306. *Addition Compounds of Gallium Trichloride. Part I. A Comparison of the Binary Systems which Acyl Chlorides form with Boron and Gallium Trichlorides.*

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The existence of the molecular addition compound boron trichloride–acetyl chloride (m. p. −54°) has been established by phase studies, but there is no evidence for a compound between boron trichloride and benzoyl chloride. Vapour pressures for the two systems at 0° show positive deviations from ideality, indicating that boron trichloride–acetyl chloride is stable only in the solid phase. Neither system shows Friedel–Crafts activity. By contrast, gallium trichloride forms compounds with both ligands (gallium trichloride–acetyl chloride, m. p. 86°, and gallium trichloride-benzoyl chloride, m. p. 46·5°), and these complexes are powerful Friedel–Crafts acylating agents. The electrical conductivity of gallium trichloride-benzoyl chloride suggests that the compound is appreciably ionized in the molten state, whereas the system involving boron trichloride and benzoyl chloride is virtually non-conducting.

The vapour pressures and heats of vaporization of highly purified boron trichloride and acetyl chloride, and the m. p. of vacuum-sublimed gallium trichloride, have been redetermined.

GALLIUM TRICHLORIDE is known to co-ordinate to ammonia,[1] trimethylamine,[2] and benzonitrile,[3] as well as to dimethyl ether [2] and *p*-nitrotoluene.[3] In all other systems the ligand contains a halogen atom, usually chlorine, and this is presumably the donor atom.[4-7] Hydrogen chloride also forms complexes providing that a subsidiary ligand such as ammonia,[4] toluene,[5] mesitylene,[5] or an ether [8, 9] is present to stabilise the proton. In all these complexes, especially those in which chlorine is the donor, gallium trichloride shows a marked resemblance to aluminium trichloride. By contrast, boron trichloride co-ordinates to several of the elements in Groups V and VI, but forms few stable complexes

[1] Klemm, Tilk, and Jacobi, *Z. anorg. Chem.*, 1932, **207**, 187.
[2] Van Dyke and Crawford, *J. Amer. Chem. Soc.*, 1950, **72**, 2829.
[3] Ulich and Heyne, *Z. phys. Chem.*, 1941, **49**, *B*, 284.
[4] Friedman and Taube, *J. Amer. Chem. Soc.*, 1950, **72**, 2236.
[5] Brown, Pearsall, and Eddy, *ibid.*, p. 5347.
[6] Brown, Eddy, and Wong, *ibid.*, 1953, **75**, 6275.
[7] Partington and Whynes, *J.*, 1948, 1952.
[8] Wiberg, Schmidt, and Galinos, *Angew. Chem.*, 1954, **66**, 442.
[9] Nachtrieb and Fryxell, *J. Amer. Chem. Soc.*, 1949, **71**, 4035.

with ligands in which chlorine is the donor atom.[10] The alkali-metal chlorides do not react to give compounds analogous to the tetrachlorogallates;[11] there are no complexes in the systems with methyl or *n*-propyl chloride, and, even when compounds are observed, as with ethyl and *iso*propyl chloride, they do not occur at the 1 : 1 ratio and melt at extraordinarily low temperatures.[12, 13]

In order to establish more clearly the reason for this difference in behaviour between boron trichloride on the one hand and aluminium and gallium trichlorides on the other, the binary systems of boron trichloride and gallium trichloride with acetyl chloride and benzoyl chloride were studied. The properties of the compounds formed between aluminium trichloride and these acyl halides are well known [14-19] and were not further investigated. A solid phase of composition $BCl_3,AcCl$ has been reported previously,[20] and some properties of the compound gallium trichloride–benzoyl chloride are known.[3, 21, 22] These results will be referred to later.

EXPERIMENTAL

Materials.—Commercial boron trichloride was purified by fractional distillation in a vacuum-line between −50° (36 mm. pressure) and −78° (5 mm. pressure). Successive fractions of the purified compound gave identical vapour pressures at a series of temperatures between −78° and 0° and these values also agreed, within the experimental error of 1 mm., with those given by Stock and Priess.[23] The m. p. was −107°.

Gallium trichloride was prepared from high-purity gallium metal (Messrs. Johnson Matthey and Co. Ltd.) by heating 28 g. in a current of dry chlorine in an all-glass apparatus similar to that described for the preparation of tellurium tetrachloride.[24] The product, which was a very pale pink,[25] was sealed in tubes under chlorine and then purified by distillation in chlorine, followed by two vacuum-sublimations at 80° in an apparatus[25] based on that described by T. W. Richards. First and last fractions were discarded and a final sublimate, from a bath held at 75°, was collected and sealed in ten receivers. The product formed large, colourless, brilliantly transparent crystals and each of the ten samples had a sharp m. p. within the range 77·75° ± 0·05°. This compares favourably with published values of 77·65°,[26] 77·0°,[27] 77·9° ± 0·2°,[28] and 78·0° ± 0·3°.[29]

Acetyl chloride was fractionated at 762 mm. through a 50 cm. column packed with glass helices, and the fraction boiling at 51·6—51·7° was collected at a take-off ratio of 1 : 70. This was further purified in the vacuum-line by distillation at −15° (37 mm. pressure) until a tensiometrically homogeneous product was obtained; this had m. p. −98°.

