CCCXL.—*Thionyl Bromide and Besson's Supposed Thionyl Chlorobromide.*

By Horace Alfred Mayes and James Riddick Partington.

In 1891, Michaelis (*Ber.*, **24**, 745) prepared thionyl bromide, apparently for the first time, by the action of bromine on thionylaniline. He described it as a brown liquid, b. p. 136° (decomp.), but was unable to obtain it pure because of the decomposition.

Hartog and Sims (*Chem. News*, 1893, **67**, 82) prepared a small quantity of thionyl bromide by the action of sodium bromide on thionyl chloride. They described it as a deep crimson liquid, $d^{18°}$ 2·68, decomposing at 150°, and so hygroscopic that it had to be kept in sealed tubes. They suggested that its colour was due to the presence of sulphur bromide.

Besson (*Compt. rend.*, 1896, **122**, 320) stated that dry hydrogen bromide has no action on cold thionyl chloride but reacts with it at its boiling point to effect substitution of bromine. He separated the products by fractionation under reduced pressure and obtained thionyl bromide and thionyl chlorobromide, $SOClBr$, which he described as a clear yellow liquid, d^{0° 2·31, distilling under ordinary pressure at about 115°. At temperatures just above its boiling point it decomposed into thionyl chloride, sulphur bromide, bromine, and sulphur dioxide. Thionyl bromide he described as a yellowish-orange liquid, b. p. 68°/4 cm., d^{0° 2·61, giving Br, 76·35, 76·19% (Calc.: 76·95%). It always contained a little sulphur chloride and was readily decomposed by heat. Together with these products a certain amount of sulphur bromide was always formed. He attempted to prepare thionyl bromide by the action of sulphur dioxide on phosphorus pentabromide, but found that decomposition occurred. Later (*Compt. rend.*, 1896, **123**, 884) Besson prepared these compounds by the action of aluminium bromide on thionyl chloride, cooled in a freezing mixture. The yield was much lower, since considerable heat was evolved and consequently decomposition occurred. He gave the freezing point of thionyl bromide as −50°.

Preparation of Thionyl Bromide.

Several unsuccessful attempts have previously been made to prepare thionyl bromide by the action of sulphur dioxide on phosphorus bromide, and, with the exception of this, all the methods of preparation were examined.

1. *The Action of Sulphur Bromide on Sulphur Trioxide.*—Sulphur trioxide was added to cooled sulphur bromide in quantities calculated from the equation $S_2Br_2 + SO_3 = SOBr_2 + SO_2 + S$, which is analogous to that for the preparation of thionyl chloride. Violent effervescence took place immediately, bromine and sulphur dioxide being given off. The considerable residue, on distillation, gave a small quantity of bromide, the major portion being unchanged sulphur bromide. This method is therefore useless.

2. *The Interaction of Bromine and Thionylaniline.*—Bromine was dropped very slowly, with stirring, into a solution of thionylaniline in light petroleum. A precipitate of tribromoaniline hydrobromide was formed, together with a dark red solution. On distillation, this gave a small quantity of thionyl bromide, $C_6H_5{\cdot}N{:}SO + 3Br_2 = C_6H_2Br_3{\cdot}NH_3Br + SOBr_2$, but the yield was poor and the liquid obtained was difficult to purify.

3. *The Interaction of Aluminium Bromide and Thionyl Chloride.*—Anhydrous aluminium bromide was added to thionyl chloride cooled in ice: the bromide dissolved with considerable evolution of heat, and decomposition occurred. The product was distilled in a vacuum on a water-bath, and the distillate fractionated. Only a small quantity of thionyl bromide was obtained, since much

bromine and sulphur bromide were formed. This confirms Besson's observation that the yield of bromide by this method is poor.

4. *The Action of Potassium Bromide on Thionyl Chloride.*—Dried, powdered potassium bromide was refluxed with 50 c.c. of thionyl chloride on a water-bath for 5 hours. The liquid was distilled in a vacuum on a water-bath, and then fractionated under reduced pressure. A small quantity of liquid, b. p. 50—60°/40 mm., was obtained, the greater part being unchanged thionyl chloride. The action is slow, and the large bulk of solid renders the first distillation in a vacuum very awkward.

