The Chemistry of Boron. Part IV.* The Boron Chlorobromides.

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The boron chlorobromides are shown to exist, in spite of earlier failure to prepare them. They can be prepared by the partial chlorination of boron tribromide with antimony trichloride, but disproportionate rapidly at temperatures as low as −50°, which explains why it has not been possible to isolate them pure. Boron trichloride and tribromide are formed from the chlorobromides until equilibrium concentrations are set up, and the mixed halides can also be prepared by keeping mixtures of the simple halides at room temperature. Equilibrium is virtually established within a few hours.

The boron chlorobromides have been identified by their Raman frequencies. The observed relative intensities for the simple and mixed halides present in an equilibrium mixture are compatible with random distribution of the halogen atoms.

THE state of knowledge concerning the mixed halides of the rather similar elements boron and silicon presents a striking contrast. Whereas mixed halides of silicon have been known for over a century, and almost all the members of this group of compounds have in recent years been prepared in quantity and adequately characterised by Anderson and his collaborators, very little is known about the corresponding compounds of boron : no mixed halide of boron has been isolated in bulk, and only the bromoiodides BBr_2I and $BBrI_2$ have been prepared in small amounts. Besson (*Compt. rend.*, 1891, **112**, 1001) made these by the action of hydrogen iodide on boron tribromide vapour in a heated tube, but he failed to prepare them from elementary boron and iodine monobromide (*ibid.*, p. 1314).

In theory, at least, the boron chlorobromides should be preparable in ways analogous to some of the numerous methods employed to produce silicon chlorobromides (Friedel and Ladenburg, *Annalen*, 1867, **143**, 118; **145**, 179; Besson, *Compt. rend.*, 1891, **112**, 788; Besson and Fournier, *ibid.*, 1911, **152**, 603; Schumb and Anderson, *J. Amer. Chem. Soc.*, 1937, **59**, 651) : of these, the most important is the interaction of chlorides with silicon tetrabromide. In the present study, therefore, the first attempts to prepare the boron chlorobromides were by the partial chlorination of boron tribromide with various chlorides. Replacement of bromine by chlorine, though without the recognised formation of either boron chlorobromide, has been shown to occur with arsenic trichloride and antimony tri- and penta-chlorides (Tarible, *Compt. rend.*, 1901, **132**, 204) as well as with carbon tetrachloride (Gustavson, *Ann. Chim. Phys.*, 1874, **2**, 200), but the investigators concerned were not looking for the intermediate compounds. However, a special search for the boron chlorobromides has been unsuccessfully made by Forbes and Anderson (*J. Amer. Chem. Soc.*, 1940, **62**, 761), who examined in turn the action of sulphur monochloride, stannic chloride, titanium tetrachloride, hydrogen chloride, and silicon dichlorodibromide on boron tribromide, as well as that of a chlorine–bromine mixture on elementary boron. No other attempt to prepare the boron chlorobromides appears to have been reported.

In the present investigation, the possibility of partially chlorinating boiling boron

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tribromide with the chlorides of silver, mercuric mercury, and tervalent antimony has been examined. Silver chloride produces a negligible reaction, but a slow reaction occurs with mercuric chloride and a moderately fast one with antimony trichloride. The last reaction is particularly convenient and occurs with gentle warming in a water-bath. By using a quantity of antimony chloride insufficient to replace all the bromine, a product containing both chlorine and bromine and boiling at a temperature intermediate between the boiling points of boron trichloride and tribromide may be obtained. One has the choice of refluxing for about two hours followed by distillation of the product, or, by adjusting the temperature of the bath, of distilling over the product boiling below a chosen temperature (say 50°) through a fractionating column as it is formed, thus preventing it from reacting with further antimony trichloride.

In the absence of air the partially chlorinated product can be kept indefinitely. It is also stable when distilled rapidly. The product does not possess the physical properties of a mixture of boron trichloride and tribromide, and only small quantities of the simple halides are obtained on a single fractionation. Rather, its physical behaviour is essentially that of a mixture of the two boron chlorobromides. However, the behaviour on repeated fractional distillation indicates progressive disproportionation, with the fairly rapid establishment of a new halogen-distribution equilibrium in each fraction. Attempts to isolate the respective boron chlorobromides pure therefore fail, and the ultimate products of repeated fractionation are the trichloride and tribromide.