Benzoyl chloride was fractionated at 8 mm. in the column described above and the fraction boiling at 70·0° was collected at a take-off ratio of 1 : 50. The m. p. was −0·5°.

Transfer of Reactants.—Unless otherwise stated, all compounds were transferred in a vacuum-line which was flamed before use. Preliminary experiments showed that boron trichloride reacted rapidly with Silicone grease, to give a gas which was not condensed at −78°, and a liquid of b. p. approx. 100°. Apiezon greases M and L were both satisfactory, but Apiezon M was considered the better. These greases darkened only slightly in the presence of the trichlorides alone but there was some attack when acetyl chloride was also present.

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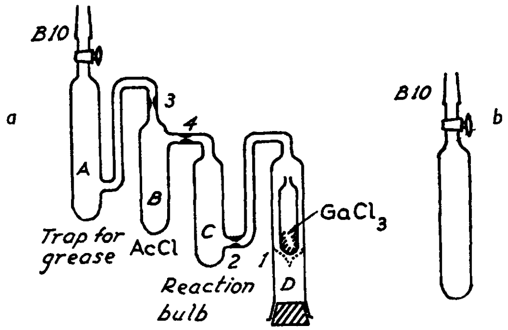
[10] Martin, *Chem. Rev.*, 1944, **34**, 461.
[11] Unpublished observations in this Laboratory.
[12] Martin and Hicks, *J. Phys. Chem.*, 1946, **50**, 422.
[13] Martin and Humphrey, *ibid.*, 1947, **51**, 425.
[14] Perrier, *Compt. rend.*, 1893, **116**, 1298.
[15] Boeseken, *Rec. Trav. chim.*, 1900, **19**, 21.
[16] Ulich, *ibid.*, 1901, **20**, 102.
[17] Menschutkin, *J. Russ. phys.-chem. Ges.*, 1910, **42**, 1310, *Chem. Zentr.*, 1911, I, 481.
[18] *Idem, Z. phys. Chem.*, Bodenstein Festband, 1931, p. 423.
[19] Nespital, *Z. phys. Chem.*, 1932, **16**, *B*, 153.
[20] Meerwein and Maier-Hüser, *J. prakt. Chem.*, 1932, **51**, 134.
[21] Ulich, *Die Chemie*, 1942, **55**, 37.
[22] *Idem, Oel u. Kohle*, 1943, **39**, 523.
[23] Stock and Priess, *Ber.*, 1914, **47**, 3109.
[24] Suttle and Smith, *Inorg. Synth.*, **3**, 140.
[25] Richards and Craig, *J. Amer. Chem. Soc.*, 1923, **45**, 1155.
[26] Craig and Drake, *ibid.*, 1934, **56**, 584.
[27] Laubengayer and Schirmer, *ibid.*, 1940, **62**, 1578.
[28] Fischer and Jübermann, *Z. anorg. Chem.*, 1936, **227**, 227.
[29] Klemm and Tilk, *ibid.*, 1932, **207**, 161.

The design of reaction vessels used for particular experiments depended on the volatility of the reactants, but the method used to prepare mixtures of gallium trichloride and acetyl chloride for m. p. determinations may be described, as typical. The apparatus (Fig. 1*a*) was flamed under vacuum and then filled with dry air. A sample tube of gallium trichloride was weakened by a file mark, weighed, broken cleanly, and placed in limb *D* which was then sealed at point 1. The apparatus was evacuated and the gallium trichloride was sublimed at 80° into limb *C* which was then sealed at 2. Tube *D* was broken open, the two halves of the sample tube were weighed, and the weight of gallium trichloride was calculated by difference. The required amount of acetyl chloride was vacuum-distilled from a bulb held at −15° into a weighing tube (Fig. 1*b*), after which it was distilled at low pressure into limb *B* which was then sealed at 3. As the acetyl chloride warmed to room temperature, its vapour was rapidly absorbed by the solid gallium trichloride in *C* with considerable evolution of heat. The transfer was completed by cooling *C* which was finally sealed at 4.

A semimicro-burette graduated in 0·01 ml. was used in the preparation of mixtures of gallium trichloride and benzoyl chloride, as both components were involatile at room temperature. The benzoyl chloride, in a burette protected by means of a phosphoric oxide guard-tube, was run on to gallium trichloride in a B14 test-tube with a side-arm which also carried a phosphoric oxide tube. Silicone grease was found to be the most suitable lubricant for the burette tap. The m. p. was determined after each addition without dismantling the apparatus.