5. *The Action of Hydrogen Bromide on Thionyl Chloride.*—Hydrogen bromide, dried by calcium chloride, was passed through thionyl chloride contained in a two-necked flask fitted with a reflux condenser. Both the lead-in tube and the condenser were ground into the necks, since thionyl chloride attacks cork and rubber. Slow reaction took place even in the cold, the liquid becoming red after about ¾ hour. It was necessary to pass the gas for about 10 hours to cause any considerable replacement of chlorine by bromine.

Hydrogen bromide was passed through 50 c.c. of cold thionyl chloride, and also 50 c.c. of boiling thionyl chloride, in each case for nearly 4 hours. On distillation, it was found that about the same amount of thionyl chloride had been changed in each case. This is in direct opposition to Besson's statement that hydrogen bromide has no effect on cold thionyl chloride. All further preparations of thionyl bromide were carried out in the cold.

During this reaction, whether carried out with boiling or cold thionyl chloride, some bromine is always liberated, and hence the fractions obtained on distillation are contaminated with it. It is rather difficult to remove the last traces, but this may be accomplished by repeated distillation.

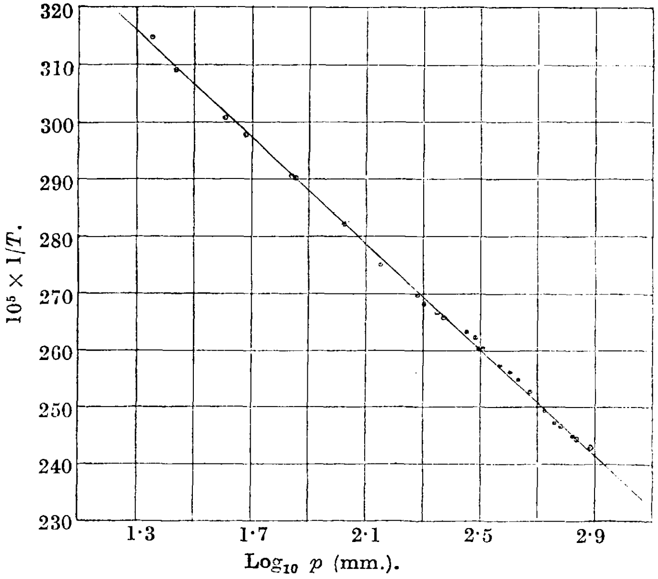
Although Besson stated that the excess of thionyl chloride could be removed by distillation on a water-bath, it was found that a considerable amount of the bromide was removed at the same time. The product was therefore always submitted to a complete fractionation under reduced pressure in a special distilling apparatus fitted with ground glass joints. It was necessary to protect the manometer by soda-lime tubes fitted in the side-arm leading to it, otherwise the mercury rapidly became corroded. The fractionation was usually carried out at about 200 mm. pressure, since the whole of the liquid then distilled between 50° and 100°; at lower pressures, a considerable proportion of the more volatile fraction was lost. At this pressure the liquid was separated into fractions boiling at 10° intervals between 40° and 100°. After prolonged fractionation, most of the liquid collected in the first and the last fraction. The latter was further separated to give pure thionyl bromide and all the residues were united and used for further bromination.

Properties of Thionyl Bromide.

As prepared by method 5, thionyl bromide is a yellowish-orange liquid (Found: Br, 77·11, 76·79, 76·68. Calc.: Br, 76·88%). The analyses were carried out by dissolving a weighed quantity of the bromide in water and precipitation with silver nitrate.

Boiling Points.—The boiling points were determined over the pressure range 22 mm. to 773 mm. The liquid boiled with very little decomposition at 250 mm., but with a considerable amount at 773 mm. This decomposition renders the higher boiling points somewhat inaccurate. These boiling points lie on a smooth curve, and if the values of log p are plotted against the reciprocals of the absolute temperatures, the points lie almost entirely on a straight line (Fig. 1).

FIG. 1.



B. p.	p (mm.).	B. p.	p (mm.).	B. p.	p (mm.).	B. p.	p (mm.).
45°	22	90°	138·5	111°	311	131°	570
50·5	27·5	98	190	111	320	132	601
59	40	99	200	115·5	365	135	660
62·5	47	101·5	219	117	395	136	680
71	67·5	103	233	120	421	138	773
71·5	70	107	274	123·5	471		
81·5	104	109	305	127·5	520		

The b. p. 59°/40 mm. does not agree with Besson's value of 68°/4 cm.; the above value has been checked many times during the distillation of different samples of thionyl bromide and is undoubtedly correct.

