

Grignard reagent and both nitroso compounds is a rearrangement product. It is the only case where the bromine is replaced by the action of the organometallic compound.

4. All the organometallic compounds except the methyl Grignard reagent, tended to some extent to split out HX.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Conductance of Non-aqueous Solutions. I. Sodium Triphenylboron and Disodium Tri- α -naphthylboron in Diethyl Ether

BY HENRY E. BENT AND MAURICE DORFMAN

Considerable work has been published recently from this Laboratory dealing with the alkali metal derivatives of various organic compounds. These compounds are salt-like in their character and conduct an electric current in non-aqueous solutions. The dissociation constants of these salts are not known but the assumption has been made that they are all of the same order of magnitude.^{1,2} The data of this paper will be used later to test this assumption and are of immediate interest in establishing the structure of disodium tri- α -naphthylboron. A preliminary report of the experimental method³ is given.

Sodium triphenylboron is a peculiar compound.⁴ Triphenylboron is saturated as far as primary valence forces are concerned. It is true that it may readily add other molecules such as ammonia by means of a coördinate covalence but this can hardly be the case for sodium. The sodium addition compound conducts an electric current in diethyl ether solution and therefore presumably the sodium ion is held to the triphenylboron ion by electrostatic force.⁵ The stability of sodium triphenylboron is therefore apparently due to a large electron affinity of triphenylboron. This in turn is probably due to the fact that the negative ion may be represented by a large number of

structures, which result in a stabilization as a result of the phenomenon of resonance.⁶

The compound disodium tri- α -naphthylboron is still more curious. The second sodium is held rather loosely.⁷ It was not possible, however, to measure ΔF for the addition of the second sodium due to the fact that an amalgam which might be in equilibrium with the compound would be solid at ordinary temperatures.

It seemed quite possible that a study of the conductance of solutions of these compounds, especially when compared with sodium triphenylmethyl, might shed some light on their structure and properties.

The method used experimentally was the ordinary a. c. procedure for resistances up to about 10^6 ohms. For higher resistance a d. c. method was adopted. The two methods were found to check in the region in which they overlapped.

Experimental Part

The cell "A," buret "B," and the tube in which the sodium addition compound was prepared are shown in Fig. 1. Two sheets of platinum, 1 cm. wide by 2 cm. long, were held rigidly about 1 mm. apart as indicated at the right in Fig. 1. Six holes were drilled in the sheets and soft glass rods pulled down to the size of the holes. A small bead was placed at the middle of each rod, the platinum sheets slipped over the ends and then by means of a small flame the end heated until sufficiently soft to allow it to be mashed down with a graphite rod. Heavy platinum wires were welded to the sheets of bright platinum and these in turn welded to No. 40 platinum ribbon, the latter being sealed into Pyrex as described by Bent and Gilfillan.⁸ The cell constant was 0.00898.

The sodium addition compound was prepared in "C" by shaking a known weight of the boron compound with 40% sodium amalgam. The product was poured into the buret quantitatively by distilling ether back into "C"

(1) Bent, *et al.*, THIS JOURNAL, **52**, 1498 (1930); **53**, 1786 (1931); **54**, 1393, 3250 (1932); **57**, 1217, 1242, 1259 (1935).

(2) Conant and Wheland, *ibid.*, **54**, 1212 (1932); McEwen, work soon to be published.

(3) This work was in progress before the first paper of Fuoss and Kraus [*ibid.*, **55**, 476 (1933)] appeared. In order to minimize the importance of polarization potentials they found it convenient to work with potentials as high as 150 v. In order to avoid the same difficulty we used potentials as small as possible, in most cases not more than 20 mv. A high sensitivity galvanometer made possible the use of these small potentials. Under these conditions polarization potentials gave no trouble.

(4) The stability of this compound has been reported in an earlier communication, Bent and Dorfman, *ibid.*, **57**, 1259 (1935).

(5) Krause and Polack [*Ber.*, **59**, 777 (1926)] state that sodium triphenylboron has a small conductivity in ether solution but give no quantitative data.

