

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

The Fluorination of Boron Trichloride

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This investigation is a continuation of the studies of this Laboratory on the fluorination of non-polar halides.¹ Boron trichloride was prepared by the chlorination of ferro-boron.² The purified boron chloride showed a sharp melting point at -107° agreeing with the value given by Stock and Priess.³

A. The Reaction of Boron Fluoride with Boron Chloride.—Passing a mixture of boron chloride and boron fluoride through a tube heated to 500° caused no rearrangement such as that found by Booth and Bozarth⁴ with similar mixtures of phosphorus trichloride and fluoride. Exposing the same mixtures to an electric discharge was also without effect.

B. Fluorination Using Calcium Fluoride.—The fluorination of non-polar halides in the vapor phase by heated calcium fluoride has been used successfully in this Laboratory in the partial fluorination of phosphorus trichloride,⁴ and of phosphoryl chloride.⁵

The apparatus consisted of a vertical tube 2 cm. in diameter filled with pellets of calcium fluoride, connected to a rectifying column with a head cooled with liquid ammonia that condensed and returned the unreacted boron chloride to an ampoule from which it again circulated through the system. An automatic stopcock which permitted the reaction products to bleed off, while most of the unreacted boron chloride, recirculated, maintained the system at the desired pressure of 14.7 cm. of mercury.

The first fluorination with calcium fluoride heated to 200° produced only boron trifluoride, showing complete fluorination. A second fluorination with the pellets at first at room temperature and then at gradually rising temperature until the reaction started, showed no reaction until the temperature reached 160° , when it proceeded quite rapidly forming only boron trifluoride. Subsequent runs in which the temperature was lowered after the reaction had started also gave boron trifluoride as the sole product.

(1) Booth and Cassidy, *THIS JOURNAL*, **62**, 2369 (1940).

(2) Mazetti and de Carli, *Atti. Acad. Lincei*, [5] **31**, ii, 119 (1938).

(3) Stock and Priess, *Ber.*, **47**, 3109 (1914).

(4) Booth and Bozarth, *THIS JOURNAL*, **55**, 3890 (1933); **61**, 2927 (1939).

(5) Booth and Dutton, *ibid.*, **61**, 2637 (1939).

With fresh calcium fluoride pellets the reaction proceeded very rapidly with almost complete conversion to boron trifluoride on a single pass. As the reaction proceeded the pellets became coated with calcium chloride and the reaction slowed. However, even then there did not seem to be any tendency to form intermediate compounds.

C. Fluorination with Antimony Fluoride and a Catalyst.—With the type of generator commonly used in this Laboratory,⁶ a run was made with the mixture, BCl_3 and SbCl_5 , maintained at 0° and at approximately half an atmosphere pressure. The generator was cooled with ice while the still-head was at room temperature. Upon addition of sublimed antimony fluoride, the reaction proceeded smoothly with pure boron trifluoride as the only product obtained.

Since lowering the temperature slowed the reaction, it was thought that it might favor the production of the intermediates, so runs were made at -15° using an ice-salt mixture for cooling, at -40° using liquid ammonia and at -78° using a solid carbon dioxide-acetone mixture. While the reaction was slowed proportionally in these runs, only the completely fluorinated product was obtained. In each of these cases the pressure was adjusted so that a little of the boron chloride could distill over. In this way any intermediate compound that was formed should have escaped immediately and should not have had opportunity to be fluorinated further.

Dilution of the boron trichloride with an equal amount of carbon tetrachloride gave only pure BF_3 . At the temperature used (-40°) none of the carbon tetrachloride was fluorinated while the boron trichloride was converted to the trifluoride.

The fluorination is thought to proceed by the formation of an addition product of antimony trifluoride with the halide which in turn decomposes forming the fluorinated compound and eventually antimony trichloride. With the thought of reducing its activity, antimony fluoride and trichloride were mixed together in the molecular proportions of antimony monofluorodichloride and fused. This mixture was used to fluorinate

(6) Booth and Morris, *ibid.*, **58**, 90 (1936).

some boron trichloride but the only effect was to slow the reaction considerably while still giving pure boron trifluoride.

Identification of the Fluorination Products.—

The products obtained from the fluorination were separated by fractional distillation and the various fractions identified by their boiling points and vapor densities according to the standard technique in this Laboratory.⁷

Discussion of Results

The fluorination of boron trichloride by antimony fluoride and pentachloride is decidedly exothermic, and proceeds quite rapidly at room temperatures and even proceeds, although considerably more slowly, at -78° . Due to the heat evolved (when the reaction starts), there is a tendency for local over-heating that makes the reaction proceed more rapidly. Also the antimony trifluoride that is added is at room temperature so that it momentarily warms the liquid with which it comes in contact and accelerates the reaction.

The theory of Booth and Swinehart⁸ for the formation of partially fluorinated products assumes that the stability of the compound of the partially fluorinated chloride and the fluorinating agent is so little at the temperature of the fluorination that dissociation takes place liberating the partially fluorinated chloride as a gas which may be removed to prevent further fluorination. However, BCl_3 and BF_3 are noted for their ability to act as acceptors for electron pairs forming unusually stable compounds.

Apparently this bond is so strong that interme-

diately fluorinated products cannot be released. If this explanation is true then fluorination at elevated temperatures (under pressure) might permit the liberation of partly fluorinated compounds. However, the fact that none were obtained by fluorination by calcium fluoride under carefully controlled conditions, nor by heating or sparking a mixture of BF_3 and BCl_3 , would suggest that under these higher temperature conditions BF_2Cl and BFCl_2 rearrange to form BF_3 and BCl_3 just as Booth and Morris found that on standing even at -78° C., GeF_3Cl , GeF_2Cl_2 and GeFCl_3 rearranged to GeF_4 and GeCl_4 .

Boron chloride represents a fourth class of reaction of non-polar halide and antimony trifluoride in the presence of pentavalent antimony in which the degree of covalent unsaturation is so great that no intermediate product can be isolated. Benzotrichloride⁹ likewise is completely fluorinated by this reagent but it is not probable that the reason is the same.

Summary

The fluorination of boron trichloride by antimony trifluoride with antimony pentachloride as a catalyst at 0° , -15° , -40° , and -78° , and by calcium fluoride heated to 160 and 200° yielded pure boron trifluoride as the sole fluorination product. This should be a useful laboratory method for preparing BF_3 free from SiF_4 .

When mixtures of boron trifluoride and boron trichloride were heated or subjected to electrical discharge, no rearrangement took place.

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(7) Booth and Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937).

(8) Booth and Swinehart, *THIS JOURNAL*, **57**, 1333, 1337 (1935).

(9) Booth, Elsey and Burchfield, *ibid.*, **57**, 2066 (1935); Booth and Burchfield, *ibid.*, **57**, 2070 (1935).