Density.—This was determined by using a pyknometer with ground glass caps. Two experiments gave $d_{4^\circ}^{15^\circ}$ 2·698, 2·697. These values do not agree with Besson's value of 2·61, but agree fairly well with that of Hartog and Sims, *viz.*, 2·68, especially as their liquid was not quite pure.

Freezing Point.—The freezing point was determined as − 52° by immersing the liquid in solid carbon dioxide, the temperature being registered by a pentane thermometer.

Molecular Weight.—The molecular weight was determined by the cryoscopic method in benzene. Three determinations with different samples of benzene gave M, 234, 246, and 237 (Calc.: 208). The deviation from the theoretical value is too great to be attributed to experimental error, and also it is consistent. Hence thionyl bromide is associated to the extent of 25% in benzene on the assumption that double molecules are formed.

The Trouton coefficient was calculated from the data already obtained; λ, the molecular heat of vaporisation, was calculated from the equation $\lambda = 4{\cdot}576(\log p_2/p_1)\{T_1T_2/(T_2 - T_1)\}$, where T_1 and T_2 are the absolute temperatures corresponding with the vapour pressures p_1 and p_2. From the straight line obtained by plotting $\log p$ against $1/T$, the following values were taken: $T_1 = 404$, $\log p_1 = 2{\cdot}7624$; $T_2 = 422$, $\log p_2 = 3{\cdot}0024$; hence $\lambda = 10{,}400$ cals. From the curve, the absolute boiling point at 760 mm. is 412·8° (139·7° C.). Hence the Trouton coefficient λ/T_0 has the rather high value of 25·2, which points to association of the liquid.

Surface Tension.—To gain further insight into the molecular complexity of thionyl bromide, surface tension measurements were made at 17° and 25°.

From the mean of two experiments (2·674, 2·669) thionyl bromide was found to have $d_{4^\circ}^{25^\circ}$ 2·672. From this value, and the density at 15°, that at 17° was calculated as 2·692. The surface tension at 17° was found to be 43·71 dynes/cm. by a comparison of the rises of benzene and thionyl bromide in a capillary tube, the value for benzene at 17° being taken as 28·43 dynes/cm. The surface tension at 25° was similarly found to be 43·08, that of benzene being taken as 27·39. The Ramsay and Shields coefficient was therefore − 0·94.

Though these figures cannot be regarded as very accurate, they serve to show that there is some association in liquid thionyl bromide. The ratio of the absolute temperatures corresponding with pressures of 760 mm. and 200 mm. is 412·8/372 = 1·108, whereas according to Ramsay and Young normal liquids have the value 1·114; association is therefore again indicated.

Chemical Properties.—Thionyl bromide is readily hydrolysed by water with the formation of hydrobromic acid and sulphur dioxide, but, contrary to the statement of Hartog and Sims, it can be kept quite well in a stoppered bottle. About 200 g. of thionyl bromide have been kept in this way for many weeks without undergoing any appreciable hydrolysis.

Decomposition, with formation of sulphur dioxide, bromine, and sulphur bromide, occurs at the ordinary temperature to a very slight extent. It is quite noticeable after a few days, and thionyl bromide which has been kept for some time is always red in colour owing to the presence of free bromine. A tube containing thionyl bromide which had been sealed for 6 months did not appear to have developed any great pressure, although the liquid was dark red. From this it would seem that the decomposition, although quite definite, takes place very slowly. This decomposition occurs readily at temperatures much above 100° so that, at the boiling point under normal pressure, quite one-third of the substance is decomposed by distillation, according to the equation $4SOBr_2 = 2SO_2 + S_2Br_2 + 3Br_2$. Thionyl bromide is a very reactive liquid, attacking both cork and rubber readily. It is soluble in the more inert organic solvents such as benzene, carbon disulphide, carbon tetrachloride, and chloroform, but with acetone it reacts violently to give a vapour having a very irritating effect on the eyes. With organic acids, it forms the acid bromides just as thionyl chloride gives the chlorides. A small quantity was warmed on a water-bath with heptoic acid; considerable effervescence took place, and a product of b. p. *ca.* 186°/760 mm. was isolated. It gave hydrobromic acid and heptoic acid on heating with water, and contained about 35% Br [$CH_3\cdot(CH_2)_5\cdot COBr$ requires Br, 41·3%]. It was not obtained pure owing to the limited quantity of heptoic acid available.