FIG. 1.



Physical Measurements.—Temperatures above −20° were read on an accurate mercury thermometer; below −20° an alcohol-in-glass thermometer which had been calibrated against a platinum resistance thermometer was used. Corrections for emergent stem were applied. In some instances (*e.g.*, boron trichloride–benzoyl chloride) it was possible to immerse the thermometer in the mixture and plot warming curves. When sealed tubes were used, the sample was heated very slowly (less than 1° in 5 min.) in a bath, the temperature of disappearance of the solid phase being taken as the m. p.

Vapour pressures were read directly on mercury manometers. In some systems >1 hr. was required for vapour-pressure equilibration, but for the pure components equilibrium was attained after a few minutes. Low temperatures were maintained by the addition of pellets of solid carbon dioxide to a stirred bath of alcohol in a Dewar flask.

Electrical conductivities in the system boron trichloride–benzoyl chloride were measured at 1000 cycles a.c. by means of a circuit and cell similar to those already described.[30, 31] The cell constant was 4·146 cm.$^{-1}$. The conductivity of the pure compound gallium trichloride–benzoyl chloride was measured with dipping electrodes in a cell of constant 0·377 cm.$^{-1}$.

RESULTS

System Boron Trichloride–Acetyl Chloride.—A partial phase diagram in the range 28—69% acetyl chloride was obtained by condensing the components from a vacuum-line into a reaction bulb at −78° and then allowing the white, crystalline product to warm slowly. The results of several experiments are presented in Table 1 and Fig. 2. The m. p. curve has a broad maximum at 50 mole % and there is no evidence of other compounds at either the 1 : 2 or the 2 : 1 ratio. The m. p. of the compound boron trichloride–acetyl chloride (−54°) is considerably above the

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[30] Greenwood, Martin, and Emeléus, *J.*, 1950, 3030.
[31] *Idem*, *J.*, 1951, 1328.

m. p.s found for the pure components (BCl_3 −107°, AcCl −98°) and may be compared with the value of −60° to −70° given by Meerwein and Maier-Hüser for the equimolar mixture.[20]

Vapour-pressure measurements at 0° over the whole composition range (Table 2) show

TABLE 1. *Melting point of the system, boron trichloride-acetyl chloride.*

AcCl (mole %)	0·0	27·8	32·5	36·9	43·3	44·3	48·6	50·0	66·1	66·5	69·0	100·0
M. p.	−107°	−58°	−57°	−55·5°	−55°	−55°	−55°	−54°	−56°	−57°	−58°	−98°

TABLE 2. *Vapour pressure of the system boron trichloride-acetyl chloride at* 0°

AcCl (mole %)	0·0	5·2	10·8	16·7	28·6	36·2	40·7	48·6	52·7
Pressure (mm. Hg)...	478	473	460	456	434	415	396	394	376
AcCl (mole %)	59·3	65·3	68·9	77·1	81·4	89·7	93·1	100·0	
Pressure (mm. Hg)...	371	341	314	289	242	210	175	86	

positive deviations from Raoult's law (Fig. 3). This unexpected result suggests that the addition compound exists only in the solid phase and that its m. p. is, in effect, the temperature at which it dissociates into its components. That this dissociation is reversible is shown by the reproducibility of both melting point and vapour pressure throughout several thermal cycles.

FIG. 2. *M.p.s of systems with* BCl_3.

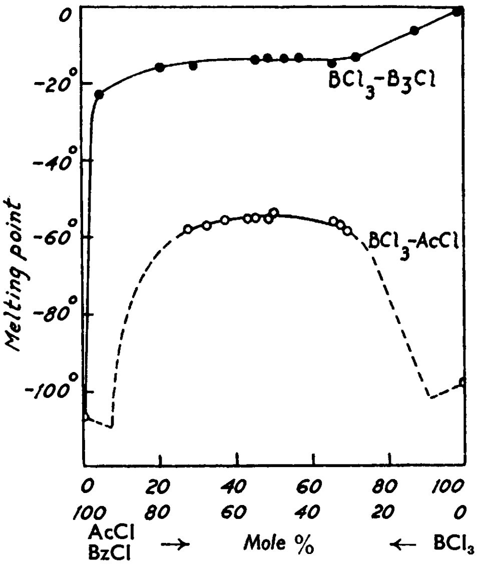
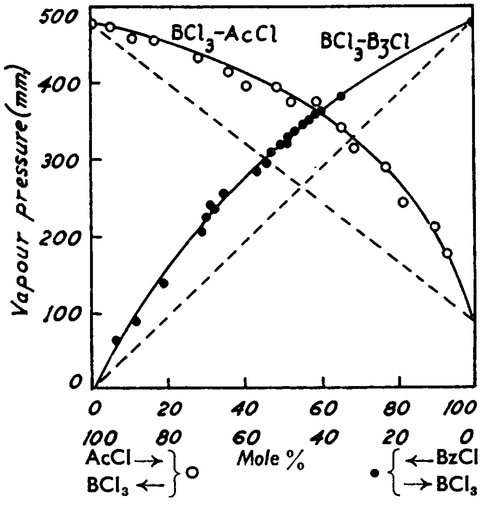


FIG. 3. *Vapour pressures of systems with* BCl_3 *at* 0°.