Attempts have therefore been made to separate the boron chlorobromides at low temperatures by fractional condensation in vacuum apparatus, but it was found that disproportionation occurred more or less as rapidly below $-50°$ as at room temperature. Clear evidence was obtained for the existence of the mixed halides as well as for progressive disproportionation. Thus, considerable quantities of material which condensed at $-84°$ in one fractional condensation failed to condense at the same temperature in a successive fractionation, while large amounts of material which originally distilled from a bath at $-57°$ became involatile at that temperature during the next fractionation. (Under the high-vacuum conditions employed, boron trichloride does not condense at $-84°$ and boron tribromide does not distil at $-57°$). Because of high mutual solubilities of all the species present, no large change in vapour pressure is observed when disproportionation proceeds in a closed system.

In view of the observed disproportionation, it should in theory be possible, if an equilibrium of the type $BCl_3 + BBr_3 \rightleftharpoons BCl_2Br + BClBr_2$ occurs, to prepare the boron chlorobromides by keeping mixtures of boron trichloride and tribromide at room temperature. This has been verified to be the case, and mixtures which had been standing only a comparatively short time could not be *rapidly* separated again by fractionation through a column that effected an immediate and almost complete separation of mixtures of other liquids of similar boiling points. From the degree of reversed disproportionation which was observed to occur in one hour, it is apparent that the rate of reaction is such as to establish effectual equilibrium within a very few hours. A similar redistribution reaction occurs between the chlorides and bromides of carbon, silicon, germanium, and tin respectively (Forbes and Anderson, *J. Amer. Chem. Soc.*, 1944, **66**, 931), although with carbon and silicon high temperatures are required—Anderson (*ibid.*, 1945, **67**, 859) found 70 hours at 140° necessary for a mixture of silicon tetrachloride and tetrabromde. It thus appears that boron resembles germanium and tin in this respect rather than silicon, since the equilibrium involving the boron chlorobromides cannot be " frozen " at room temperature, as is the case with the silicon chlorobromides. The distillation curve observed for the trichloride–tribromide mixture of boron is identical in principle with the curve obtained by Forbes and Anderson (*loc. cit.*, 1944) for the mixture of the stannic compounds. Their failure to find evidence for the existence of the boron chlorobromides (*loc. cit.*, 1940) must therefore be attributed to the adoption of too stringent means of separating the products of their reactions.

Two physical methods were employed to attempt to verify the formation of the chlorobromides. The first was to study the change of dielectric constant of boron trichloride–boron tribromide liquid mixtures with time. In theory, the molecules of the mixed halides

should possess small dipole moments, while the simple halides do not, so that the formation of the mixed halides should increase the dielectric constant. Although an increase was detected in preliminary experiments at 0° in a cell of the type described by Le Fèvre ("Dipole Moments," Methuen, London, 2nd Edn., 1948, p. 35), the effect observed within 24 hr. of mixing the boron trichloride and tribromide was so small, being only about five times the minimum change observable with the apparatus available, that the experiments were abandoned as inconclusive.

The second method involved the study of the Raman frequencies of partially chlorinated boron bromide. Here the effect was unmistakable. A number of new frequencies were observed which belonged neither to the trichloride nor to the tribromide, and for a mixture containing roughly equal quantities of chlorine and bromine, the strongest at 347 and 408 cm.$^{-1}$ were more pronounced than the frequencies due to the trichloride and tribromide, which were also present. This confirms that all species are simultaneously present in equilibrium, and further indicates that the equilibrium (p. 4458) lies somewhat over to the right. The frequency 347 cm.$^{-1}$ is relatively stronger in bromine-rich, and that at 408 cm.$^{-1}$ in chlorine-rich, mixtures. The position of these frequencies relative to the symmetric or "breathing" frequencies of the simple halides suggests that they can be identified with the corresponding frequencies for the species $BClBr_2$ and BCl_2Br respectively :

Species	BCl_3	BCl_2Br	$BClBr_2$	BBr_3
"Breathing" frequency, cm.$^{-1}$ ...	471	408	347	279
Δ, cm.$^{-1}$		63	61	68

For a mixture in which half the halogen was chlorine and half bromine, random distribution would involve all four species in the ratio 1 : 3 : 3 : 1. The observed intensities for such a mixture imply that the distribution of halogen is indeed random, or at least nearly so. Precisely the same Raman frequencies are observed whether measurements are taken on partially chlorinated boron tribromide or on boron trichloride–tribromide mixtures. Because of the long exposures required (several hours), study of the kinetics of the redistribution reaction is not possible by this method.

The establishment of the existence of the boron chlorobromides in this way after earlier failure finds a parallel in the similar case of the chlorobromides of tin (Trumpy, *Z. Physik*, 1930, **66**, 790; Delwaulle and Francois, *Compt. rend.*, 1944, **219**, 64), and one that emphasises the danger of drawing hasty conclusions. The corresponding compounds of silicon (*idem, ibid.*, p. 335) and, very recently, those of germanium (Delwaulle, *ibid.*, 1954, **238**, 84) have also been identified by Raman spectroscopy.

