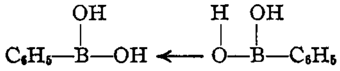
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI]

Association of the Organoboric Acids

BY H. E. FRENCH AND SAM DAVIS FINE[1]

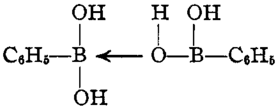
The behavior of organic acids in general, as well as the specific properties of boron, would suggest the possibility of association among the organo boric acids. Such association conceivably might take place in either of two ways, with the formation of molecular complexes which would be represented by such formulas as the following



$$C_6H_5-\overset{OH}{\overset{|}{B}}-OH \longleftarrow \overset{H}{\overset{|}{O}}-\overset{OH}{\overset{|}{B}}-C_6H_5$$

and

I



$$C_6H_5-\underset{OH}{\underset{|}{\overset{OH}{\overset{|}{B}}}} \longleftarrow \overset{H}{\overset{|}{O}}-\overset{OH}{\overset{|}{B}}-C_6H_5$$

II

Compounds of formula I would be produced in accordance with the theory of hydrogen bond formation, while those of formula II would be formed as a result of the known tendency of boron in certain of its compounds to coördinate with other molecules such as alcohols, ethers, esters, etc.[2]

The question of the association of the organoboric acids has been discussed by other investigators. Kinney and Pontz[3] determined the molecular weights of several of the acids in nitrobenzene and found them to be monomolecular. Otto[4] determined the dipole moments of certain of these acids and their esters in dioxane and in benzene, and concluded that in neither solvent did association of the acids take place, and that there was no compound formation between dioxane and the solute in any case.

In order to investigate this problem further, the present authors determined the molecular weights by freezing point depression methods in benzene, nitrobenzene, and in dioxane of the following compounds: phenylboric acid, *n*-butylboric acid, *n*-amylboric acid, and *n*-butyl borate.

The compounds used in this investigation were prepared according to the method of Bean and Johnson,[5] and had the following physical constants: *n*-butyl borate, b. p. 114–115°, 15 mm.; phenylboric acid, m. p. 214° (corr.); *n*-butylboric acid, m. p. 93–94° (corr.); *n*-amylboric acid, m. p. 91–92° (corr.). The benzene was washed with concentrated sulfuric acid, with water, then dried and fractionally distilled. The nitrobenzene was the best grade of Eastman product redistilled. The dioxane was purified by the method suggested by Oxford.[6] The results are summarized in Table I.

TABLE I

SUMMARY OF MOLECULAR WEIGHT DETERMINATIONS

Moles per 1000 g. solvent	Solvent	Molecular weight Calcd.	Molecular weight Found	Multiple of simple m. w.
	Phenylboric acid			
0.0573	Benzene	122	243	1.99
.0236	Benzene		202	1.65
.0202	Nitrobenzene		132	1.08
.0208	Nitrobenzene		136	1.11
.0649	Nitrobenzene		142	1.16
.0418	Dioxane		128	1.04
.0383	Dioxane		132	1.08
	n-Butylboric acid			
0.0228	Benzene	102	249	2.44
.0192	Benzene		250	2.45
.0228	Benzene		253	2.48
.0242	Benzene		264	2.58
.0203	Nitrobenzene		111	1.08
.0188	Nitrobenzene		108	1.05
.0220	Dioxane		110	1.07
.0184	Dioxane		117	1.14
	n-Amylboric acid			
0.0108	Benzene	116	214	1.84
.0155	Benzene		229	1.97
.0066	Nitrobenzene		119	1.02
.0082	Nitrobenzene		102	0.87
.0073	Dioxane		124	1.06
.0078	Dioxane		132	1.13
	n-Butylborate			
0.0202	Benzene	230	238	1.03
.0462	Benzene		242	1.05
.0145	Nitrobenzene		212	0.92
.0253	Nitrobenzene		193	0.83
.0178	Dioxane		240	1.04
.0298	Dioxane		241	1.04

The organoboric acids did not show a very high solubility in benzene, which made it impossible to determine the molecular weights over any considerable range of concentration. The results, nevertheless, indicate association of the acids in

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[1] This paper is an abstract of the Master's thesis submitted by Sam Davis Fine.

[2] Bowlus and Nieuwland, THIS JOURNAL, **53**, 3835 (1931).

[3] Kinney and Pontz, *ibid.*, **58**, 196 (1936).

