860. *Reactions of Heptasulphur Imide with the Boron Trihalides.*

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Heptasulphur imide with boron trichloride gives dichloro(heptasulphur imido)boron and with boron tribromide the corresponding bromine compound. It does not react with boron trifluoride. Boron tri-iodide destroys the sulphur–nitrogen ring. Dichloro(heptasulphur imido)boron forms a crystalline adduct with pyridine.

IN a recent note [1] we described how heptasulphur imide and boron trichloride yield dichloro(heptasulphur imido)boron, $S_7N \cdot BCl_2$, at appreciable rates at temperatures down to $-40°$. We now report the corresponding reaction with boron tribromide occurring in carbon disulphide down to $-55°$; with boron tri-iodide reaction was observed even at $-78°$. With boron trifluoride, on the other hand, there was little reaction in carbon disulphide at $30°$, or, in absence of a solvent, at $80°$. This order of reactivities cannot be fully explained at present but may depend upon the fact [2] that Lewis bases with nitrogen as donor atom add to the boron trihalides with increasing ease as the atomic weight of the halogen increases.

The reaction $S_7NH + BCl_3 \longrightarrow S_7NBCl_2 + HCl$ is almost quantitative in carbon disulphide at $-40°$. Evaporation of the reaction mixture *in vacuo* leaves colourless needles of dichloro(heptasulphur imido)boron, which melt at 42—$44°$ to a red, viscous liquid (m. p. $25°$ reported earlier [1] was for a less pure sample). The melt decomposed only slowly at 45—$47°$; a solution of the compound in carbon disulphide was unchanged after a week at room temperature. Vapour-pressure measurements showed the compound to be monomeric in carbon disulphide solution. In this respect it contrasts with the di-chlorodialkylamidoborons with small alkyl groups, which dimerise in order to raise the co-ordination number of the boron to four: and it resembles the compounds of this class with bulky alkyl groups, in which dimerisation appears to be sterically hindered. [3]

Dichloro(heptasulphur imido)boron readily added pyridine, forming an adduct, $S_7N \cdot BCl_2,py$, m. p. $150°$ (decomp.), which is quantitatively hydrolysed when refluxed with carbon disulphide and water:

$$S_7N \cdot BCl_2,py + 3H_2O \longrightarrow S_7NH + H_3BO_3 + 2Cl^- + H^+ + pyH^+$$
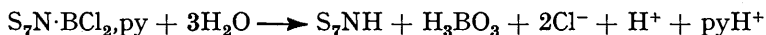
Formation of this adduct shows that the boron atom has some acceptor power, but the dichloro-compound does not add heptasulphur imide. Thus we could not replace a second chlorine atom in boron trichloride by the S_7N group. Though heptasulphur imide reacted slowly with the dichloro-compound at room temperature, yet, for reasons given on p. 4446 we think that this reaction destroyed the S_7N ring of the dichloride and did not lead to chloro bis(heptasulphur imido)boron.

The orange carbon disulphide solution resulting from the reaction of boron tribromide with heptasulphur imide left, when evaporated, a viscous red substance. We believe that this contained much dibromo(heptasulphur imido)boron, first, because the infrared spectrum of its solution in carbon disulphide closely resembled that of the dichloride (see below) and, secondly, because the product yielded heptasulphur imide (about one-third of the starting amount) when hydrolysed. The failure of the dibromide to crystallise must be attributed to contamination; a probable cause was the secondary reaction $S_7NH + 3HBr \longrightarrow NH_4Br + (probably)$ bromosulphanes, which we found to take place at $-50°$. No such reaction occurred with hydrogen chloride, but a similar reaction with

[1] Heal, *J. Inorg. Nuclear Chem.*, 1961, **20**, 165.
[2] Stone, *Chem. Rev.*, 1958, **58**, 101.
[3] Coates, " Organo-Metallic Compounds," 2nd edn., Methuen and Co. Ltd., London, 1960, p. 108.

hydrogen iodide has been reported.[4] Dibromo(heptasulphur imido)boron decomposed very little in 16 hr. at room temperature in carbon disulphide solution.