Absence of association or compound-formation in the liquid phase was further indicated by the fact that the heat of vaporization of the equimolar mixture was less than that of either component, so that vaporization of the mixture could clearly not also involve the concurrent dissociation of a chemical bond. Thus, the vapour-pressure measurements by Stock and Priess on boron trichloride[23] imply a heat of vaporization of 6·28 kcal. mole^{-1} at 0° and this value was confirmed by the present work in which vapour pressures between −78° and 0° were related to the absolute temperature by the equation,

$$\log p\ (\text{mm.}) = 7{\cdot}700 - 1372/T$$

This equation represents the pressures to within ±1 mm. and by extrapolation gives b. p. 11·5°. The only determination of the vapour pressure of acetyl chloride over a range of temperatures appears to be that of Kireev and Popov[32] who express their results by the equation

$$\log p\ (\text{mm.}) = 17{\cdot}16999 - 0{\cdot}023636T + 1{\cdot}75 \log T - 3570{\cdot}87/T$$

This implies that the heat of vaporization varies from 10·29 to 6·16 kcal. mole^{-1} in the range −20° to +50° and is 9·22 kcal. mole^{-1} at 0°. As these figures differ from the value of 6·84 kcal.

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[32] Kireev and Popov, *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 1399.

mole^{-1} obtained directly at the b. p.,[33] the vapour pressure of acetyl chloride was redetermined between −40° and +20°. The results are given in Table 3; above −20° they may be represented to within ±1 mm. by the equation

$$\log p \text{ (mm.)} = 8{\cdot}094 - 1684/T$$

This leads to a heat of vaporization of 7·68 kcal. mole^{-1} at 0° and an extrapolated b. p. of 49·9°.

The temperature dependence of the vapour pressure of a mixture containing 1·000 mol. of boron trichloride and 1·001 mol. of acetyl chloride was measured between −70° (supercooled) and +15°. The results, which are given in Table 4, may be represented by the following equation which is valid above −30°; at lower temperatures the measured pressures fall somewhat below this curve:

$$\log p \text{ (mm.)} = 7{\cdot}294 - 1294/T$$

The heat of vaporization at 0° is 5·92 kcal. mole^{-1} which is lower than the heat of vaporization of either component and is consistent with the positive deviation from ideality.

TABLE 3. *Vapour pressure of acetyl chloride between* −40° *and* +20°.

Temp.	−37°	−28°	−21·0°	−19·0°	−16·7°	−13·8°	−10·8°	−8·3°	−6·5°	−3·5°
Pressure (mm.)	8	15	26	29	34	40	48	55	61	72
Temp.	−2·0°	−0·4°	0·0°	2·2°	4·7°	7·3°	12·4°	15·5°	17·6°	
Pressure (mm.)	77	84	86	96	111	124	159	183	200	

TABLE 4. *Vapour pressure of an equimolar mixture of boron trichloride and acetyl chloride between* −70° *and* +15°.

Temp.	−72°	−68°	−59°	−54°	−49°	−43°	−38°	−35°	−31°	−24°	−20·5°	−17·5°
Pressure (mm.)	8	9	16	23	29	42	55	66	86	132	150	174
Temp.	−13·0°	−8·5°	−6·0°	−3·5°	−0·5°	+1·5°	+3·0°	+6·5°	+8·0°	+10·7°	+13·4°	
Pressure (mm.)	217	261	287	322	359	391	420	473	500	552	604	

The Friedel–Crafts activity of an equimolar mixture of boron trichloride and acetyl chloride was investigated by treating the mixture with an excess of pure, sodium-dried benzene for 5 days at room temperature and then refluxing it for a further 3 hr. The product was worked up in the usual way but no trace of acetophenone was obtained.

The phase diagram, vapour-pressure curves, and catalysis experiment indicate that, whereas boron trichloride and acetyl chloride form a well-defined solid addition compound, there is no evidence for compound formation in the liquid or vapour phase.

System Boron Trichloride–Benzoyl Chloride.—When successive amounts of boron trichloride were condensed from the vacuum-line on to a weighed quantity of benzoyl chloride, the liquid, originally colourless, changed through pale yellow to deep green. However, experiments on separate samples showed that this gradual darkening of colour had no significant effect on the m. p. The m. p. was obtained for each composition from warming curves measured in triplicate. The data, given in Table 5 and plotted in Fig. 2, show no evidence of compound formation; there is a broad plateau at −13·8° between 30 and 70 mole %, but no maximum.