The low activation energy required for the redistribution reaction of boron trichloride–tribromide mixtures in order that it may proceed at and far below room temperature, suggests an intermediate step, which may be the effect of a slight tendency to dimerise : $BCl_3 + BBr_3 \rightleftharpoons B_2Cl_3Br_3 \rightleftharpoons BCl_2Br + BClBr_2$, but there is a possibility that a slight degree of ionisation of the type $BBr_3 + BCl_3 \rightleftharpoons BBr_2^{\cdot} + BCl_3Br' \rightleftharpoons BClBr_2 + BCl_2Br$ might be responsible. Either mode of rearrangement would exhibit an unusual temperature-dependence.

EXPERIMENTAL

Materials.—Boron trifluoride was at first prepared by methods described by Booth ("Inorganic Syntheses," McGraw-Hill, New York, Vol. I, 1939, p. 21), but was later available in cylinders under pressure. The boron trichloride was from a commercial source containing much dissolved hydrogen chloride which was readily removed by a number of fractional condensations *in vacuo*. For the preparation of boron tribromide, bromination of the trifluoride according to Gamble, Gilmont, and Stiff's method (*J. Amer. Chem. Soc.*, 1940, **62**, 1257) was found to be the most convenient, except that it proved to be simpler not to distil the aluminium bromide into the reaction flask but to prepare it *in situ* from the elements and remove excess of bromine by redistilling the resultant boron tribromide over mercury before refractionation.

Attempts to effect Partial Chlorination of Boron Tribromide.—In general, pure boron tribromide was refluxed for several hours in the absence of moist air with a quantity of the anhydrous metal chloride sufficient to replace two-thirds of the bromine present, complete

reaction being assumed. The product was then distilled off through an efficient fractionating column. A guard trap cooled in liquid oxygen was employed, but in no case did a significant quantity of boron trichloride (b. p. 12·5°) condense in it.

With silver chloride. Boron tribromide (24·9 g.) was refluxed with silver chloride (28·6 g.) for 2½ hr. No appreciable reaction occurred and most of the boron tribromide was subsequently recovered, although it began to distil 4° below its true b. p. of 90·5°.

With mercuric chloride. Boron tribromide (20·2 g.) was refluxed with coarsely crystalline mercuric chloride (22 g.). After 30 min. the liquid became cloudy, suggesting a slow reaction. After 12 hr. the product was fractionated, yielding 0·75 ml. of a more volatile head fraction which commenced to distil at 40°. Repetition using a larger proportion of mercuric chloride, finely crushed, did not materially improve the yield of the more volatile fraction, suggesting that the rate of reaction may be limited by the low solubility of the salt in boron tribromide.

The volatile head fraction was transferred to a high-vacuum apparatus for examination. After the presence of chlorine as well as bromine had been proved qualitatively, weighed samples were analysed by determining (*a*) the vapour density and (*b*) the number of moles present by hydrolysis and subsequent titration of the total hydrogen halide produced against standardised sodium hydroxide :

Weight of substance taken (g.)	0·2546	0·2142
No. of moles present (by titration)	0·001734	0·001513
Hence moles % of Br replaced by Cl	77·8	81·7
Mean mol. wt. (calc.)	146·8	141·6
Mean mol. wt. (from v.d.)	143·8	139·6

With antimony trichloride. Boron tribromide (25 g.) was refluxed for 11 hr. with antimony trichloride (15 g.). Reaction was much more pronounced than with mercuric chloride. On subsequent distillation all the liquid distilled over the temperature range 32—50°, leaving 23 g. of solid containing all the elements participating in the reaction. The distillate contained boron, chlorine, and bromine, but no antimony. Later experiments indicated a refluxing time of 2—3 hr. to be sufficient.

Behaviour of Partially Chlorinated Product on Fractional Distillation.—The distillate from the previous experiment could be redistilled without noticeable change, but progressive disproportionation occurred on attempting to isolate the chlorobromides by slow fractional distillation. Thus a total of 106·8 g. of the partially chlorinated product from a number of experiments yielded on the first slow fractionation (several hours) through a long and efficient column the following fractions : b. p. 25—35° (20·1 g.), 35—55° (21·4 g.), 55—80° (19·4 g.), 80—90° (40·0 g., mainly BBr₃). The three lighter fractions were each refractionated through the same column, cuts being made at 25°, 32·5°, and 70°. The combined fractions obtained were : b. p. 21·5—25° (14·6 g.), 25—32·5° (10·5 g.), 32·5—70° (13·0 g.), 70—90° (15·9 g.). Thus far only small quantities of boron trichloride had condensed in a liquid-oxygen guard trap. With successive refractionations the amount of material boiling in the range 30—70° decreased, while appreciable quantities of almost pure boron trichloride and boron tribromide were isolated.