The carbon disulphide solution from the reaction of heptasulphur imide with boron tri-iodide contained one mol. of iodine per mol. of the tri-iodide that reacted; there were no bands in its infrared spectrum between 670 and 4000 cm.$^{-1}$, and the product yielded no heptasulphur imide when hydrolysed. These results indicate practically total destruction of the S_7N rings, and imply that di-iodo(heptasulphur imido)boron is very unstable.

The infrared spectra of dichloro(heptasulphur imido)boron and its presumed dibromide analogue had, as sole prominent features between 670 and 4000 cm.$^{-1}$, two strong doublet bands (see Table). Each doublet consisted of a high-frequency component which we attribute to the ^{10}B isotope (19% of natural boron), and a low-frequency component about four times more intense, which we attribute to ^{11}B (81% of natural boron). We assign the doublets designated X in the Table to the B–N stretching vibration, since, first, the wavenumber ratio of the components was near 1·028 (the square root of the ratio of reduced masses of the ^{11}B–^{14}N and the ^{10}B–^{14}N system) and, secondly, the wavenumbers of B–N stretching vibrations in other molecules fall in this general region.[5] The doublets designated Y we assign to an asymmetric boron–halogen stretching vibration, because in wavenumber and in isotopic splitting they agree approximately with bands so assigned in the spectra of the boron trihalides (see Table) and of other molecules $R\cdot BCl_2$.[5]

Wavenumbers (cm.$^{-1}$) of principal infrared bands between 670 and 4000 cm.$^{-1}$, with wave-number ratio for the components of each doublet (all compounds in CS_2).

$S_7N\cdot BCl_2$				$S_7N\cdot BBr_2$				BCl_3		BBr_3		BI_3	
X		Y		X		Y							
1198 1232 }	1·029	968 1005 }	1·038	1190 1220 }	1·026	869 899 }	1·035	941 980 }	1·041	810 845 }	1·044	697 728 }	1·045

The molar extinction coefficients (ε) at the band maxima of dichloroheptasulphur imidoboron were approximately:

Band (cm.$^{-1}$)	968	1005	1198	1232
ε	920	230	2080	470

ε values of comparable magnitude were found for the doublets of the dibromide and the boron trihalides.

Our results point to the following general conclusions. Heptasulphur imide must be a very weak Brönsted base, since it does not combine with hydrogen chloride. However, its destructive decomposition by the stronger Brönsted acids hydrogen bromide and hydrogen iodide might be initiated by salt formation. It is also a weak Lewis base, as its failure to combine with boron trifluoride shows. Nevertheless, it does react with boron trichloride and tribromide, and also with sulphur dichloride and disulphur dichloride,[6] halogen atoms being replaced by S_7N groups and hydrogen halide eliminated. These reactions almost certainly begin with co-ordination of the imide-nitrogen atom to the central atom of the halide. A reaction of this type would probably take place with any covalent halide having both strong acceptor character and space to admit a bulky extra ligand. In sulphur dichloride, where the co-ordination number of the central atom is only two, there can be little steric impediment to reaction and both chlorine atoms are

[4] Goehring, " Ergebnisse und Probleme der Chemie der Schwefelstickstoffverbindungen," Akademie-Verlag, Berlin, 1957, p. 58.
[5] Herzberg, " Infrared and Raman Spectra," Van Nostrand Co. Inc., Princeton, 1945, pp. 178, 298; Gerrard, " The Organic Chemistry of Boron," Academic Press, London, 1961, pp. 226, 229.
[6] Becke-Goehring, *Progr. Inorg. Chem.*, 1959, **1**, 221; *Adv. Inorg. Chem. Radiochem.*, 1960, **2**, 163.

replaced. Our own results with the three-co-ordinate boron halides suggest that here the substitution of an S_7N group for one halogen atom raises a steric barrier against further similar replacement. No experiments with four-co-ordinate halides have been reported but, if the halide has a large central atom and is a strong Lewis acid [*e.g.*, tin(IV) chloride], one halogen atom should be readily replaceable by S_7N.

