm. to the equilibrium dissociation pressure at 25°, *viz.*, 2 mm.

Minor specific-heat corrections being neglected, term (ii) is the sum of the entropy of fusion (1977/231·4 = 8·6 e.u.) and the entropy of vaporization at the b. p. (8493/388·8 = 21·8 e.u.). The thermal data were taken for convenience from ref. 8. Similarly, apart from deviations from ideality, term (iii) is given by $2{\cdot}303\,\boldsymbol{R}\log(p_1/p_2) = 11{\cdot}8$ e.u. The sum of terms (ii) and (iii) is therefore approximately 42·2 e.u. The change of entropy in step (i) is not easy to calculate but, as it involves a condensed-phase reaction in which one solid phase gives two solid phases, an entropy change of 10—20 e.u. might be expected. The value calculated by difference between the observed total entropy change, 59·9 e.u., and the estimated entropy changes in steps (ii) and (iii) is 17·7 e.u.

The heats of solution of gallium tribromide and gallium tribromide–pyridine in excess of pyridine can be calculated from the data in Table 1 and are given in equations (7) and (8). Equation 9 shows that the derived heat of formation of the crystalline 1 : 1 complex is nearly 5 kcal. mole^{-1} greater than the heat of formation of the corresponding complex of gallium trichloride (eqn. 4):

(7) $GaBr_3(c) + xC_5H_5N(l) = GaBr_3,C_5H_5N(\text{in soln.})$; $-\Delta H = 54{\cdot}8 \pm 0{\cdot}3$ kcal. mole^{-1}

(8) $GaBr_3,C_5H_5N(c) + xC_5H_5N(l) = GaBr_3,C_5H_5N(\text{in soln.})$; $-\Delta H = 20{\cdot}3 \pm 0{\cdot}1$ kcal. mole^{-1}

(9) $GaBr_3(c) + C_5H_5N(l) = GaBr_3,C_5H_5N(c)$; $-\Delta H_f = 34{\cdot}5 \pm 0{\cdot}4$ kcal. mole^{-1}

The large heat of solution of gallium tribromide–pyridine in excess of pyridine (eqn. 8) may indicate the formation of a 1 : 2 or higher complex in solution, though no definite evidence for such compounds was obtained from a partial phase diagram of the system.[9]

Piperidine, like pyridine, forms two complexes with gallium trichloride.[10] The calorimetric data in Table 1 lead to the following heats of solution:

(10) $GaCl_3(c) + xC_5H_{11}N(l) = GaCl_3,2C_5H_{11}N(\text{in soln.})$; * $-\Delta H = 64{\cdot}7 \pm 1{\cdot}7$ kcal. mole^{-1}

(11) $GaCl_3,C_5H_{11}N(c) + xC_5H_{11}N(l) = GaCl_3,2C_5H_{11}N(\text{in soln.})$; * $-\Delta H = 31{\cdot}0 \pm 1{\cdot}0$ kcal. mole^{-1}

(12) $GaCl_3,2C_5H_{11}N(c) + xC_5H_{11}N(l) = GaCl_3,2C_5H_{11}N(\text{in soln.})$; * $-\Delta H = 12{\cdot}6 \pm 0{\cdot}3$ kcal. mole^{-1}

From these values, the heats of formation of the crystalline 1 : 1 and 1 : 2 complexes from gallium trichloride and piperidine, and the heat of formation of the 1 : 2 complex from the 1 : 1 complex and piperidine are:

(13) $GaCl_3(c) + C_5H_{11}N(l) = GaCl_3,C_5H_{11}N(c)$; $-\Delta H_f = 33{\cdot}7 \pm 2{\cdot}7$ kcal. mole^{-1}

(14) $GaCl_3(c) + 2C_5H_{11}N(l) = GaCl_3,2C_5H_{11}N(c)$; $-\Delta H_f = 52{\cdot}1 \pm 2{\cdot}0$ kcal. mole^{-1}

(15) $GaCl_3,C_5H_{11}N(c) + C_5H_{11}N(l) = GaCl_3,2C_5H_{11}N(c)$; $-\Delta H = 18{\cdot}4 \pm 1{\cdot}3$ kcal. mole^{-1}

* See following paragraphs.

