The Chemistry of Transition-metal Vapours. Part II.[1] The Preparation of Diboron Tetrachloride from Copper Vapour and Boron Trichloride

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Copper vapour has been shown to react with boron trichloride on condensation at low temperatures to give good yields of diboron tetrachloride. The method has been developed into a laboratory preparation of diboron tetrachloride on a 10 g scale.

DIBORON TETRACHLORIDE is a valuable starting material for the synthesis of a number of boron compounds, but its use has been restricted because it is difficult to make in large quantities. The usual preparation involves an electrical discharge in boron trichloride with copper or mercury electrodes.[2,3] There have been no reports of rates of formation of the compound of greater than *ca.* 1 g/h by these methods and commonly the rate is only 100—300 mg/h.

This work describes the synthesis of diboron tetrachloride on a 10 g scale by the reaction of copper vapour with boron trichloride on a surface cooled at −196°. The formation of small amounts of diboron tetrachloride by this route was reported in a preliminary communication.[4]

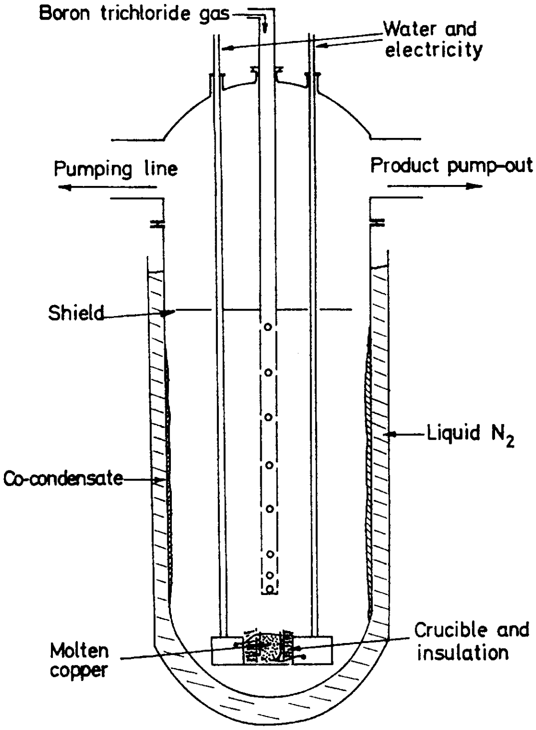
EXPERIMENTAL

The apparatus used is shown in the Figure.

The glass reaction vessel was connected through a 2 in. butterfly valve to a liquid-nitrogen cooled trap and a mercury diffusion pump. The vessel was easily pumped down to *ca.* 10^{-5} Torr. Although the pumping system used gave a speed of 18 l/s at the vessel, the pumping speed was found to be uncritical in the preparation of diboron tetrachloride and a much lower speed through a smaller valve or stopcock would have been satisfactory.

Copper was vaporized from electrical-resistance heated crucibles each made by coating a spiral of 18 s.w.g. molybdenum wire with alumina cement.[1] The crucibles were insulated with molybdenum radiation shields and refractory wool (Triton Kaowool, A. D. Wood, Ltd.). They were mounted in a water-cooled copper jacket with an open top.

The largest crucibles used had an internal diameter of 15 mm and a capacity of 5 ml. Each was charged with a length of a commercial grade copper (B.S. 2874) weighing *ca.* 30 g. Under high vacuum, 20 g of copper was vaporized in an hour with a power input of 320 W (17 V at 19 A). The amount of copper vaporized was found from the weight of the crucible. During vaporization the surface temperature of the copper was *ca.* 1480°. Roughly 150 W were radiated from the open top of the crucible, the remaining heat was absorbed in the water cooling. These large crucibles generally survived five to eight runs before the molybdenum wire broke. Crucibles of 1 or 2 ml capacity were made for the smaller scale experiments.



Apparatus for co-condensing boron trichloride gas and copper vapour on a cold surface

Traces of permanent gas were removed from commercial boron trichloride (Matheson, 99·9% pure) and then it was used without further purification direct from a lecture

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[1] Part I, P. L. Timms, *J. Chem. Soc.* (*A*), 1970, 2526.

[2] T. Wartik, R. Rosenberg, and W. B. Fox, *Inorg. Synth.*, 1967, **10**, 118.

[3] G. Urry, T. Wartik, R. E. Moore, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1954, **76**, 5293.

[4] P. L. Timms, *Chem. Comm.*, 1968, 1525.

bottle. For the large-scale preparations it was passed into the reaction vessel *via* a 4 l ballast volume, at the rate of *ca.* 5 g/min.

The sequence of operations in the preparation of diboron tetrachloride was as follows. The reaction vessel was first evacuated to a pressure below 2×10^{-5} Torr. The crucible was then heated until the copper was just molten. Traces of gases evolved from the copper were pumped away. The lower portion of the reaction vessel was immersed in liquid nitrogen and the flow of boron trichloride was started. Finally, the temperature of the crucible was increased to vaporize the copper.

With a rate of introduction of boron trichloride of greater than 2 g/min, it was observed that over part of the cold surface the compound did not solidify immediately on condensation, but formed a liquid layer in which the copper vapour condensed. However, the cryogenic pumping effect of other parts of the surface receiving a lower flux of condensing vapours, was sufficient to keep the pressure at the top of the vessel below 5×10^{-4} Torr.