[4] Otto, *ibid.*, **57**, 1476 (1935).

[5] Bean and Johnson, *ibid.*, **54**, 4417 (1932).

[6] Oxford, *Biochem. J.*, **28**, 1328 (1934).

benzene solution. In nitrobenzene and in dioxane the acids were found to be monomolecular. The *n*-butyl borate was monomolecular in all three solvents.

Normal butyl borate should, in the absence of steric effects, be able to polymerize according to formula II, but not according to formula I. That it does not polymerize suggests, but of course does not prove, that the association of the acids likewise does not involve the atom of boron. In that case, hydrogen bond formation would be the principal factor in that association.

The dissociating effect of both nitrobenzene and dioxane would be expected, since both possess the structures necessary for hydrogen bond formation with an hydroxyl containing solute, as well as for coördination with boron. Should either reaction take place between solvent and solute to any considerable extent, a monomolecular form of the acid would be indicated by the experimental results.

Summary

1. The molecular weights by freezing point depression of three organoboric acids and one ester have been determined in benzene, nitrobenzene, and in dioxane.

2. In benzene, the acids were found to be associated, and in the other solvents monomolecular. Normal butyl borate was found to be monomolecular in all three solvents.

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Isomerization Accompanying Alkylation: Alkylation of Benzene with Isopropylethylene in the Presence of Sulfuric Acid[1]

BY V. N. IPATIEFF, HERMAN PINES AND LOUIS SCHMERLING

The shifting of the double bond in olefins under the influence of catalysts is well known. Butene-1 is isomerized completely to butene-2 at 249° in the presence of phosphoric acid.[2]

In the presence of phosphorus pentoxide on a silica gel at 300°, *unsym*-methylisopropylethylene, tetramethylethylene, and *t*-butylethylene each yields identical equilibrium mixtures of the three isomers in the ratio 31:61:3, respectively.[3]

Isopropylethylene is converted to trimethylethylene in about 80% yield[4] when passed over alumina at 525°; the same isomerization occurs in the presence of aluminum sulfate[5] and of phosphoric acid[5] at 450°. Norris and Reuter[5] also observed that the isomerization takes place to a very slight extent in the presence of 60% sulfuric acid at 38°.

In the present investigation it was found that complete isomerization of the isopropylethylene occurs at 0° during the alkylation of benzene, using 96% sulfuric acid as catalyst.

Due to the shifting of the double bond to form trimethylethylene, the alkylation product was *t*-amylbenzene and not 2-methyl-3-phenylbutane. The same product also was obtained by the alkylation of benzene with a mixture of trimethylethylene and *unsym*-methylethylethylene. That the two amylbenzenes were identical was shown by the fact that both yielded the same mono- and diacetamino derivatives.[6] Proof that these were derivatives of *t*-amylbenzene consisted in comparing them with the derivatives of a sample of *t*-amylbenzene obtained from *p*-*t*-amylphenol. Hydrogenation of the phenol with a nickel catalyst at 150° gave the cyclic alcohol. This was dehydrated over alumina at 427°. Hydrogenation then gave *t*-amylcyclohexane. Dehydrogenation by platinum at 250° gave the authentic specimen of *t*-amylbenzene. This was used because the commercial material was found to contain other amylbenzenes.

In order to compare the derivatives of 2-methyl-3-phenylbutane with those of *t*-amylbenzene, the former hydrocarbon[7] was synthesized by treating acetophenone with isopropylmagnesium bromide, dehydrating the resulting carbinol with oxalic acid, and hydrogenating the olefins with a nickel catalyst in the usual way.

The melting points of the derivatives of the amylbenzenes are given in the table.

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[1] Presented before the Division of Organic Chemistry of the American Chemical Society at Rochester, New York, September 6–10, 1937.

[2] Ipatieff, Pines and Schaad, THIS JOURNAL, **56**, 2696 (1934).

[3] Laughlin, Nash and Whitmore, *ibid.*, **56**, 1395 (1934).

[4] Ipatieff, *Ber.*, **36**, 2003 (1903).

[5] Norris and Reuter, THIS JOURNAL, **49**, 2624 (1927).

[6] Ipatieff and Schmerling, *ibid.*, **59**, 1056 (1937).

[7] Auwers and Eisenlohr, *J. prakt. Chem.*, [2] **82**, 93 (1910).