[7] Herington and Martin, *Trans. Faraday Soc.*, 1953, **49**, 154.

[8] Weissberger, Proskauer, Riddick, and Toops, "Organic Solvents," 2nd edn., Interscience Pub Inc., 1955.

[9] Greenwood and Worrall, *J.*, 1960, 353.

[10] Greenwood and Wade, *J.*, 1958, 1663, 1671.

It is evident that more heat is evolved in the formation of these complexes than is evolved for the corresponding pyridine adducts (eqns. 4, 5, 6). Addition of the first mole of ligand is again more exothermic than addition of the second.

In all the piperidine systems the solution reactions were accompanied by formation of a white precipitate. This was not eliminated either by rigorous drying of the ligand or by repeated fractionation. The effect of an inhomogeneous final state was minimized by adjusting the amount of ligand so as always to have a constant mole ratio (about 1930 : 1). In the experiments with gallium trichloride itself (series 10) reaction was rapid but several runs were necessary to obtain a consistent mean value. In the case of the 1 : 1 complex (series 11) reaction was extremely slow and the temperature rose over a period of 2 hr. or more; for this reason the heats of reaction given in Table 1 are only approximate. The heat of solution of the 1 : 2 complex (series 12) was more precise.

In an attempt to identify the white precipitate, larger amounts of it were prepared in separate experiments. The same product was obtained independently of whether gallium trichloride, gallium trichloride–piperidine, or gallium trichloride–di(piperidine) was dissolved in excess of piperidine, and independently of the mole ratio used. The solid melted at 207—211° with slight decomposition. Mixed m. p.s of all combinations of products fell in the same range, whereas a mixture of the precipitate and the 1 : 1 complex (m. p. 134°) melted at 85°, and a mixture of the precipitate and the 1 : 2 complex (m. p. 112°) melted at 95°. Typical analytical data were: C, 47·15; H, 9·2; N, 10·5; Cl, 28·15; Ga, 6·1. The corresponding empirical formula is $C_{45}H_{105}N_9Cl_9Ga$, *i.e.*, $GaCl_3,9C_5H_{11}N,6HCl$. It will be noticed that the ratio Cl : Ga in the precipitate is 9 : 1, implying that the supernatant solutions were correspondingly richer in gallium. The matter was not pursued further.

Discussion

The similarity in the physical properties of the 1 : 1 complexes of pyridine with boron trichloride, aluminium trichloride, and gallium trichloride has already been noted;[10] *e.g.*, their m. p.s are 115°, 118°, and 126° respectively. It is now seen that this similarity extends in some measure to the thermochemistry of these complexes, their heats of formation being 40·7,[4] 31·8,[5] and 29·8 kcal. mole^{-1}, respectively. The difference between boron trichloride on the one hand and aluminium and gallium trichlorides on the other is due partly to the fact that the former is a covalent liquid under the conditions of the experiment whereas the last two acceptors are ionic solids. Of more significance is the comparison between the heats of reaction of pyridine vapour and the monomeric acceptors in the gas phase. For the complex $GaCl_3,C_5H_5N$ this energy can be computed from the following cycle:

$$\begin{tikzcd}
GaCl_3(c) + & C_5H_5N(l) \arrow[r, "29\cdot8^{d}"] \arrow[dd, "-9\cdot7"] & GaCl_3,C_5H_5N(c) \arrow[d, "ca.\,-3\cdot0"] \\
\tfrac{1}{2}Ga_2Cl_6(g) \arrow[d, "-10\cdot5^{b}"] \arrow[from=u, "-8\cdot5^{a}"] & & GaCl_3,C_5H_5N(l) \arrow[d, "-20\cdot3^{f}"] \\
GaCl_3(g) + & C_5H_5N(g) \arrow[r, "-\Delta H_g"] & GaCl_3,C_5H_5N(g
\end{tikzcd}$$

[a] Ref. 11. [b] Ref. 12. [c] Ref. 7. [d] Eqn. (4). [e] Estimated by analogy with the heat of fusion of $AlCl_3,NH_3$, *viz.*, 2·6 kcal. mole^{-1}.[13] [f] Ref. 10.