(6) Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

(7) Bent and Dorfman, *loc. cit.*

(8) Bent and Gilfillan, THIS JOURNAL, **55**, 3989 (1933).

thereby washing the amalgam. Tube "C" was sealed off at the constriction. Solution was then poured into "A." Dilutions were accomplished by pouring a given quantity into "B" and distilling ether back into the cell. This procedure made it possible to work with extremely dilute solutions without introducing uncertainty due to water given off by the glass. The small amount of water liberated during the early part of a run would not affect appreciably the concentration of the original concentrated solution. Experiments on the most dilute solutions were then made in glass which had been in contact with the solution so long as to introduce no further appreciable error from this source.⁹ The procedure of pouring all of the material into the cell and repeating the run with the same sample of material served as a check on the unimportance of decomposition due to water given off by the glass.

In making d. c. measurements a Wolf potentiometer, direct reading to 0.01 mv., was used to apply a variable potential to the cell. In series with the cell was a Leeds and Northrup type HS galvanometer, mounted on a Julius suspension. This instrument has a sensitivity of 1 mm. for 10^{-11} amp. The procedure consisted in determining the potential necessary to produce 10 cm. deflection of the galvanometer when applied through a standard resistance. The cell was then added to the circuit and the potential determined which would give the same deflection of the galvanometer. The accuracy of the measurement, therefore, is essentially that of the Wolf potentiometer. With the technique described above it was quite easy to obtain an accuracy of from 1-5% in the measurement of the resistance of the cells over the range from 2×10^4 to 5×10^8 ohms. When the specific conductance became as small as 5×10^{-10} further dilution had no effect. This was probably due to adsorbed material as the specific conductance of ether is less than 4×10^{-12} . This final value of 5×10^{-10} was taken as the specific

TABLE I
CONDUCTANCE OF DISODIUM TRI- α -NAPHTHYLBORON IN DIETHYL ETHER SOLUTION AT 0°

Equiv. per liter $\times 10^7$	Λ	Equiv. per liter $\times 10^7$	Λ
792,000	0.00674	792,000	0.00672
162,000	.00539	368,000	.00544
34,900	.00742	66,300	.00636
6,560	.0143	8,500	.0126
1,204	.040	272	.0116
144.4	.187	29.6	.0510
2.92	3.1	1.27	.036

TABLE II
CONDUCTANCE OF SODIUM TRIPHENYLBORON IN DIETHYL ETHER SOLUTION AT 0°

Equiv. per liter $\times 10^7$	Λ	Equiv. per liter $\times 10^7$	Λ
26,860	0.0284	26,860	0.0284
14,000	.0357	5,290	.0517
3,210	.0588	332	.117
695	.0921	34.4	.286
106	.146	2.50	1.07
9.8	.476	0.257	3.07

(9) Bent and Lesnick, THIS JOURNAL, 57, 1246 (1935).

TABLE III
CONDUCTANCE OF DISODIUM TRI- α -NAPHTHYLBORON IN DIETHYL ETHER SOLUTION AT 25°

Equiv. per liter $\times 10^7$	Λ
758,000	0.00598
154,400	.00455
32,840	.00598
7,260	.00955
1,150	.0318
136	.170

TABLE IV
CONDUCTANCE OF SODIUM TRIPHENYLBORON IN DIETHYL ETHER SOLUTION AT 25°

Equiv. per liter $\times 10^7$	Λ
25,990	0.0243
13,500	.0296
3,100	.0491
665	.0778

conductance of the solvent and subtracted from the observed reading for the most dilute solutions where it would begin to be important.

The experimental results are given in Tables I, II, III and IV and in Fig. 2.