After an hour, the crucible was allowed to cool and the mixture of diboron tetrachloride and unchanged boron trichloride was pumped out of the vessel and through two traps at −90° in which the diboron tetrachloride was retained. The product was finally purified on a low-temperature distillation column [5] and its purity was checked by its vapour pressure [2] (43 Torr at 0°) and its mass spectrum.

The same apparatus and type of crucible was used in trial experiments on the reactions of other metal vapours with boron trichloride, although the temperature of vaporization was different for each metal.[1]

RESULTS AND DISCUSSION

When copper vaporizes under equilibrium conditions it forms mainly monatomic copper gas. Trace amounts of the dimer, Cu_2, have been observed mass spectrometrically.[6] With the rapid, non-equilibrium vaporization used in this work it seems probable that the concentration of polymers in the vapour was insignificant.

Analysis of the residue in the reaction vessel after copper vapour had been condensed with boron trichloride and the volatile products pumped off, showed that it contained less than 1% boron and was essentially a mixture of cuprous chloride and metallic copper. Thus, the overall reaction can be represented by the equation,

$$2Cu(g) + 2BCl_3(g) \longrightarrow B_2Cl_4(l) + 2CuCl(s) \quad (1)$$

The results of four typical runs for the preparation of diboron tetrachloride are shown in the table below.

Expt.	Moles Cu *	Moles BCl_3	BCl_3 : Cu Ratio	Moles B_2Cl_4	% Yield
(a)	0·04	0·80	20 : 1	0·014	70
(b)	0·04	0·24	6 : 1	0·008	40
(c)	0·30	1·80	6 : 1	0·046	30
(d)	0·30	2·70	9 : 1	0·057	38

* Evaporated over a period of 1 h.

The yield of the compound, based on the copper used and the stoicheiometry assumed in equation (1), appears to have been influenced by two factors. First, by the ratio of boron trichloride to copper condensed on the cold surface. A large excess of boron trichloride favoured the formation of diboron tetrachloride, presumably by reducing the probability of copper atoms reacting with each other to form metallic copper. Second, by the rate of deposition. Runs (a) and (b) on a small scale with a lower deposition rate gave slightly higher yields than the large-scale runs (c) and (d). In (c) and (d), the boron trichloride was seen to condense as a liquid indicating a surface temperature greater than −107°, the melting point of the compound. Under these conditions, copper atoms must have been very mobile with a higher chance of reacting with each other than when frozen directly into a solid matrix as in (a) and (b).

In practice, it was inconvenient to have a huge excess of boron trichloride in large-scale experiments because it was then difficult to handle the volume of liquid and separate it from diboron tetrachloride on a vacuum line. The ratio of BCl_3 : Cu of 9 : 1 [Expt. (d)] was found suitable for the routine preparation of diboron tetrachloride on a 10 g scale.

The success of the reaction between copper vapour and boron trichloride to form diboron tetrachloride can be attributed partly to thermodynamic factors. Gaseous copper is an energetic species ($\Delta H_f°$ from the solid at 298 K is +338 kJ/mol [7]). Taking enthalpy data from reference 7, the reaction of Eqn. (1) is exothermic by 665 kJ/mol. However, chromium, iron, cobalt, nickel, and tin vapours, each with an affinity for chlorine comparable to that of copper, formed no diboron tetrachloride when condensed with boron trichloride. Thus, as suggested by its use in the discharge preparation, kinetic and mechanistic factors must be particularly favourable with copper. Silver vapour gave a small amount of diboron tetrachloride, *e.g.* a 5% yield using a 20 : 1 BCl_3 : Ag ratio.

As reported earlier, copper vapour will also react with methyldichloroborane [4] and the generality of such reactions with alkylchloroboranes will form part of later papers in this series. However, no reaction was detected when copper vapour was condensed with diboron tetrachloride vapour at a low temperature. It was hoped that B_4Cl_4 would be formed, a compound obtained in low yield from the discharge preparations of diboron tetrachloride.[2,3]

CONCLUSIONS

Although most transition-metal vapours are likely to be reactive chemical species,[8] it is only a few which can

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[5] For a description see D. F. Shriver, 'The Manipulation of Air Sensitive Compounds,' McGraw-Hill, 1969, p. 91.

[6] M. Ackerman, F. E. Stafford, and J. Drowart, *J. Chem. Phys.*, 1960, **33**, 1784.

[7] D. D. Wagman, W. H. Evans, V. B. Parker, I. Harlow, S. M. Bailey, and R. H. Schumm, *Nat. Bur. Stan. Tech.*, note 270—3 (1968) and 270—4 (1969).

[8] P. L. Timms, *Advan. Inorg. Rad. Chem.*, 1972, **14**, in the press.

be evaporated easily, which lend themselves to becoming useful reagents in synthetic chemistry.

This work describes one of the first applications of a reaction of a transition-metal vapour to a practical synthesis on a 10 g scale. The apparatus is no more complex than required for the electrical discharge preparations of diboron tetrachloride,[2,3] but it enables the compound to be made more quickly.

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