A similar cycle, with data from refs. 5, 7, and 14, gives the value shown in equation (17) for aluminium chloride–pyridine, if the heat of sublimation of the complex is taken

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[11] Laubengayer and Schirmer, *J. Amer. Chem. Soc.*, 1940, **62**, 1578.
[12] Fischer and Jübermann, *Z. anorg. Chem.*, 1936, **227**, 227.
[13] Klemm, Tilk, and Jacobi, *Z. anorg. Chem.*, 1932, **207**, 187.
[14] Fischer and Rahlfs, *Z. anorg. Chem.*, 1932, **205**, 1.

to be the same as that of gallium trichloride–pyridine; the corresponding figure for boron trichloride–pyridine [4] is given in equation (18):

(16) $GaCl_3(g) + C_5H_5N(g) = GaCl_3,C_5H_5N(g)$; $-\Delta H_g \simeq 35{\cdot}2$ kcal. mole^{-1}

(17) $AlCl_3(g) + C_5H_5N(g) = AlCl_3,C_5H_5N(g)$; $-\Delta H_g \simeq 46{\cdot}2$ kcal. mole^{-1}

(18) $BCl_3(g) + C_5H_5N(g) = BCl_3,C_5H_5N(g)$; $-\Delta H_g \simeq 37{\cdot}9$ kcal. mole^{-1}

These figures, which are probably accurate to ± 2 kcal. mole^{-1}, imply that the acceptor strength of the monomeric Group III trichlorides towards pyridine is a maximum at aluminium trichloride–pyridine, the heat of formation of this complex in the gas phase being some 10 kcal. mole^{-1} greater than that for the boron and gallium analogues. This difference arises principally from the high heat of sublimation of aluminium trichloride into monomeric molecules, which is 9·0 kcal. greater than the corresponding quantity for gallium trichloride.

The m. p.s of the pyridine complexes of the tribromides are likewise similar to each other and are also close to those of the trichloride complexes: BBr_3,C_5H_5N, 127°; [4] $AlBr_3,C_5H_5N$, 115°; [15] and $GaBr_3,C_5H_5N$, 126°.[9] The heats of formation of these crystalline complexes are 45·6,[4] 31·9,[5] and 34·5 kcal. mole^{-1}, respectively, each value being greater than that for the corresponding chloride complex. Data for the gas-phase reactions are summarized in equations (19), (20), and (21):

(19) $BBr_3(g) + C_5H_5N(g) = BBr_3,C_5H_5N(g)$; $-\Delta H_g \simeq 43{\cdot}5$ kcal. mole^{-1}

(20) $AlBr_3(g) + C_5H_5N(g) = AlBr_3,C_5H_5N(g)$; $-\Delta H_g \simeq 39{\cdot}6$ kcal. mole^{-1}

(21) $GaBr_3(g) + C_5H_5N(g) = GaBr_3,C_5H_5N(g)$; $-\Delta H_g \simeq 38{\cdot}3$ kcal mole^{-1}

The value for boron tribromide-pyridine is from ref. 4, and that for aluminium tribromide–pyridine was obtained by combination of the relevant data in refs. 5, 7, and 14, on the assumption that the heat of sublimation of the complex was the same as the heat of sublimation of gallium tribromide–pyridine. This was estimated to be *ca.* 25 kcal. mole^{-1} on the grounds that it was probably similar to, but slightly greater than, that of gallium trichloride–pyridine, an assumption consistent with the somewhat greater activation energy of viscous flow of the bromide complex.[10] The calculation of the gas-phase heat of formation of gallium tribromide–pyridine also employed 9·3 kcal. mole^{-1} for the heat of dissociation of $\frac{1}{2}Ga_2Br_6$ into monomeric $GaBr_3$,[12] and 9·8 kcal. mole^{-1} for the heat of sublimation of gallium tribromide (comprising 7·2 kcal. mole^{-1} for the heat of vaporization of the liquid [12] and 2·6 kcal. mole^{-1} for the heat of fusion, this being taken to be the same as for the trichloride,[11] since both processes involve a change from an ionic solid to a covalent liquid [16]).