EXPERIMENTAL

Apparatus.—Reactions were carried out in a simple vacuum-line equipped with greaseless Springham valves with fluorocarbon-rubber diaphragms. The reaction vessel was a bulb of 12 ml. capacity, coupled to the line by a long glass tube of 4 mm. bore, which was flexible enough to permit shaking.

Materials.—Heptasulphur imide [7] was purified as in our earlier work by repeated recrystal-lisation from methanol. For removal of the last 2—3% of sulphur, this proved inefficient, so we later resorted to chromatography.* Crude heptasulphur imide (3 g.) was passed through chromatographic silica gel (25 × 8 cm.) and eluted with 1 : 1 v/v carbon disulphide–cyclohexane. Sulphur (S_8) was eluted first, followed by, and cleanly separated from, heptasulphur imide. The latter was obtained practically colourless and free from impurities detectable by thin film chromatography (see below). In particular, ≪1% of sulphur was present. In melted at 113·5° (lit., 113·5°) and gave satisfactory nitrogen analyses and infrared spectra.

Immediately before use, boron trichloride and tribromide, in small batches, were fractionated repeatedly *in vacuo* to remove hydrogen halide. The vapour pressures at 0° and −78° then agreed accurately with recorded values.[8] Boron tri-iodide was sublimed into the reaction vessel *in vacuo*. Boron trifluoride was prepared as described by Brauer,[9a] as were hydrogen chloride and hydrogen bromide.[9b]

Carbon disulphide was distilled from a stock of 20 ml. of the solvent of spectroscopic grade, stored over about 75 mg. of fresh phosphoric oxide at −78° *in vacuo*.

Analytical Methods.—Boric acid was determined by titration with carbonate-free sodium hydroxide in presence of mannitol.

Fairly pure samples of heptasulphur imide were assayed for sulphur content by subjecting them, together with S_8 as standards, to thin-film chromatography on silica gel, in the Desaga apparatus [Camlab (Glass) Limited, Cambridge]. On elution with 1 : 1 v/v carbon tetrachloride–cyclohexane, R_F was ∼0·5 for heptasulphur imide and 1 for sulphur. The chromatograms were developed by spraying them with 0·1M-silver nitrate.

Heptasulphur imide in the products of reactions was identified by examining the infrared spectra [10] of carbon disulphide solutions in 0·1 or 0·2 mm. cells, concentrations being calculated from the optical density of the band at 810 cm.$^{-1}$ (in a 0·2 mm. cell, 0·1m-heptasulphur imide gave an optical density of 0·497 at 810 cm.$^{-1}$); the error in such analyses was ±2—3%.

Infrared Spectra.—A Perkin–Elmer Infracord spectrophotometer, covering the range 670—4000 cm.$^{-1}$, was used.

Heptasulphur Imide and Boron Trifluoride.—Solid heptasulphur imide (0·38 mmole) was heated from −78° to +80° in 1½ hr. in contact with gaseous boron trifluoride (0·38 mmole). The appearance of the crystals did not change. 0·38 mmole of gas was still present at the end, and the solid was found to contain 0·34 mmole of heptasulphur imide.

Heptasulphur imide (0·21 mmole) in carbon disulphide (20 mmoles) was shaken for 15 min. at 30° with boron trifluoride (0·49 mmole). The solution became slightly yellow and deposited a trace of flocculent matter. The volatile materials were then distilled off. The solid residue contained 0·20 mmole of heptasulphur imide.

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* We gratefully acknowledge the help of Drs. Tavs and Schultze-Steiner at the Shell Research Laboratories at Thornton, Cheshire, who told us about the chromatographic methods of purification and analysis described in this paper.

[7] Becke-Goehring, Jenne, and Fluck, *Chem. Ber.*, 1958, **91**, 1947.

[8] Landolt–Börnstein, " Physikalisch-chemische Tabellen," Springer, Berlin, 1923, p. 1341.

[9] Brauer, " Handbuch der präparativen anorganischen Chemie," Enke, Stuttgart, 1954, (*a*) p. 176 (Method II), (*b*) pp. 218, 221 (Method III).

[10] Goehring and Zirker, *Z. anorg. Chem.*, 1956, **285**, 70.