TABLE 5. *Melting point of the system boron trichloride–benzoyl chloride.*

BzCl (mole %)	0·0	4·8	20·4	28·9	45·3	48·1	52·9
M. p.	−107°	−22·8°	−15·8°	−14·8°	−13·8°	−13·6°	−13·7°
BzCl (mole %)	56·2	65·5	71·7	87·1	98·3	100	
M. p.	−13·3°	−14·5°	−12·8°	−5·8°	−0·5°	−0·5°	

TABLE 6. *Vapour pressure of the system boron trichloride–benzoyl chloride at* 0°.

BzCl (mole %)	0·0	34·3	35·4	39·6	41·1	42·8	44·6	46·5	48·2	48·5	50·5	52·7
Pressure (mm.)	478	380	378	361	358	351	344	336	324	328	319	308
BzCl (mole %)	53·9	56·2	65·4	68·1	68·3	70·0	70·9	81·4	88·3	93·6	100·0	
Pressure (mm.)	295	285	254	238	240	223	207	139	92	64	0·1	

The vapour-pressure measurements on the system boron trichloride–benzoyl chloride are summarized in Table 6. Fig. 3 shows that these values correspond to a positive deviation from ideality very similar to that obtained in the system of boron trichloride with acetyl chloride.

[33] Mathews and Fehlandt, *J. Amer. Chem. Soc.*, 1931, **53**, 3212.

The electrical conductivity of the system confirmed that there was but little interaction between the components. The conductivity of pure benzoyl chloride was below the limit of detectability of the apparatus used (5×10^{-7} ohm^{-1} cm.$^{-1}$); addition of boron trichloride increased the conductivity to about 10^{-6} ohm^{-1} cm.$^{-1}$, but variation of the concentration of boron trichloride from 17·8 to 29·4 mole % left the conductivity unaffected to within 1 part in 200.

Friedel–Crafts activity was not to be expected in such a system and an experiment with benzene, parallel to the one described for the boron trichloride–acetyl chloride system, gave negative results. When undried, commercial toluene was substituted for the purified benzene, a trace of 4-methylbenzophenone (m. p. 58°; 2 : 4-dinitrophenylhydrazone, m. p. 190°) was obtained after 10 weeks under pressure.

System Gallium Trichloride–Acetyl Chloride.—The phase diagram of the system gallium trichloride–acetyl chloride was difficult to obtain because melting was always accompanied by decomposition and chemical reaction (as distinct from reversible dissociation observed in the system with boron trichloride). This necessitated the preparation of separate mixtures for each m. p. determination by the rather tedious procedure outlined in the Experimental section. If, instead, successive amounts of acetyl chloride were condensed on to a given mixture which had previously been melted, then the m. p.s always fell below the true values characteristic of an unmelted mixture of the two components. A typical example is shown by the small dotted curve in Fig. 4, which refers to five successive additions of acetyl chloride to a mixture originally containing 36 mole %. It is seen that the full curve, obtained on samples individually prepared and melted only once, gives a maximum at the 1 : 1 ratio which is 12° higher than that of the sample which had been remelted several times. Similarly, the effect of repeated fusion on the m. p. of a given mixture at constant composition may be illustrated by the results on the pure 1 : 1 addition compound itself. This melts, with evolution of gas, at 86° (see Table 7), but does not solidify completely when cooled to room temperature. On being reheated, the compound melted at 75° and after a further thermal cycle the m. p. was 60°. Under such conditions the measurement of vapour pressure has little significance, but it was established that the vapour pressure of the solid 1 : 1 compound at 20° was 6 mm. when freshly prepared (cf. acetyl chloride 222 mm.).

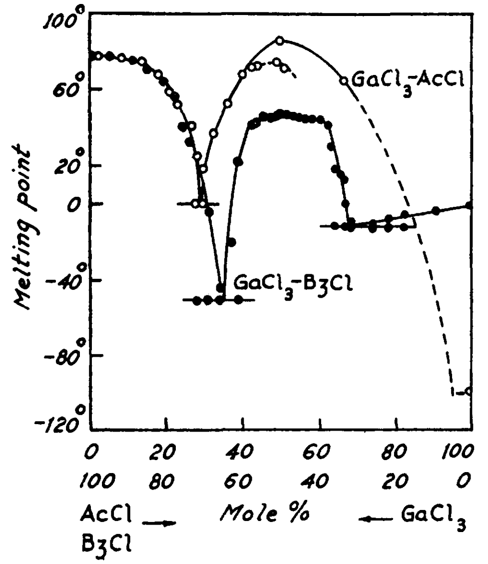

Fig. 4. *M.p.s of systems with* $GaCl_3$.

