

NOTES

Association of Boron Trifluoride Addition Compounds with Amines in Non-Polar Solvents

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During the course of some work on molecular addition compounds of tertiary amines, trimethylamine-boron trifluoride was prepared and its apparent molecular weight in benzene solution (cryoscopic method) determined. The compound is associated in solution by an amount which varies with concentration (Fig. 1A; Table I). Association constants were calculated assuming that each of the following equilibria occurred independently of all others: (1) $2AB \rightleftharpoons (AB)_2$, *i. e.*, monomer and dimer; (2) $3AB \rightleftharpoons (AB)_3$, *i. e.*, monomer and trimer; and (3) $4AB \rightleftharpoons (AB)_4$, *i. e.*, monomer and tetramer. In no case were the values for the association constants entirely consistent, least so in the case of the monomer-dimer equilibrium. Similar results were ob-

TABLE I
APPARENT MOLECULAR WEIGHT^a OF $(CH_3)_3N:BF_3$ IN BENZENE

Solute, g.	Solvent, g.	Mole fraction	ΔT_f , °C.	Apparent mol. wt.			
				K_{1-2}	K_{1-3}	K_{1-4}	$K_{1-4} (\times 10^{-4})$
(a)							
0.2412	24.2623	0.0060 ^b	0.220	230	566	1061	1.2
.2412	34.8229	.0042	.160	220	351	277	2.4
.2412	45.3965	.0032	.130	208	198	1587	3.4
.2412	55.9184	.0026	.115	191	93	1204	3.1
(b)							
.1860	30.2917	.0037	.150	209	176	1210	2.2
.1860	40.6296	.0028	.120	194	102	1207	2.9
.1860	51.1000	.0024	.100	185	82	1329	4.0
.1860	70.5882	.0016	.085	158	26	659	2.5

^a Formula weight = 126.8. ^b Solution nearly saturated. (a)-(b) Separate runs.

TABLE II
APPARENT MOLECULAR WEIGHT^a OF $C_6H_5(CH_2)_2N:BF_3$ IN BENZENE

Solute, g.	Solvent, g.	Mole fraction	ΔT_f , °C.	Apparent mol. wt.			
				K_{1-2}	K_{1-3}	K_{1-4}	$K_{1-4} (\times 10^{-4})$
0.0997	48.2624	0.00085	0.030	351	7354	6.7	5.4
.0997	58.8882	.00071	.025	345	5786	8.8	8.5
.0499	39.1257	.00052	.020	325	2354	8.9	11.9
.0499	49.4572	.00043	.017	302	1142	9.7	13.2
.0499	59.7369	.00035	.015	284	696	6.9	13.7
.0232	38.6415	.00024	.012	255	352	5.6	14.7
.0232	49.0848	.00019	.010	241	268	5.6	17.9

^a Formula weight = 188.87.

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tained for dimethylaniline-boron trifluoride (Fig. 1B, Table II). Such association is to be expected from the dipole character of such addition compounds.

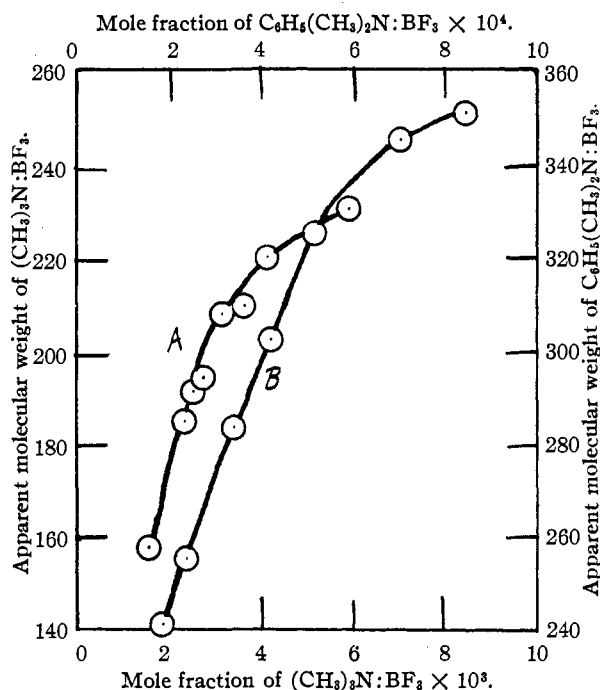


Fig. 1.—Apparent molecular weight (cryoscopic) of addition compounds of boron trifluoride with amines in benzene solution: A, $(CH_3)_3N:BF_3$; B, $C_6H_5(CH_2)_2N:BF_3$.

The molecular weight data of Kraus and Brown³ for triethylamine-boron trifluoride (cryoscopic in benzene) and ethylamine-boron trifluoride (ebullioscopic in ether) indicate similar association, although these investigators do not comment on this fact.