Thionyl Chlorobromide.

According to Besson this compound is formed, together with thionyl bromide, when hydrogen bromide reacts with thionyl chloride. Attempts to prepare it in this way were unsuccessful.

Dry hydrogen bromide was passed through thionyl chloride, and the product distilled under reduced pressure. After the unchanged thionyl chloride had passed over, the temperature rose steadily with no interruption, until it attained the boiling point of thionyl bromide. During many preparations, there was never any indication of the formation of a compound intermediate between thionyl chloride and thionyl bromide. On continued fractionation, the middle fractions always separated gradually to give the chloride and the bromide.

Thionyl chloride was treated with dry hydrogen bromide for a few hours, and the product (75 c.c.) fractionated at 200 mm. pressure; there were finally obtained 26 c.c. of fairly pure thionyl bromide and 35 c.c. of fairly pure chloride (contaminated with some bromine), together with very small quantities of each of the four intermediate fractions, amounting altogether to 10 c.c. These fractions were so small that it was impossible to distil them further. Thus there were recovered 71 c.c. out of 75 c.c. of the brominated product.

From Besson's statements it would be expected that, as the bromide and chloride were present in such proportions, there would have been a considerable quantity of thionyl chlorobromide, but it is obvious from the above experiment that only a very small amount, if any, of chlorobromide was present.

The product from the action of potassium bromide on thionyl chloride was also distilled carefully, and gave results precisely similar to those above.

The aluminium bromide method was unsuitable for this investigation owing to the poor yield and impurity of the product obtained.

Although the above facts offer considerable evidence for the non-existence of thionyl chlorobromide, it seems that the question cannot be settled by any purely chemical method, since the reactions of an equimolecular mixture of thionyl chloride and bromide must necessarily be very similar to those of thionyl chlorobromide. Accordingly, various physical measurements were made, all of which showed that the so-called thionyl chlorobromide is exactly the same as a mixture of the chloride and bromide.

Thionyl chloride was treated with hydrogen bromide, and the product distilled under reduced pressure. From an examination of the boiling point of thionyl " chlorobromide " and those of the bromide and chloride under ordinary pressure, it would appear that the chlorobromide should boil at about 70—80°/200 mm., so this fraction was collected separately. The liquid was analysed for total halogen by the method used for thionyl bromide, and found to contain 30·46% $SOCl_2$ and 69·54% $SOBr_2$, whereas thionyl chlorobromide would have given 36·5% and 63·5%, respectively, corresponding to an equimolecular mixture of the chloride and bromide.

No substance other than thionyl chloride, bromide, or chlorobromide could have been present, since pure hydrogen bromide and pure thionyl chloride were used, and the only by-products, bromine and sulphur bromide, were removed in the distillation, bromine in the first fractions and sulphur bromide in the residue.

A mixture of thionyl bromide and chloride corresponding with the above was prepared containing exactly 30·46% of thionyl chloride. The only possible difference between this mixture and the brominated product would be that the latter might contain some chlorobromide, if it existed, whereas the former might contain only the bromide and the chloride.

The physical properties of these two mixtures were then determined. (The ready hydrolysis of the liquids, combined with their chemical activity, made all work with them difficult, and prevented an accurate determination of the refractive index, for instance.)

Comparison of Physical Properties of Mixtures at 17°.

	Density.	Surface tension.	Viscosity.
1. Brominated product	2·290	40·35	0·01652
2. Mixture of $SOCl_2$ and $SOBr_2$	2·270	40·0	0·01622

These figures agree within the limits of experimental error, which is affected, in addition, by that due to analysis.

These results show that the liquid, which, according to Besson, should contain a large proportion of thionyl chlorobromide, has the same physical properties (density, surface tension, and viscosity) as those of a mixture of thionyl chloride and thionyl bromide containing the same amount of total halogen. Also, the mixture prepared from thionyl chloride and bromide boiled at about the same temperature as the brominated product, and was just as difficult to separate into its constituents by distillation.