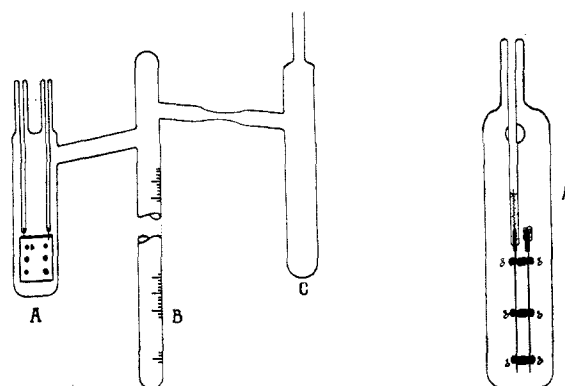
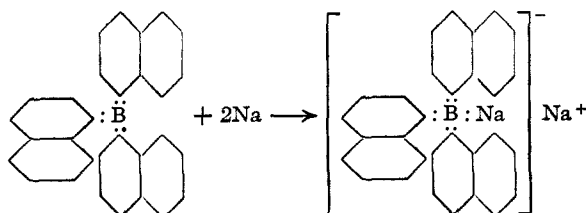


Fig. 1.

Discussion of Results

The fact that tri- α -naphthylboron can add two electrons suggested that the reaction with two atoms of sodium might be represented by the structural formulas



The two electrons from the sodium atoms are here assumed to complete a group of eight about a boron atom. One of the sodium ions is drawn to the boron atom by the strong electrostatic

force but the other is unable to approach so closely on account of the three phenyl groups attached to the boron. If this picture is correct, one would expect one of the sodium ions to dissociate very readily, giving rise to a relatively strong electrolyte.

A second possibility is that a quinonoid structure results in the localization of the negative charge at the para position of one of the benzene rings. If such a structure represents the molecule the absence of steric hindrance would permit both sodium ions to come close to the carbon atom, one on either side of the ring. A further argument in favor of the quinonoid structure is to be found in

tained the curves reported in Fig. 2. The curve for sodium triphenylboron (curve No. 1) which was run for comparison seems quite normal. There is a little kink in the curve at a rather smaller concentration than one might expect. The slope of the curve is -0.5 , as one would expect for a uni-univalent electrolyte.¹¹

It follows from Oswald's dilution law that if we are working at concentrations such that only a small fraction of the material is ionized we may write

$$K = \frac{(\text{Na}^+)(\text{R}^-)}{(\text{NaR})} = \frac{\alpha^2 C}{(1-\alpha)} = \alpha^2 C = \frac{\Lambda^2}{\Lambda_\infty^2} C$$

$$\text{or } \log \Lambda = \log \Lambda_\infty K^{1/2} - 1/2 \log C$$

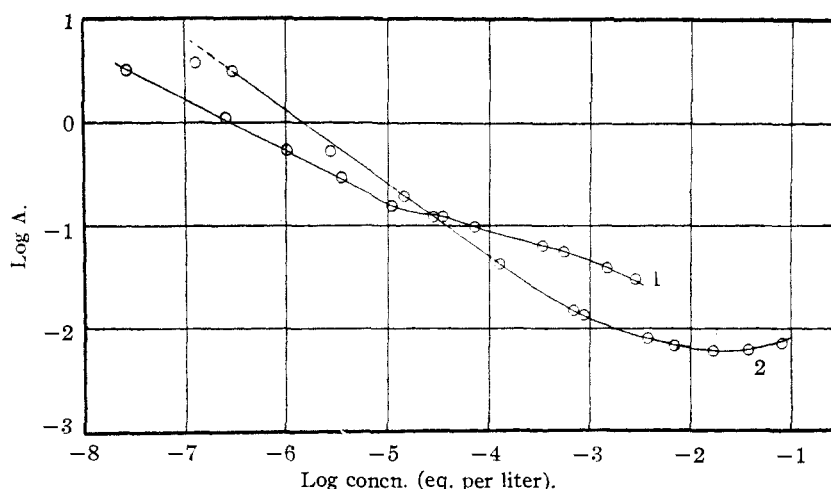


Fig. 2.—Curve 1, sodium triphenylboron; curve 2, disodium tri- α -naphthylboron.

the fact that triphenylboron is not able to add a second atom of sodium. The oxidation potential of 1,4-naphthoquinone is 0.495 and of 1,4-benzoquinone is 0.711 v.¹⁰ The larger oxidation potential is exhibited by that compound for which the quinonoid structure is relatively less stable. If this second hypothesis is correct then we would expect triphenylboron to add a second atom of sodium less readily than tri- α -naphthylboron. We attempted to prepare trianthracylboron (9, 10-anthraquinone has a potential of 0.157 v.) in order to test the influence of the oxidation-reduction potential. However, the methods used in preparing triphenylboron and tri- α -naphthylboron were not successful.