Table 7. *Melting point of the system gallium trichloride–acetyl chloride.*

AcCl (mole %)	0·0	2·1	8·3	13·9	18·0	21·2	23·2	26·5
M. p.	77·8°	77·6°	76·5°	75°	68°	59°	53°	40°
AcCl (mole %)	28·0	29·4	32·6	36·2	40·4	50·0	66·7	100·0
M. p.	25° *	19° *	37°	53°	68°	86°	65°	−98°

* And a eutectic at ~0°.

The compound gallium trichloride–acetyl chloride is an excellent acetylating agent. The complex (1·3 g.) was refluxed for 3 hr. with 6 ml. of pure, dry benzene under a phosphoric oxide guard-tube. The product, when washed with dilute alkali and water and then dried ($CaCl_2$), gave a 32% yield of acetophenone based on the acetyl chloride used (acetophenone, m. p. 19°; 2 : 4-dinitrophenylhydrazone, m. p. 235°, mixed m. p. 236°; semicarbazone, m. p. and mixed m. p. 198°).

System Gallium Trichloride–Benzoyl Chloride.—The existence of the compound gallium trichloride–benzoyl chloride was established by the m. p. data presented in Table 8 and Fig. 4.

TABLE 8. *Melting point of the system gallium trichloride–benzoyl chloride.*

BzCl (mole %)	0·0	5·4	11·7	15·3	19·2	22·2	24·4	26·0	28·0 *	31·3 *
M. p.	77·8°	77°	75°	71°	65°	57°	41°	33°	25°	−5°
BzCl (mole %)	33·9 *	36·7	38·9 *	42·6	43·8	45·8	47·4	49·0	49·7	50·4
M. p.	−44°	−20°	~22°	~41°	~42°	46°	46°	46·5°	46·5°	46·5°
BzCl (mole %)	51·8	53·3	54·7	56·4	58·4	60·3	62·0	63·1	64·3	65·8
M. p.	46·5°	46°	45·5°	45°	44·5°	44°	42°	30°	~18°	~15°
BzCl (mole %)	66·5	66·9 †	68·1 †	74·1 †	78·3 †	84·4 †	90·2	100·0		
M. p.	~13°	0°	−10°	−10°	−8°	−6°	−4°	−0·5°		

* And a eutectic at −50°. † And a eutectic at −12°.

The pure compound melts at 46·5°, presumably with some dissociation as 5 mole % excess of either component lowers the m. p. by only 1°. There are eutectics at 34 mole % of benzoyl chloride (−50°) and at 68 mole % (−12°). These results confirm and extend the observations of Ulich and Heyne[3] who found that an addition compound of m. p. 46° was precipitated by mixing solutions of the components in carbon tetrachloride. Fig. 3 also shows a slight irregularity at 64 mole % benzoyl chloride which might suggest an incongruently melting compound $GaCl_3,2BzCl$, but in this region supercooling and the viscous nature of the mixture make accurate observations difficult and the effect is probably within the experimental error. Moreover, the constancy of the eutectic temperature between 64 and 84 mole % of benzoyl chloride seems to preclude the existence of a second compound in this region, and the diagram may be taken as establishing only the equimolar addition compound unambiguously. As with the system gallium trichloride–acetyl chloride, the mixtures tended to discolour through pale straw to green, but melting was not accompanied by comparable decomposition and there was no evolution of gas during fusion.

The addition compound was shown to be ionic in the molten state by a preliminary measurement of its electrical conductivity, which gave a value of $1·08 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$ at the m. p. This is greater than the conductivity of molten gallium trichloride[29] by a factor of more than 10^6 and is also well above the conductivity of benzoyl chloride which has been shown to be certainly less than 5×10^{-7} ohm^{-1} cm.$^{-1}$.

A Friedel–Crafts reaction between 10 ml. of benzene and 6 g. of benzoyl chloride containing 10 mole % of gallium trichloride yielded 27% of benzophenone after refluxing under anhydrous conditions for 4 hr. (benzophenone, m. p. 45°, b. p. 305°; 2 : 4-dinitrophenylhydrazone, m. p. 236°, mixed m. p. 237°; semicarbazone, m. p. and mixed m. p. 165°). The yield could undoubtedly be improved in the presence of a higher concentration of gallium trichloride.[21, 22]

DISCUSSION

The principal results obtained on the addition compounds of acetyl and benzoyl chlorides with the trichlorides of Group III are summarized in Table 9. The trends are towards increased stability, increased ionic nature, and increased catalytic activity of the addition compound with increasing atomic number of the electron-deficient atom. However, these trends are unlikely to continue to indium and thallium; the trihalides of these elements form few addition compounds (Gmelin), and there are indications that indium trichloride has no catalytic activity, at least in the alkylation of benzene by ethylene, under conditions where aluminium and gallium trichlorides are effective.[34] It will also be noted from Table 9 that aluminium trichloride stands much closer to gallium trichloride in its acceptor properties than it does to boron trichloride. This is due, in part, to the small size of the boron atom and the consequent anomalous properties which arise in common

[34] Ulich, Keutmann, and Geierhaas, *Z. Elektrochem.*, 1943, **49**, 292.

with all elements in the first Short Period. The effect is enhanced by the close similarity in size of aluminium and gallium due to a "*d*-block contraction" analogous to the lanthanide (or *f*-block) contraction. As a result the radii for tetrahedral covalent bonding are boron 0·89, aluminium 1·26, and gallium 1·26 Å. The similarity between the trichlorides of aluminium and gallium is also illustrated by the fact that both are dimeric, whereas boron trichloride is monomeric.