No attempt was made to ascertain the variation of the vapour pressure of mixtures of thionyl chloride and bromide with composition, owing to the hygroscopic and chemically active nature of the liquids, but some idea of the nature of this curve was obtained from the manner in which mixtures of the two compounds distilled: the boiling point rose perfectly evenly from that of the chloride to that of the bromide.

Finally, the freezing-point curve of mixtures of thionyl chloride and bromide was investigated. Mixtures of the pure liquids were prepared by weighing, and the freezing point of each mixture was determined with a pentane thermometer. The first few points on the curve were obtained by cooling in solid carbon dioxide, but it was then found necessary to use much lower temperatures and a special cooling bath was applied.

The apparatus consisted of a Dewar vessel containing alcohol and stirred by hand. Immersed in this were two test-tubes, one containing the liquid mixture under consideration, and the other a small plug of cotton wool. A thermos flask, used as a liquid-air reservoir, was fitted with a doubly-bored cork through which passed two glass tubes. One was a short, right-angled bend connected with a bicycle pump, and the other a long tube dipping into the liquid air and bent so as to pass into the second test-tube in the Dewar vessel. This end was drawn out so that, when the bicycle pump was worked slowly, a fine spray of liquid air was thrown on to the cotton wool. This cooled the alcohol by evaporation, and thus the temperature of the bath was lowered at will. When the temperature fell much below — 100°, the alcohol became so viscous that stirring was difficult, consequently some of the lowest freezing points were not very accurate.

During these experiments the freezing point of thionyl chloride was observed as — 104·5° ; it seems that this has never been recorded before. The following table shows the results obtained.

$SOBr_2$ (%).	F. p.	$SOBr_2$ (%).	F. p.	$SOBr_2$ (%).	F. p.	$SOBr_2$ (%).	F. p.
100	−52°	74·62	−76°	44·82	−96·5°	14·97	−107·5°
94·15	58·6	68·86	79·7	40·04	99	9·06	109
90·77	61·5	67·65	80·9	28·9	104·5	5·29	107 5
83·36	68·9	59·69	85·5	20·8	108	0	104·5
79·8	71·5	50·30	92·5	16·1	108		

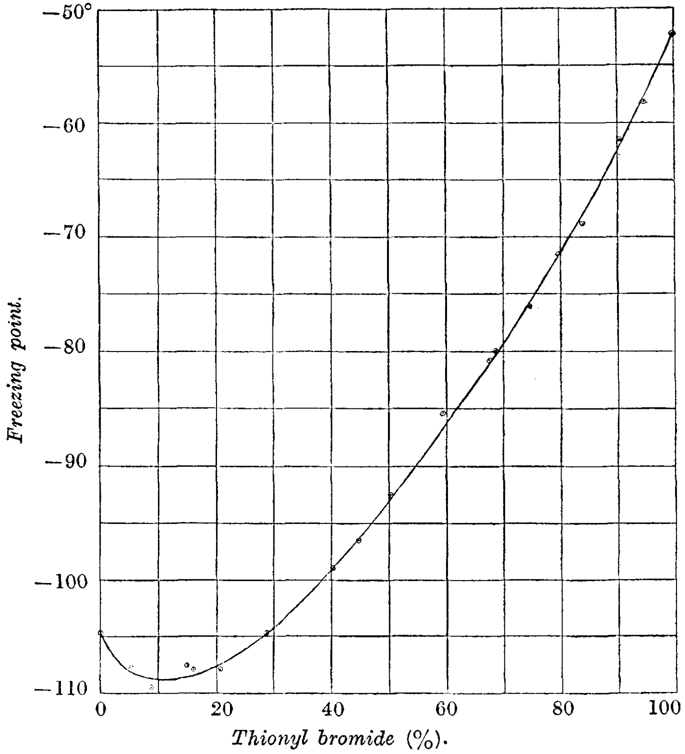
All these freezing points were repeated, three determinations of each being made. The necessary correction for emergent stem has also been made.

