

Summary

1. *d*-Talonic amide is levorotating as would be predicted from Hudson's amide rule.

2. The sodium and ammonium salts of *d*-talonic acid show a small dextrorotation. The rotation is much less dextro than the rotation of solutions of the free acid.

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PYRIDINE BORON TRIFLUORIDE

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Boron trihalides are extremely reactive toward ammonia and amines, and Kraus and Brown¹ have recently studied a number of reactions with boron trifluoride. They showed that true addition compounds are formed with ammonia, ethylamine, diethylamine and triethylamine.

All of these compounds can be shown to be examples of coördinate covalency, in which the boron atom acts as acceptor and the nitrogen atom acts as donor. Since the nitrogen atom in pyridine has one lone pair of electrons it should be possible to prepare a similar compound of boron trifluoride and pyridine. The purpose of this investigation was to prepare and study such a compound. After the work was nearly completed, Bowlus and Nieuwland² reported experimental work in which they measured the absorption of boron trifluoride by pyridine, and obtained a solid product which they believe to contain two molecules of boron trifluoride to one of pyridine. While the existence of such a compound in the solid state is not inconsistent with modern valence theory, it is probably not simply a case of coördinate covalency. In the present investigation a compound of boron trifluoride and pyridine was prepared, in which the molecular ratio is 1:1.

Experimental

Preparation of Materials.—Boron trifluoride was prepared by heating a mixture of ammonium fluoborate and boric oxide with concentrated sulfuric acid. The boric oxide was prepared by fusing boric acid in an iron crucible.

The pyridine was twice redistilled through an efficient fractionating column, and a constant boiling fraction was used without further purification.

The benzene was likewise redistilled twice using a column in order to ensure the complete absence of water from the reaction chamber.

Preparation of the Compound.—The all-glass apparatus shown in Fig. 1, made of Pyrex glass, was thoroughly dried in an electric oven before use. Eighteen grams of an-

¹ Kraus and Brown, *THIS JOURNAL*, **51**, 2690 (1929).

² Bowlus and Nieuwland, *ibid.*, **53**, 3835 (1931).

hydrous ammonium fluoborate and 9 g. of pulverized boron trioxide were thoroughly mixed and placed in the generator flask, A. Fifty cubic centimeters of concentrated sulfuric acid (sp. gr. 1.83) was added and the flask was heated. The boron trifluoride passed through two bulbs, one empty, B, and the other, C, filled with coarsely ground boric oxide. The pure dry boron trifluoride then entered the reaction tube, D, which contained a solution of 10 g. of pyridine in 20 cc. of benzene. It was found necessary to cool the reaction tube with a bath of running water, as considerable heat was evolved. The boron trifluoride was rapidly absorbed by the benzene solution of pyridine, and the action was continued until after absorption had apparently ceased. The final bulb, F, containing soda lime and calcium chloride, was used to exclude atmospheric moisture.

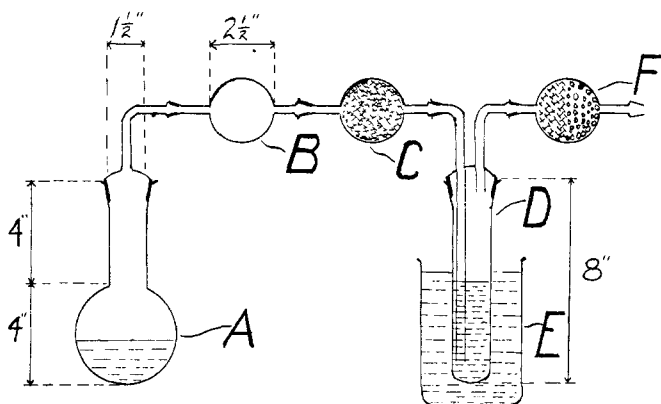


Fig. 1.

Purification of the Compound.—The crude product was crystallized with difficulty from the benzene. The solution had a marked tendency to remain supersaturated, but after prolonged cooling and agitation, crystallization took place. The compound was purified by solution in pure dry benzene, and evaporation of the solvent in a vacuum desiccator over sulfuric acid. Two such treatments yielded a colorless product with a very faint odor of pyridine. The compound was stored in a vacuum desiccator over sulfuric acid.

Analysis of the Compound.—Pyridine was determined by distilling a weighed sample with a solution of sodium hydroxide, collecting the distillate in standard acid and titrating the excess acid, using brom phenol blue as the indicator. Fluorine was determined gravimetrically as calcium fluoride. Boron was determined by the method recommended by Morgan and Tunstall.³ The molecular weight determined cryoscopically in benzene was 148 (m. w. $C_5H_5NBF_3 = 146.8$). The melting point, determined by heating 4 g. of the solid in a dry test-tube, with the bulb of a thermometer embedded in the melting solid was $45 \pm 1^\circ$. The boiling point was $300 \pm 5^\circ$.

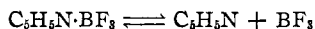
Pyridine boron trifluoride was found to be very soluble in benzene and in pyridine, fairly soluble in absolute alcohol, slightly soluble in boiling chloroform and practically insoluble in petroleum ether. Hot 95% alcohol converts it, by hydrolysis, into the pyridine salt of fluoboric acid.

Analysis of the compound gave the following results: pyridine, 53.42% (calcd. 53.81); fluorine, 38.47% (calcd. 38.83); boron, 7.21% (calcd. 7.36).

Dissociation of Gaseous Pyridine Boron Trifluoride.—Measurements of the vapor

³ Morgan and Tunstall, *J. Chem. Soc.*, **125**, 1963 (1924).

density of pyridine boron trifluoride above its boiling point by the Victor Meyer method were carried out. It was found that the vapor density decreased with rising temperature, showing that the compound is dissociated, and that an equilibrium exists between the gaseous products. The dissociation may be represented by the equation



The substances used as heating liquids were boiling mercury, phenanthrene and phenyl benzoate. The actual temperature of the vapor was read from a thermometer hung inside the inner tube of the Victor Meyer apparatus. The degree of dissociation of the vapor was calculated from the apparent molecular weight. The results are given in Table I.

TABLE I
DISSOCIATION OF PYRIDINE BORON TRIFLUORIDE BY HEAT

Temp., °C.	Apparent molecular weight	Degree of dissociation, %
356	89.9	63.3
333	108.2	35.7
313	124.1	18.2

Heat of Dissociation.—The variation in the degree of dissociation of the compound was used to calculate the heat of dissociation.⁴ The average value obtained for ΔH is 50,600 cal.

Summary

Pyridine boron trifluoride, $\text{C}_5\text{H}_5\text{N}\cdot\text{BF}_3$, has been prepared and some of its properties have been studied. It is a white crystalline compound, melting at 45° and boiling at approximately 300° under atmospheric pressure. It is soluble in benzene, pyridine and in hot absolute alcohol. In 95% ethyl alcohol it undergoes hydrolysis. It is dissociated in the vapor state and in the temperature range 313 to 356° its heat of dissociation is 50,600 calories.

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⁴ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 298.