TABLE 9. *Properties of addition compounds in the binary systems of acyl chlorides with Group* III *trichlorides.*

System	M. p. of 1 : 1 compound	Vap. press. (mm. at t°)	Elec. cond. (ohm^{-1} cm.$^{-1}$ at t°)	Dipole moment (D) (solvent)	Catalytic activity
BCl_3–AcCl	−54° (dissoc.) [a]	385 (0°)	—	—	Absent
BCl_3–BzCl	No compound	320 (0°)	$<10^{-6}$ (25°)	—	Absent
$AlCl_3$–AcCl	Decomp.[16]	Low	—	—	Strong
$AlCl_3$–BzCl	95° [19, b]	Low	—	9·04 (C_6H_6) [19, d]	Strong
$GaCl_3$–AcCl	86° (decomp.)	6 (20°)	—	—	V. strong
$GaCl_3$–BzCl	46·5° [c]	0 (20°)	$1{\cdot}08 \times 10^{-3}$ (45°)	6·85 (CCl_4)[3]	V. strong

[a] Ref. 20 gives −60° to −70°. [b] Ref. 17 gives 93°. [c] Ref. 3 gives 46°. [d] This value is affected by the Friedel–Crafts benzoylation of the solvent by the solute. The dipole moment [19] in carbon disulphide is 7·93 D.

The electron-donor properties of acetyl chloride enable it to co-ordinate to a variety of metal halides (magnesium bromide,[35] boron trichloride, boron trifluoride,[20, 36] aluminium trichloride,[16] gallium trichloride, titanium tetrachloride,[37, 38] tin tetrachloride,[20] and antimony pentachloride [20]), and the properties of some of these complexes may be compared with advantage. Thus, the phase diagram of the system which acetyl chloride forms with boron trichloride (Fig. 2) is strikingly similar to that of its system with titanium tetrachloride, which shows the same type of broad maximum at the equimolar ratio.[38] Again, the vapour pressure of the compound boron trichloride–acetyl chloride may be compared with that of the corresponding compound with boron trifluoride: [36]

$$BF_3,\mathrm{AcCl},\ \log p\ (\mathrm{mm}).\ = 15{\cdot}762 - 2877/T \text{ between } -80° \text{ and } -60°$$

$$BCl_3,\mathrm{AcCl},\ \log p\ (\mathrm{mm}.) = 7{\cdot}294 - 1294/T \text{ between } -70° \text{ and } +13°$$

The pressure above the boron trifluoride compound is always greater, and its heat of vaporization is about 2·2 times as large as that of its boron trichloride analogue. By contrast, boron trifluoride–acetyl fluoride has zero vapour pressure even at −50°; it dissociates quantitatively at room temperature without melting.[39] The simple and reversible dissociation into donor and acceptor components which is shown by these systems is not paralleled by the behaviour of the compounds which acetyl chloride forms with aluminium and gallium trichloride. Here, melting is accompanied by decomposition due to self-acetylation. For the complex with aluminium trichloride this may be represented by the equation [16] $3\mathrm{Me{\cdot}CO{\cdot}Cl} + AlCl_3 \rightleftharpoons \mathrm{Me{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}COCl},AlCl_3 + 2HCl$. A similar reaction is considered to take place, to a much smaller extent, in the system with gallium trichloride investigated in the present work.

Benzoyl chloride forms addition compounds with all the electron acceptors mentioned in the preceding paragraph except the boron trihalides.[35, 17, 40, 38, 20] In addition, compounds have been reported with aluminium tribromide [17] and ferric chloride,[41] but a detailed comparison of properties does not appear profitable at present. It will, however, be apparent from Table 9 that the complexes of benzoyl chloride with aluminium and gallium trichloride are more stable than are the corresponding complexes of acetyl chloride with these acceptors. The reverse is true for the systems with boron trichloride as the electron acceptor molecule.

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[35] Menschutkin, *Chem. Zentr.*, 1906, *II*, 1720.

[36] Brown, Schlesinger, and Burg, *J. Amer. Chem. Soc.*, 1939, **61**, 673.

[37] Bertrand, *Bull. Soc. chim. France*, 1880, **33**, 403.

[38] Cullinane, Chard, and Leyshon, *J.*, 1952, 4106.

[39] Seel, *Z. anorg. Chem.*, 1943, **250**, 331.

