68. *Thermochemistry of the Systems which Boron Trichloride and Gallium Trichloride form with Acetone and Acetyl Chloride, and the Heat of Solution of Boron Tribromide in Acetone.*

By N. N. GREENWOOD and P. G. PERKINS.

Gallium trichloride forms a 1 : 1 complex, m. p. 42·2° (decomp.), with acetone; this is the first reported complex of gallium trichloride with a ketone. Its heat of formation is 15·3 ± 0·9 kcal. mole^{-1} compared with 4·1 ± 0·1 kcal. mole^{-1} for gallium trichloride–acetyl chloride. The 1 : 1 mixture of boron trichloride and acetyl chloride, which exists as a complex only in the solid phase at low temperatures, has an even lower heat of formation: 0·7 ± 0·1 kcal. mole.$^{-1}$ A complex between boron trichloride and acetone could not be isolated because of polymerizing side reactions, but the total heat of solution of boron trichloride in this ligand was 44·9 ± 0·1 kcal. mole^{-1}, compared with 68·4 ± 0·03 kcal. mole^{-1} for boron tribromide.

THE properties of the 1 : 1 complex between gallium trichloride and acetyl chloride suggest [1] that it has the structure $Me{\cdot}CO^+GaCl_4^-$, and the absence of a similar complex between boron trichloride and acetyl chloride has been ascribed [1] to the difficulty of forming the corresponding tetrachloroborate ion, though this ion is now known in other compounds.[2] The present experiments were designed to find out whether this difference was

---

[1] Greenwood and Wade, *J.*, 1956, 1527.

[2] Kynaston and Turner, *Proc. Chem. Soc.*, 1958, 304, and references therein.

reflected in the thermochemistry of the two systems and to determine the influence of replacing the chlorine atom in the ligand by a methyl group, thus ensuring that any co-ordination occurs through the oxygen atom of the carbonyl group. A partial statement of some of the results, without the supporting experimental data, has appeared in the Proceedings of recent conferences.[3,4]

EXPERIMENTAL AND RESULTS

The preparation and purification of gallium trichloride [1] and the purification of boron trichloride,[1] boron tribromide,[5] and acetyl chloride [1] have been previously described. Acetone, m. p. −95°, b. p. 56·5°, was dried by refluxing it over anhydrous potassium carbonate and then fractionated twice.

The phase diagram of the system gallium trichloride–acetone was determined by means of the apparatus shown in Fig. 1. A sample tube containing gallium trichloride was weighed, broken, and sealed in limb *A*. The apparatus was then evacuated and the chloride quantitatively sublimed into compartment *B*, the weight taken being found by weighing the empty pieces of sample tube after the apparatus had been sealed at *C*. Successive known weights of acetone were then condensed into *B* which could be detached from the vacuum line and shaken to ensure a homogeneous mixture. Heating and cooling curves were obtained by immersing the apparatus in a magnetically stirred oil-bath fitted with a 40-w heater, cooling being obtained, when required, by pellets of solid carbon dioxide. Temperatures were measured to 0·025° by means of a single-junction copper–constantan thermocouple in conjunction with a Pye precision vernier potentiometer. The results are given in Fig. 2 which shows a maximum m. p. of 38° at the 1 : 1 ratio. It was observed that repeated melting and freezing tended to decompose the compound, and the maximum on the phase diagram is lower than the m. p. of a freshly prepared sample of the complex, *viz.*, 42·2°. This is the first reported complex between gallium trichloride and a ketone, though several such compounds of aluminium trichloride are well known. The system is similar to that between gallium trichloride and acetyl chloride, in which the 1 : 1 complex melts with some decomposition at 86°.[1] However, in contrast to gallium trichloride–acetyl chloride which rapidly yielded acetophenone when refluxed with benzene, the complex gallium trichloride–acetone showed no Friedel–Crafts activity under the same conditions and no acetophenone was detected.

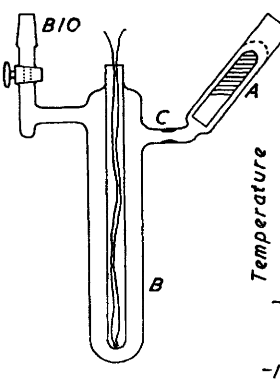

FIG. 1.
Melting-point apparatus.