These freezing points plotted against composition (Fig. 2) agree with a simple mixed-crystal curve showing a minimum but no eutectic. It would be possible to draw a curve containing a maximum and two eutectics in the region of 10 to 20% of thionyl bromide, but this would indicate the existence of a very unlikely compound. Moreover, the general shape of the curve is not what would be expected if a eutectic were present, since it is slightly concave, whereas eutectic curves are generally convex. Work in this particular region was found very difficult, and it is considered that the slight irregularities are due to experimental errors. The main object of the experiments was fulfilled, since it is clear that no indication of the existence of the compound SOClBr is evident. The so-called thionyl chlorobromide corresponds with a composition of 63·5% bromide. The freezing-point curve at this point is quite smooth and shows no maximum or break such as would be expected if the chlorobromide were present.

It might be objected that the mixture obtained on bromination of thionyl chloride is not the same as a mere mixture of chloride and bromide. The physical measurements given above suggest, however, that the two types of mixtures are identical, but to remove all doubt the following experiments were carried out.

Hydrogen bromide was passed through boiling thionyl chloride for some hours, and the product distilled under reduced pressure. The first fractions were rejected, as they contained bromine, but two fractions boiling in the region of 70°/200 mm. were collected. These had been prepared exactly according to the directions of Besson, and should be nearly pure thionyl chlorobromide [Found : (i) 64·09, (ii) 62·21% of thionyl bromide]. The freezing points of these two liquids, taken as before, were : (i) $-82·75°$, (ii) $-84·5°$. These

FIG. 2.



two points lie almost exactly on the curve, and, further, the figures for the analyses of the fractions show that they should be very nearly pure thionyl chlorobromide.

Thus the liquids obtained on bromination of thionyl chloride are absolutely identical with the corresponding mixtures of thionyl chloride and thionyl bromide. The freezing-point curve shows that there is no chlorobromide in mixtures of chloride and bromide, and hence we may conclude that thionyl chlorobromide is not present in the product formed by the bromination of thionyl chloride.

It only remains to explain the apparent preparation of thionyl chlorobromide by Besson. He describes it as a clear yellow liquid, d^{0° 2·31, which " distille, sous la pression normale, *aux environs* de 115° C."

The middle fractions obtained during the distillation of brominated thionyl chloride are, after removal of bromine, clear yellow liquids. One fraction, containing 69·54% of thionyl bromide as compared with 63·53% for the " chlorobromide," has d^{17° 2·29, comparing fairly well with Besson's value of 2·31 at 0°. This fraction boiled at about 110—120° at normal pressure, with some decomposition, thus corresponding with Besson's boiling point.

Besson states that thionyl chlorobromide decomposes, on heating much above 100°, into thionyl chloride, sulphur bromide, bromine, and sulphur dioxide : $8SOClBr = 4SOCl_2 + 2SO_2 + S_2Br_2 + 3Br_2$. This would be expected to happen with a mixture of thionyl chloride and bromide, since the latter decomposes above 100° : $4SOBr_2 = 2SO_2 + S_2Br_2 + 3Br_2$, whilst thionyl chloride is stable up to 400—500°.

Besson gives no figures for the analysis of thionyl chlorobromide, and it is noteworthy that Hartog and Sims, who prepared thionyl bromide by the action of sodium bromide on thionyl chloride, apparently found no indication of an intermediate compound.

There seems no doubt that the liquid described by Besson as thionyl chlorobromide is merely a mixture of thionyl chloride and thionyl bromide, and that thionyl chlorobromide has never been prepared. It may be inferred, from the absence of compounds of similar type, that it probably does not exist.

Summary.

1. The properties of thionyl bromide and the freezing point of thionyl chloride have been determined.

2. The evidence showing that thionyl chlorobromide does not exist may be summarised as follows :

(*a*) It is impossible to separate any constant-boiling liquid, other than thionyl chloride and thionyl bromide, from the product of bromination of thionyl chloride with hydrogen bromide.

(*b*) The freezing-point curve shows that no intermediate compound is present in mixtures of thionyl chloride and bromide.

(*c*) Physical properties show that the product of bromination of thionyl chloride is exactly the same as mere mixtures of thionyl chloride and bromide.

(*d*) From (*b*) and (*c*) it is obvious that thionyl chlorobromide is not formed on bromination of the chloride.

In conclusion, the authors wish to acknowledge their indebtedness to Mr. W. H. Patterson for the design of the very convenient type of cooling bath used.

East London College,
University of London.

[*Received, July* 30*th*, 1926.]