[40] Bertrand, *Bull. Soc. chim. France*, 1880, **34**, 631.

[41] Nencki, *Ber.*, 1899, **32**, 2414; Boeseken, *Rec. Trav. chim.*, 1903, **22**, 315.

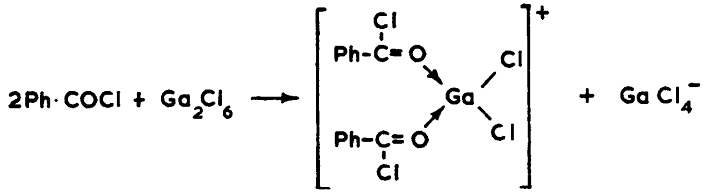
The curious phenomenon of a system which simultaneously exhibits a melting-point maximum and a positive deviation from Raoult's law has already been alluded to in presenting the results on the system boron trichloride–acetyl chloride. It appears that the 1 : 1 complex is a lattice compound which is stabilized in the solid state by favourable packing conditions but dissociates completely on melting. This demonstration of solid-compound formation between two components which show no association whatever in the liquid phase may resolve a controversy which has arisen from the apparent discrepancy that, whereas vapour pressure–composition curves for solutions of aluminium halides in alkyl halides gave no indication of compound formation at room temperature,[42] yet solid compounds each with a definite dissociation pressure were obtained [5] on similar systems at −80°. The former experiments were presumably carried out above the melting point of the labile compounds so that only positive deviations in the vapour-pressure curves were obtained.

It only remains to discuss the structure of the complexes which gallium trichloride forms with acetyl and benzoyl chloride in the solid and the liquid phases. Any elucidation of chemical constitution by means of physical properties depends for its success on the care with which the components are purified and handled. In the present work, vacuum-line techniques have been used to ensure purity of reactants and the absence of subsequent contamination by moisture. Despite these precautions, the inherent instability of molten gallium trichloride–acetyl chloride precludes the accurate measurement of significant physical properties, but the corresponding compound with benzoyl chloride is free from this drawback and reproducible results can be obtained. The high electrical conductivity of molten gallium trichloride–benzoyl chloride indicates extensive ionic dissociation and several hypothetical structures may be considered for the ions formed. The simplest of these would arise from the donation of a pair of electrons from a chloride ion to the gallium trichloride to give benzoyl tetrachlorogallate :

$$\mathrm{Ph{\cdot}CO{\cdot}Cl{\rightarrow}GaCl_3 \rightleftharpoons Ph{\cdot}CO^+ + GaCl_4^-}$$

This structure would explain the electrical conduction and catalytic action in a straightforward way which is now generally accepted.[43] It is also consistent with the fact that the corresponding compounds with boron trichloride do not occur in the liquid phase, since these would involve the unstable tetrachloroborate anion, the existence of which has yet to be established unambiguously in any compound. This instability of the tetrachloroborate ion is presumably related to the small size of the boron atom as mentioned earlier in the Discussion, but it is not a direct steric effect, for a simple model will demonstrate that it is possible to pack even four iodine atoms tetrahedrally about boron (cf. also the existence of carbon tetraiodide).

An alternative structure for the addition compounds of Group III elements has been suggested by Lebedev [44] on the basis of properties which are shown by the complexes of aluminium bromide with acyl bromides. However, the arguments used do not appear to be conclusive, nor the experiments crucial. Applied to the present system the structure would be written as follows :



This structure has no advantages over the previous one and makes the interpretation of catalysis more complicated. Two further structures involving either chlorine or oxygen as the ligand are conceivable, $\mathrm{[Ph{\cdot}CO{\cdot}Cl{\rightarrow}GaCl_2]^+Cl^-}$ and $\mathrm{[Ph{\cdot}CCl{=}O{\rightarrow}GaCl_2]^+Cl^-}$.

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[42] Van Dyke, *J. Amer. Chem. Soc.*, 1950, **72**, 3619.

[43] Burton and Praill, *Quart. Rev.*, 1952, **6**, 302.

[44] Lebedev, *J. Gen. Chem.* (*U.S.S.R.*) (U.S. Transl.), 1951, **21**, 1975.

However, these suffer the defect that the gallium atom is still electron-deficient and therefore unlikely to exist in the presence of a dissociating chloride ion unless a more powerful electron-donor solvent were present to stabilize the gallium by co-ordination.[45] In the absence of a solvent, such systems would tend to form quadricovalent molecules, which does not accord with the high conductivity of the molten complex. The principal structural feature which distinguishes the first mode of ionization as benzoyl tetrachlorogallate from the other hypothetical modes is that only for this first scheme does all the gallium appear in the anion. Tracer experiments with ^{72}Ga have been designed to follow the migration of the ions during electrolysis of the molten complex and the results will be published later.

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[45] Van Dyke, *J. Amer. Chem. Soc.*, 1950, **72**, 2823.