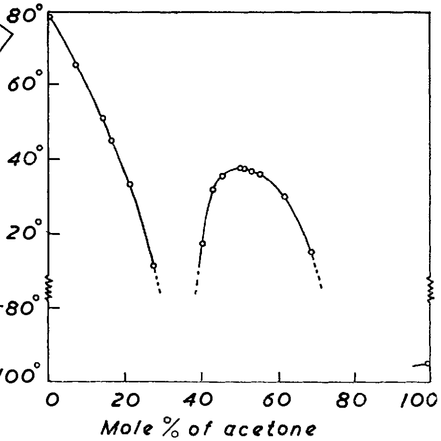

FIG. 2.
Phase diagram of the system $GaCl_3$–Me_2CO

The heat of formation of crystalline gallium trichloride–acetone from crystalline gallium trichloride and liquid acetone at 25° was determined from the difference between the heats of

---

[3] Greenwood, Wade, and Perkins, Proc. 16th Congress I.U.P.A.C. (Inorganic Section), Paris, 1957, 491.

[4] Greenwood, *J. Inorg. Nuclear Chem.*, 1958, **8**, 234.

TABLE 1. $GaCl_3$(c) + *excess of* Me_2CO(l) = $GaCl_3,Me_2CO$ (*in excess of* Me_2CO).

Me_2CO (g.)	$GaCl_3$ (g.)	Mole ratio	$\Delta T(\mu v)$	Calibration (cal. per μv)	$-\Delta H$ (kcal. mole^{-1})
80	0·0767	3160 : 1	127·0	0·1065	31·1
80	0·1022	2370 : 1	182·5	0·1040	32·7
80	0·0887	2740 : 1	153·0	0·1051	31·9
					Mean 31·9

TABLE 2. $GaCl_3,Me_2CO$(c) + *excess of* Me_2CO(l) = $GaCl_3,Me_2CO$ (*in excess of* Me_2CO).

Me_2CO (g.)	$GaCl_3,Me_2CO$ (g.)	Mole ratio	$\Delta T(\mu v)$	Calibration (cal. per μv)	$-\Delta H$ (kcal. mole^{-1})
101	0·6424	620 : 1	390	0·1177	16·7
103·5	0·6354	655 : 1	373	0·1202	16·5
					Mean 16·6

TABLE 3. $GaCl_3$(c) + *excess of* Me·COCl(l) = $GaCl_3$,Me·COCl (*in excess of* Me·COCl).

Me·COCl (g.)	$GaCl_3$ (g.)	Mole ratio	$\Delta T(\mu v)$	Calibration (cal. per μv)	$-\Delta H$ (kcal. mole^{-1})
130	0·1252	2330 : 1	182·5	0·1229	31·5
133	0·0757	3880 : 1	125·5	0·1080	31·5
					Mean 31·5

TABLE 4. $GaCl_3$,Me·COCl(c) + *excess of* Me·COCl(l) = $GaCl_3$,Me·COCl (*in excess of* Me·COCl).

Me·COCl (g.)	$GaCl_3$,Me·COCl (g.)	Mole ratio	$\Delta T(\mu v)$	Calibration (cal. per μv)	$-\Delta H$ (kcal. mole^{-1})
133	0·3190	1350 : 1	320	0·1079	27·5
133	0·3427	1260 : 1	322	0·1141	27·3
					Mean 27·4

TABLE 5. BCl_3(l) + *excess of* Me·COCl(l) = {BCl_3 + Me·COCl} (*in excess of* Me·COCl).

Me·COCl (g.)	BCl_3 (g.)	Mole ratio	$\Delta T(\mu v)$	Calibration (cal. per μv)	$-\Delta H$ (kcal. mole^{-1})
133	0·1694	1170 : 1	292·0	0·1056	21·3
132	0·1142	1725 : 1	201·5	0·1037	21·4
					Mean 21·4

TABLE 6. {BCl_3 + Me·COCl}(l) + *excess of* Me·COCl(l) = {BCl_3 + Me·COCl} (*in excess of* Me·COCl).