Equations (19), (20), and (21) suggest that, for the bromide complexes, there is a small decrease in the gas-phase dissociation energy with increasing atomic number of the Group III element, though this decrease is not far outside the possible errors incurred in the estimates of sublimation energies. If the figures are accepted, they would imply, again, that the dissociation energy of aluminium chloride–pyridine in the gas phase (eqn. 17) is unusually high. It is also noticeable that, whereas the heats for the bromide complexes of boron and gallium are greater than those for the chloride complexes, the reverse is true for the aluminium trihalides in the gas phase. This point is discussed in the next section.

Information on the complexes of piperidine is less complete, and we know of no thermochemical study on the complexes of this ligand with the aluminium halides. The heat of formation of crystalline boron trichloride–piperidine [4] is 84·4 kcal. mole^{-1} compared with only 33·7 kcal. mole^{-1} for the corresponding complex of gallium trichloride (eqn. 13).

[15] Eley and Watts, *J.*, 1952, 1914.

[16] Greenwood and Worrall, *J. Inorg. Nuclear Chem.*, 1957, **3**, 357.

This large difference persists when estimates are made for the gas-phase reactions by using a value of 8·9 kcal. mole^{-1} for the heat of vaporization of piperidine,[17] 18·2 kcal. mole^{-1} for the heat of sublimation of boron trichloride–piperidine,[18] and other relevant data cited above. The measured heat of vaporization of liquid gallium trichloride–piperidine [10] is 20·5 kcal. mole^{-1}, and if a value of 3 kcal. mole^{-1} is assumed for the heat of fusion, then the heat of sublimation becomes ~23·5 kcal. mole^{-1}. Hence:

(22) $BCl_3(g) + C_5H_{11}N(g) = BCl_3,C_5H_{11}N(g)$; $-\Delta H_g = 80{\cdot}6$ kcal. mole^{-1}

(23) $GaCl_3(g) + C_5H_{11}N(g) = GaCl_3,C_5H_{11}N(g)$; $-\Delta H_g \simeq 38{\cdot}1$ kcal. mole^{-1}

The exceptionally large energy involved in reaction (22) is unexplained.[4]

The Relative Acceptor Strengths of Chlorides, Bromides, and Iodides.—The superior acceptor strength of boron tribromide as compared with the trichloride and trifluoride is now well established both for reactions in solution [3] and in the gas phase,[4] and also for the formation of the crystalline complexes themselves.[4] This order is determined mainly by the extent of π-bonding in the trihalides which, in turn, influences the energy of reorganization of the electron acceptor from the planar to the tetrahedral configuration. Estimated values of this reorganization energy [2] are BF_3 48·3 kcal. mole^{-1}, BCl_3 30·3 kcal. mole^{-1}, and BBr_3 26·2 kcal. mole^{-1}, the difference between the last two figures being close to the difference between the gas-phase heats of formation of the pyridine complexes (eqns. 18 and 19).

The estimated reorganization energies of monomeric $AlCl_3$ (31·6 kcal. mole^{-1}) and $AlBr_3$ (27·9 kcal. mole^{-1}) [2] are very similar to the values for the corresponding boron halides but the acceptor strength of these compounds is also influenced by their heats of dimerization. Complications also arise when the heats of formation of complexes from crystalline aluminium trichloride and tribromide are compared, for the chloride is an ionic solid [19] whereas the bromide forms a lattice of dimeric molecules.[20] Nevertheless, in the absence of data for the gas-phase reactions it is interesting to compare the heats of formation of iualuminm trihalide complexes in condensed-phase reactions. The heats of formation * of the pyridine complexes of aluminium trichloride, tribromide, and tri-iodide are 31·8, 31·9, and 31·5 kcal. mole^{-1}, respectively,[5] and the corresponding heats of mixing in chlorobenzene solution [5] are 42·6, 60·1, and 70·1 kcal. mole^{-1}, the larger values in the second series being ascribed to the formation of higher complexes in solution. The heats of formation of the crystalline complexes of the aluminium halides with trimethylamine show a similar increase with increasing atomic number of the halogen: [5] 30·8, 33·0, and 33·1 kcal. mole^{-1}. From the vapour pressures above the 1 : 2 complexes of aluminium trichloride and tribromide with trimethylamine [21] the energies of dissociation of these complexes into the 1 : 1 complex and gaseous trimethylamine are 10·4 and 15·2 kcal. mole^{-1}, implying that the heats of formation of the crystalline 1 : 2 complexes from the parent donor and acceptors are 41·2 and 48·2 kcal. mole^{-1}, the value for the bromo-complex again being the larger.