Experimental

Trimethylamine-Boron Trifluoride.—Dry boron trifluoride⁴ was passed slowly into a cold (0°) solution of anhydrous trimethylamine in carefully dried petroleum ether (boiling range 30–60°). The insoluble product was filtered quickly on a Büchner funnel, washed with cold petroleum ether, and dried *in vacuo* over concd. sulfuric acid. The dry solid was purified by crystallization from hot benzene: m. p. 138° (sealed tube) although some of the material sublimed as low as 125–130°; solubility *ca.* 0.995 g./100 g. of benzene at room temperature; mol. wt.

(3) C. A. Kraus and E. H. Brown, *THIS JOURNAL*, **51**, 2690 (1929).

(4) H. S. Booth, "Inorganic Syntheses," McGraw-Hill Book Company, New York, N. Y., 1939, Vol. 1, p. 23.

see Table I. Additional material may be obtained during purification by addition of petroleum ether to the cold benzene solution.

Dimethylaniline-Boron Trifluoride.—This substance was prepared and purified in the same manner as the trimethylamine compound: m. p. 90–92° (sealed tube); solubility *ca.* 0.266 g./100 g. of benzene; mol. wt. see Table II.

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A Color Reaction for Natural Pigments and Phenols

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Recently Tauber, Laufer and Goll¹ described a color test for the anti-bacterial mold pigment citrinin. We are now able to report on certain

TABLE I
SHOWING CHEMICAL DIFFERENCES BETWEEN CITRININ AND ITS OXIDATION PRODUCT

Reagent	Citrinin	Oxidation product
Color (in dry state)	Yellow	Reddish-brown
Color (in solution at pH 7.0)	Yellow	Wine red
FeCl ₃	Brown	Dark blue
NaOH	Yellow	Wine red
H ₂ SO ₄	Yellow	Almost colorless (slightly yellow)
AgNO ₃ , on boiling	No reaction	Silver mirror
(Ag ₂ O-NH ₃ , in cold)	No reaction	Black precipitate in cold
Basic lead acetate	No precipitate	Heavy reddish-brown
Neutral lead acetate	No precipitate	Precipitate

chemical properties concerning the oxidation product of citrinin. We have also applied this reaction, oxidation with hydrogen peroxide, etc., to a series of natural pigments, and to phenols. We found that some of these substances also give typically colored oxidation products under similar conditions. This indicates that certain phenolic groups are indispensable for this reaction.

Experimental

Oxidation of Citrinin by Hydrogen Peroxide and Preparation of the Oxidation Product.—100 mg. of citrinin¹ was dissolved in 1 cc. of dioxane. The solution was brought to 34° and 0.1 cc. of 30% hydrogen peroxide was added. The mixture was stirred for one minute and then cooled in ice water. Thereafter 10 cc. of distilled water was added and the orange red solution was extracted once with 16 cc. of ether and three times with 10-cc. portions of ether. The ether extracts were combined and washed with 10 cc. of distilled water. After evaporation of the ether a yield of 60 mg. of a reddish-brown hygroscopic material was obtained. It was soluble in ether, chloroform, ethyl alcohol, dioxane and slightly soluble in water. It could not be obtained, however, in crystalline form from these solvents. An alcoholic solution of this substance gave a wine red color when adjusted to pH 7.0 with dilute sodium hydroxide and on slight acidification the solution turned light yellow, almost colorless. Citrinin solutions are yellow under these conditions. It should be noted that continuous exposure of citrinin to dioxane or boiling citrinin in dioxane effects a gradual oxidation of the substance. It may be seen from Table I that the oxidation product differs in many respects from citrinin; the former appears to be a polyphenolic compound while the latter apparently is a quinoid compound containing one phenolic group only. The structural formula of citrinin is not definitely known yet.²

TABLE II
SHOWING COLOR REACTIONS OBTAINED WITH NATURAL PIGMENTS

Pigment tested	Color with H ₂ O ₂ + NaOH		Color on acidification	
			Experiment	Control
Anthocyanins				
Red beet	Violet	Yellow	Red	Red
Red rose	Intense yellow	Dark brown	Red	Red
Deep red dahlia	Light lemon yellow	Deep lemon yellow	Red	Red
Red gladiola	Yellow	Dark brown	Pink	Brick red
Orange-red dahlia	Deep yellow	Reddish-brown	Brick red	Brick red
Blue grape	Yellow	Green	Red	Red
Flavones				
White dahlia	Yellow	Orange red	Almost colorless	Almost colorless
White carnation	Yellow	Yellow	Colorless	Colorless
Other Natural Pigments				
Citrinin (originally yellow)	Wine red	Orange yellow	Orange yellow	Yellow
Penicillin (originally yellow)	Yellow	Yellow	Yellow	Yellow
Pigment of <i>P. Chrysogenum</i> (originally yellow)	Yellow	Yellow	Yellow	Yellow
Actinomycin (originally yellow)	Slightly yellow, almost colorless	Yellow	Yellow	Yellow

(1) H. Tauber, S. Laufer and M. Goll, *THIS JOURNAL*, **64**, 2228 (1942).

(2) F. P. Coyne, H. Raistrick and R. Robinson, *Trans. Roy. Soc. (London)*, **220**, 297 (1931).