Behaviour of Partially Chlorinated Product on Fractional Condensation at Low Temperatures.— A grease-free vacuum system was employed. In order to start with a liquid boiling almost exactly halfway between the b. p.s of boron trichloride and tribromide (and hence likely to contain the two chlorobromides in approximately equal proportion), the method of preparing the partially chlorinated product was modified. Boron tribromide (90 g.) and antimony trichloride (55 g.) were heated in a Kon flask over a water-bath until a distillate began to come over through the fractionating arm. Raising the temperature of the water-bath caused the temperature registered by the thermometer in the fractionating arm to rise, and *vice versa*. By carefully controlling the bath temperature, it was possible to keep the product distilling as it was formed at a temperature close to 50°, thus avoiding complete chlorination to boron trichloride while preventing appreciable quantities of boron tribromide from distilling. The distillate was collected in a trap cooled in liquid oxygen.

About 9 ml. of the distillate were transferred to the vacuum apparatus and subjected to fractional condensation *in vacuo* with the baths at the following temperatures (±2°) : trap *A* −57°, trap *B* −84°, trap *C* −183° (liquid oxygen), these having been chosen so that practically no boron tribromide would distil from trap *A*, while most of the chlorobromide would condense in trap *B* and almost all the trichloride pass on to trap *C*. At the end of the first fractional condensation (requiring close on 3 hr.), approximately 2 ml. of material had collected in trap *C* and 5 ml. in trap *B* (liquid), while 2 ml. remained in trap *A* (mostly solid). (Had the

mixture consisted entirely of boron trichloride and tribromide, the final distribution would have been very different, and trap B would have been almost empty.) The head portion of the tail fraction in trap A had v. p. 71 mm., and the tail portion of the head fraction in trap C 294 mm. at 0° (cf. 19·3 and 475 mm. at 0° for BBr_3 and BCl_3 respectively). The evidence from this is that, in addition to boron trichloride, trap C contained a fair amount of less volatile material, which however could hardly be boron tribromide uncondensed by trap B at −84°.

The middle fraction in trap B was subjected to two further fractional condensations as before with the following results (v. p.s at 0° given in parentheses) : Second fractionation, trap A ~1 ml. (45 mm.), trap B ~3 ml. (150 mm.), trap C ~1 ml. (321 mm.); third fractionation, trap A ~0·7 ml. (38 mm.), trap B ~1·6 ml. (138 mm.), trap C ~0·7 ml. (297 mm.). These results indicate progressive disproportionation. Vapour-density determinations on the middle fraction from the final fractional condensation gave : Found (most volatile portion), 75·1; (least volatile portion), 100·9 (BCl_2Br requires v.d. 80·8; $BClBr_2$, 103·1). This is consistent with the presence of both chlorobromides in this fraction.

Behaviour of Boron Trichloride and Boron Tribromide on Mixing.—Pure boron tribromide (20 ml.) was added to an equal volume of pure boron trichloride and the mixture kept in a Kon flask for only 30 min. On distillation, the temperature in the side arm rose continuously from 22° to 90°. More than half of the liquid distilled below 50°, and only 3 ml. of boron bromide distilling at 90° were recovered at the end of the fractionation (about 1 hr. after mixing). With a difference in b. p.s of 78°, had there been no interaction the separation into boron trichloride and tribromide would have been nearly complete. To test the efficiency of the column, a mixture of ethyl chloride and ethyl iodide (difference in b. p.s 61°) was similarly treated, and almost complete separation was obtained at a single fractionation.

Raman Spectra.—A partially chlorinated boron bromide product boiling at about 50° and prepared as before was distilled into an optical vessel for comparing its Raman spectrum with the spectra of samples of pure boron trichloride and tribromide in identical vessels. Whereas with the apparatus employed and exposures of several hours' duration two frequencies were observed for the trichloride (253, 471 cm.⁻¹) and two for the tribromide (151, 279 cm.⁻¹), yet the product containing both bromine and chlorine exhibited ten frequencies, namely, these four frequences weakly and six new frequencies (168, 197, 212, 223, 347, 408 cm.⁻¹), those at 347 and 408 cm.⁻¹ being particularly strong. The same lines were observed when the tubes were filled with mixtures of boron trichloride and boron tribromide. By varying the trichloride–tribromide ratio, it was possible from the change in relative intensities to associate the frequencies 212, 223, and 408 cm.⁻¹ with BCl_2Br and those at 168, 197, and 347 cm.⁻¹ with $BClBr_2$. A fuller account of the Raman studies of these compounds will be published elsewhere.

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