Me·COCl (g.)	{BCl_3 + Me·COCl} (g.)	Mole ratio	$\Delta T(\mu v)$	Calibration (cal. per μv)	$-\Delta H$ (kcal. mole^{-1})
134	0·3292	1010 : 1	321·0	0·1082	20·6
132	0·2017	1630 : 1	208·5	0·1027	20·8
					Mean 20·7

TABLE 7. BCl_3(l) + *excess of* Me_2CO(l) = {BCl_3 + *products*} (*in excess of* Me_2CO).

Me_2CO (g.)	BCl_3 (g.)	Mole ratio	$\Delta T(\mu v)$	Calibration (cal. per μv)	$-\Delta H$ (kcal. mole^{-1})
96·5	0·2918	670 : 1	987	0·1130	44·8
95	0·2027	945 : 1	739	0·1059	44·9
95	0·3119	615 : 1	1124	0·1067	45·0
					Mean 44·9

TABLE 8. BBr_3(l) + *excess of* Me_2CO(l) = {BBr_3 + *products*} (*in excess of* Me_2CO).

Me_2CO (g.)	BBr_3 (g.)	Mole ratio	$\Delta T(\mu v)$	Calibration (cal. per μv)	$-\Delta H$ (kcal. mole^{-1})
98·5	0·1685	2520 : 1	433	0·1064	68·4
98·5	0·5181	820 : 1	1288	0·1101	68·4
					Mean 68·4

solution of gallium trichloride and of the complex in excess of acetone. The thermochemical data were obtained as previously described [5,6] and are summarized in Tables 1 and 2. These lead to the following heat of formation:

$$GaCl_3(c) + Me_2CO(l) = GaCl_3,Me_2CO(c); \quad -\Delta H_f = 15{\cdot}3 \pm 0{\cdot}9 \text{ kcal. mole}^{-1}$$

The corresponding data for the system gallium trichloride–acetyl chloride are given in Tables 3 and 4 and lead to the following heat of formation of the complex:

$$GaCl_3(c) + Me{\cdot}COCl(l) = GaCl_3,Me{\cdot}COCl(c); \quad -\Delta H_f = 4{\cdot}1 \pm 0{\cdot}1 \text{ kcal. mole}^{-1}$$

The high value for the heat of solution of this complex is probably due to the acetylation which occurs in solution. This should take place to the same extent in the solution of both gallium trichloride itself and the complex and therefore should not affect the derived heat of formation of the complex. However, some inaccuracy arises from the fact that the maximum temperature rise, which is usually attained in 2—3 min., occurred only after 5—10 min.

Boron trichloride, in contrast to gallium trichloride, does not form a complex with acetyl chloride,[1] and this is reflected in the low heat of interaction of the two components to give the 1 : 1 mixture:

$$BCl_3(l) + Me{\cdot}COCl(l) = \{BCl_3 + Me{\cdot}COCl\}(l); \quad -\Delta H_f = 0{\cdot}7 \pm 0{\cdot}1 \text{ kcal. mole}^{-1}$$

The supporting experimental data are recorded in Tables 5 and 6.

Boron trichloride forms neither a 1 : 1 adduct nor a stable mixture with acetone because of rapid resinification of the ligand, with elimination of hydrogen chloride. Preparation of an unstable complex in solution was accomplished but this always polymerized before the product could be isolated. Accordingly only the total heat of interaction of boron trichloride and acetone could be measured (Table 7), and the final calorimetric liquid was yellow-brown owing to the presence of the polymerization and condensation products in solution. The value obtained was $44{\cdot}9 \pm 0{\cdot}1$ kcal. mole^{-1}.