Dichloro(heptasulphur Imido)boron.—Annexed are typical results (in mmoles) obtained when this substance was prepared according to ref. 1 and then hydrolysed:

Reactants				Hydrolysis products			
S_7NH	BCl_3 total	BCl_3 consumed	HCl evolved *	S_7NH	H_3BO_3	HCl *	
0·739	0·822	0·758	0·714	—	—	—	
0·590	0·636	0·586	0·590	0·567	0·611	1·23	
0·838	1·11	0·818	0·801	0·783	0·820	1·64	

* H+ determined by titration with sodium hydroxide to pH 6, and Cl− gravimetrically as silver chloride.

In a number of preparations with similar quantities, traces ($<\sim$2 mg.) of an unidentified flocculent substance were precipitated and the yields of hydrogen chloride were slightly below theoretical.

Degree of Aggregation of Dichloro(heptasulphur Imido)boron in Carbon Disulphide.—Carbon disulphide was distilled on to a pure sample of the dichloride in measured portions. Vapour pressures of the resulting solutions were:

Solution: $S_7N·BCl_2$ (mmole)	0·739	0·739	0·739	—
CS_2 (mmoles)	3·09	4·96	6·79	(100%)
V. p. (mm.) at 0°	104·1	111·5	115·0	127·2
Degree of aggregn.	1·09	1·06	1·03	—

The degrees of aggregation were calculated by assuming Raoult's law to hold.

Pyridine Adduct of Dichloro(heptasulphur Imido)boron.—Dry pyridine (1·24 mmoles) was added to dichloro(heptasulphur imido)boron (1·11 mmole) in carbon disulphide (40 mmoles). The solution at once became warm and soon deposited colourless rhombs of the *adduct*, which were collected and washed with carbon disulphide (yield 0·88 mmole). The compound dissolved sparingly in carbon disulphide, began to darken at 130°, and melted with decomposition at 150—152° (Found, for 3 samples: C, —, 14·9, —; H, —, 1·0, —; N, —, 7·5, —; B, 2·7, —, 2·8; Cl, —, 18·4, 18·1; S_7N, 59·3, —, 57·6; C_5H_5N, —, 20·0, 20·3. BCl_2NS_7,C_5H_5N requires C, 15·5; H, 1·3; N, 7·0; B, 2·7; Cl, 17·8; S_7N, 59·7; C_5H_5N, 19·8%). Carbon, hydrogen, and nitrogen were determined by combustion. To obtain the other figures, the sample was refluxed for 0·5 hr. with carbon disulphide and water; the resulting boric acid was titrated in presence of mannitol; chloride ion was determined gravimetrically as silver chloride, the heptasulphur imide from its infrared spectrum (see above), and pyridine spectrophotometrically (band of the pyridinium ion at 257 mμ).

Heptasulphur Imide and Hydrogen Chloride.—Heptasulphur imide (0·14 mmole), carbon disulphide (30 mmoles), and hydrogen chloride (0·95 mmole) were shaken together for 30 min. at room temperature. No reaction was seen. Volatile materials were distilled off, and with water yielded H+ 0·92 mmole and Cl− 0·93 mmole. The nearly white, crystalline residue contained 0·13 mmole of heptasulphur imide.

Heptasulphur Imide and Dichloro(heptasulphur Imido)boron.—Heptasulphur imide (0·81 mmole), carbon disulphide (70 mmoles), and boron trichloride (0·41 mmole) were shaken together at −30° for 1 hr. Volatile materials were distilled off and treated with water; 0·41 mmole of hydrochloric acid and no boric acid were found in the water. The infrared spectrum of a solution of the residue in carbon disulphide showed the presence of 0·41 mmole of unchanged heptasulphur imide, and 0·27 mmole of dichloro(heptasulphur imido)boron. Strong unidentified bands at 1280 and 1350 cm.$^{-1}$ were also present. After the solution had been kept for 94 hr. at room temperature, the bands of the dichloride had disappeared, but 0·2 mmole of heptasulphur imide was still present. The band at 1350 cm.$^{-1}$, and less so that at 1280 cm.$^{-1}$, had increased in intensity; neither band showed the doublet structure expected for a three-co-ordinate boron compound.