The heats of reaction of aluminium trichloride [22] and tribromide [23] with acetophenone

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* Strictly, the heats of formation were not determined by the measurements in ref. 5. The reactions studied were (L = ligand; X = Cl, Br, I):

$L,AlX_3(c)$ + excess of 2N-HCl soln. = {L + AlX_3} (in soln.); . . . $-\Delta H_1$

L(l) + excess of 2N-HCl soln. = L (in soln.); . . . . . $-\Delta H_2$

$AlX_3(c)$ + excess of 2N-HCl soln. = AlX_3 (in soln.); . . . . $-\Delta H_3$

The heat of formation of the reaction $L(l) + AlX_3(c) = L,AlX_3(c)$ was then taken to be $-\Delta H_2 - \Delta H_3 + \Delta H_1$. This tacitly assumes zero heat of mixing for the reaction

L (in soln.) + AlX_3 (in soln.) = {L + AlX_3} (in soln.); . . . . $-\Delta H_4$

[17] Riley and Bailey, *Proc. Roy. Irish Acad.*, 1929, **38**, *B*, 450.

[18] Greenwood and Wade, *J.*, 1960, 1130.

[19] Ketelaar, MacGillavry, and Renes, *Rec. Trav. chim.*, 1947, **66**, 501.

[20] Renes and McGillavry, *Rec. Trav. chim.*, 1945, **64**, 275.

[21] Van Dyke and Crawford, *J. Amer. Chem. Soc.*, 1950, **72**, 2829.

[22] Dilke, Eley, and Sheppard, *Trans. Faraday Soc.*, 1950, **46**, 261.

[23] Lebedev, *Zhur. obshchei Khim.*, 1951, **21**, 1788.

(19·2 and 22·4 kcal. mole^{-1}) and with benzophenone (15·4 and 19·5 kcal. mole^{-1}), and their heats of solution in nitrobenzene [24] (12·2 and 24·5 kcal. mole^{-1}) show the same order. Likewise, the heat of reaction with acetaldehyde in chlorobenzene solutions increases from aluminium trichloride (24·7),[22] through aluminium tribromide (36·0), to the tri-iodide (42·4 kcal. mole^{-1}).[25] The generality of the phenomenon is shown by the heats of formation (in kcal. mole^{-1}) of the following pairs of ionic complexes: [26]

$AlCl_3,NaCl$	6·65;	$AlCl_3,NaBr$	3·32;	$AlCl_3,KCl$	12·42
$AlBr_3,NaCl$	9·93;	$AlBr_3,NaBr$	10·1;	$AlBr_3,KCl$	14·6;

It is therefore curious that the reverse order is observed for the heats of formation of the 1 : 1 complexes of ammonia with both the aluminium [27,13] and the gallium trihalides.[13] The heats of dimerization of the aluminium trihalides [14] and gallium trihalides [12] in the gas phase also decrease in the sequence Cl $>$ Br $>$ I, but here one is changing both the donor and the acceptor simultaneously and the results are not comparable with those above, in which the acceptor strength is measured relative to the same ligand in each series. In summary, it can be said that, with few exceptions, the heat of complex formation of the Group III trihalides in condensed-phase reactions increases in the order Cl $<$ Br $<$ I. Where data are available, the same sequence appears to hold for the gas-phase reactions of the trihalides of boron and gallium but not always for those of the aluminium trihalides.

We thank the Royal Society and the Chemical Society for financial support and the D.S.I.R. for a Maintenance Grant to P. G. P.

THE UNIVERSITY, NOTTINGHAM. [*Received, August* 14*th*, 1959.]

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