In the same way it was found that complexes of boron tribromide with acetone could not be isolated, either as products of direct reaction or by interaction of the components in an inert solvent such as carbon tetrachloride. Table 8 shows that the heat of interaction was $68{\cdot}4 \pm 0{\cdot}03$ kcal. mole^{-1}. In view of the side reactions which occur on dissolution it is not possible to say anything definite about the relative heats of formation of the fugitive complexes in the two systems though it is noticeable that the heat of interaction of acetone with boron tribromide is greater than that with boron trichloride. The same order is observed when pyridine, piperidine, methyl cyanide, and nitrobenzene are used as ligands.[5]

DISCUSSION

The heat of formation of gallium chloride–acetone is similar to that of other complexes between gallium trichloride and oxygen-containing ligands (*e.g.*, $GaCl_3,Et_2O$ 15·4 kcal. mole^{-1};[4] and $GaCl_3,POCl_3$ 10·2 kcal. mole^{-1}).[6] It seems likely that boron trichloride–acetone would have a somewhat higher heat of formation if it were possible to isolate the complex before the interfering side-reactions occurred (cf. BF_3,Me_2CO,[7] m. p. 35—40°). Comparison with aluminium chloride–acetone is also difficult because here again a numerical value is not available; the heat evolved has been stated to be " marked " [8] and the value is likely to be greater than 20 kcal. mole^{-1} since, in chlorobenzene solution, the heat of formation of the complexes $AlCl_3,Ph_2CO$ and $AlCl_3,PhMeCO$ are 15·4 and 19·2 kcal. mole^{-1} respectively.[8] A complex $3AlCl_3,5Me_2CO$, m. p. 110—114°, has been claimed in this system.[9]

Acetyl chloride is a much weaker ligand than acetone but this difference cannot be ascribed to the differing inductive effects of the chlorine atom and the methyl group on the electron-density of the carbonyl oxygen atom as the structures of the two sets of complex are different. There is no reason to suppose that the acetone complexes are other than

[5] Greenwood and Perkins, *J.*, in the press.
[6] *Idem, J. Inorg. Nuclear Chem.*, 1957, **4**, 291.
[7] Lombard and Stéphan, *Bull. Soc. chim. France*, 1957, 1369.
[8] Dilke, Eley, and Sheppard, *Trans. Faraday Soc.*, 1950, **46**, 261.
[9] Uschakow, *Z. anorg. Chem.*, 1929, **183**, 140.

simple donor–acceptor addition compounds $Me_2C{=}O{\rightarrow}MX_3$ and this is consistent with the infrared spectrum of boron trifluoride–acetone.[10] On the other hand acyl halides tend to be halide-ion donors as shown by the infrared spectra[11] of the complexes $Me{\cdot}CO^+BF_4^-$ and $Me{\cdot}CO^+AlCl_4^-$, and the properties[1] of the complex $Me{\cdot}CO^+GaCl_4^-$.

The value of 0·7 kcal. mole^{-1} for the heat of formation of the 1 : 1 mixture of boron trichloride and acetyl chloride confirms the view[1] that there is no complex formation between these two compounds at room temperature. This can be seen by considering the free energy of formation of such a complex, which is given by the expression $\Delta G = \Delta H - T\Delta S$. The entropy of formation of a donor–acceptor complex in a gas-phase reaction is usually[12] about —40 to —45 cal. deg.$^{-1}$ mole^{-1} and, if the usual (Trouton's rule) allowance of about +20 to +25 cal. deg.$^{-1}$ mole^{-1} is made for the entropy of vaporization of the components and the complex, then completion of the thermochemical cycle leads to an entropy of complex formation of about —20 cal. deg.$^{-1}$ mole^{-1} for the liquid-phase reaction. This figure is intended merely to convey a very approximate idea of the entropy change involved. At room temperature the term $-T\Delta S$ is therefore about +6 kcal. mole^{-1} and, since $\Delta H = -0{\cdot}7$ kcal. mole^{-1}, it is seen that ΔG is positive to the extent of about 5 kcal. mole^{-1}, implying that the complex is virtually completely dissociated.

We thank the Royal Society for generous financial support and the D.S.I.R. for a maintenance grant to P. G. P.

THE UNIVERSITY, NOTTINGHAM. [*Received, August 6th*, 1959.]

---

[10] Chalandon and Susz, *Helv. Chim. Acta*, 1958, **41**, 697.
[11] Susz and Wuhrmann, *ibid.*, 1957, **40**, 722, 971.
[12] Stone, *Chem. Rev.*, 1958, **58**, 101.