In another experiment, heptasulphur imide (0·98 mmole), boron trichloride (0·49 mmole), and carbon disulphide (80 mmoles) were shaken together for 3 hr. at −35° to −40°. 0·50 mmole of hydrogen chloride was formed. After 16 hr. at 0°, 0·02 mmole more of hydrogen chloride had been formed, and after 16 hr. more at 19° a further 0·02 mmole. At this stage, the

infrared spectrum of the solution showed dichloro(heptasulphur imido)boron to be practically absent, while 0·28 mmole of heptasulphur imide remained. Shaking the solution with water increased the content of heptasulphur imide only to 0·54 mmole. Thus, of the original 0·98 mmole of this compound, 0·44 mmole had been converted into substances which were not hydrolysed back to heptasulphur imide.

Heptasulphur Imide and Hydrogen Bromide.—Heptasulphur imide (0·19 mmole), hydrogen bromide (0·76 mmole), and carbon disulphide (40 mmoles) were shaken together at −55° to −45° until all the heptasulphur imide had disappeared. An orange solution and a bulky, flocculent precipitate resulted. The volatile materials were distilled off at −45° and treated with water. 0·23 mmole of hydrogen ion and 0·23 mmole of bromide ion were found in the water. The residue contained 0·01 mmole of heptasulphur imide; the portion of it insoluble in carbon disulphide dissolved in water and was probably mostly ammonium bromide (0·12 mmole of ammonium ion determined by the " formol " titration, and 0·14 mmole of bromide ion).

In this experiment 3 moles of hydrogen bromide were consumed per mole of heptasulphur imide destroyed, the same ratio as in the previously known reaction, $S_7NH + 3HI \longrightarrow 7S + I_2 + NH_4I$. In the reaction with hydrogen bromide, however, any elemental sulphur and bromine formed would have combined to give bromosulphanes, which were probably responsible for the orange colour of the solution.

Heptasulphur Imide and Boron Tribromide.—Heptasulphur imide (0·54 mmole), boron tribromide (0·54 mmole), and carbon disulphide (30 mmoles) were shaken together at −55° to −40° for 2 hr. Volatile materials were distilled off at −40° and treated with water. 0·03 mmole each of hydrogen ion and bromide ion, and no boric acid, were found in the water. The red, viscous residue was shaken with carbon disulphide (79 mmoles), giving an orange solution and an insoluble brownish substance. The infrared spectrum of the solution showed the doublet bands attributed to dibromo(heptasulphur imido)boron, while the bands of heptasulphur imide were absent; it was practically unchanged after 16 hr. at room temperature. The solution was shaken thoroughly with water. The resulting aqueous layer contained H⁺ 0·54, Br⁻ 0·74, and boric acid 0·42 mmole. The carbon disulphide layer was still orange, contained 0·19 mmole of heptasulphur imide, and showed no infrared bands due to any other substance. On evaporation, however, it left a gummy red residue which yielded 0·28 mmole of silver bromide when refluxed with concentrated nitric acid and silver nitrate. The product of the original reaction which had not dissolved in carbon disulphide weighed 0·0302 g. When treated with water, it gave H⁺ 0·12, boric acid 0·10, and Br⁻ 0·25 mmole, along with a little insoluble white matter resembling sulphur. It probably consisted of ammonium salts.

Heptasulphur Imide and Boron Tri-iodide.—Boron tri-iodide (0·24 mmole), heptasulphur imide (0·22 mole), and carbon disulphide (60 mmoles) were shaken together at −78°. A deep purple colour developed, and a brown solid was deposited. The temperature was raised to 0° in 1 hr., with shaking at intervals. The materials volatile at −25° were fractionated (to remove a trace of iodine) and treated with water. No hydrogen ion and no boric acid were found in the aqueous layer. The infrared spectrum of an extract of the residue with 60 mmoles of carbon disulphide showed no bands between 670 and 4000 cm.⁻¹. The purple extract was added to water and titrated with 0·1N-thiosulphate, which showed the presence of 0·44 mg.-atom of elemental iodine. The carbon disulphide layer left after the titration contained no heptasulphur imide.

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