It was in order to test these hypotheses with regard to the nature of the union of the two sodium atoms that the conductance experiments were initiated. To our great surprise we ob-

Plotting $\log \Lambda$ against $\log C$ the slope should be -0.5 . As is evident from the figure, however, disodium tri- α -naphthylboron is neither a much stronger electrolyte than sodium triphenylboron nor is the slope of the curve -0.5 . On the contrary, the slope of the curve plotting $\log \Lambda$ against $\log C$ is -0.69 ± 0.02 . This slope of approximately $2/3$ can be accounted for in the following way. If we assume that both sodium atoms ionize simultane-

ously, then we obtain the following equations.

$$K = \frac{(\text{Na}^+)^2(\text{R}^-)}{\text{Na}_2\text{R}} = \frac{(\alpha C)^2(\alpha C)}{(1-\alpha)C} = \alpha^3 C^2 = \frac{\Lambda^3}{\Lambda_\infty^3} C^2$$

$$\text{or } \log \Lambda = \log \Lambda_\infty K^{1/3} - 2/3 \log C$$

This gives an explanation for the slope of the conductance curve of $-2/3$ but leads to the very surprising conclusion that here we are dealing with a weak electrolyte presumably capable of ionizing in steps and yet both sodium atoms come off simultaneously. This cannot be accounted for by assuming simply that the two atoms are distantly located in the molecule, for, as has been shown by Adams,¹² such an assumption leads to the conclusion that the statistical factor would only double the apparent ionization constant. Evidently there must be possible some rearrangement of the molecule which can take place only when both sodium ions have been removed, or which, taking place when one ion is gone, suffi-

(10) "I. C. T.," Vol. 6, p. 334. These values are for 0.5 N HCl, 95% ethyl alcohol.

(11) Kraus and Fuoss, *This Journal*, **55**, 21 (1933).

(12) Adams, *ibid.*, **38**, 1503 (1916).

ciently weakens the force of attraction for the second ion that it ionizes readily. The energy change for this rearrangement must be sufficiently large to more than offset the coulomb energy which would normally make the second sodium ion ionize with much less ease.

On the basis of these facts the following hypothesis is suggested. The two electrons furnished by the two sodium atoms are localized in the ion, on a carbon atom in a quinonoid ring. The two sodium ions are held closely to the negative charge, one on either side of the atom on which the electrons are localized. When one of the sodium ions leaves, the coulomb force of the single sodium ion then becomes too small to cause this localization of the electrons to continue. The pair of electrons then resonates among all of the various quinonoid structures which can be written for the molecule with the result that the effective size of the ion is greatly increased, the coulomb force weakened and the second sodium ionizes as though the salt were a strong electrolyte.

Referring now to the equilibrium data¹³ we find what at first glance would appear to be a contradiction. One of the sodium atoms can be removed easily by shaking disodium tri- α -naphthylboron with an amalgam while the other sodium atom is removed only by shaking with a more dilute amalgam. This turns out not to be a contradiction, however, but is quite capable of being explained without modifying the above theory. If we are right in assuming that both electrons are located on the same atom and that they

(13) Bent and Dorfman, *loc. cit.*

resonate together, then we would expect a large coulomb repulsion term on account of the proximity of the two negative charges. This would account for the difficulty of adding a second sodium atom to monosodium tri- α -naphthylboron. When we consider the process of ionization, however, we are not removing electrons and hence this coulomb term does not enter into the dissociation constants of the ions.

The theory which has just been outlined is in harmony with all of the observations which we have made on these compounds. It is of course desirable to have more data in order to test further the theory.

In a later communication the significance of the temperature coefficient of conductance will be considered. It is not unusual for weak electrolytes in non-aqueous solution to exhibit a negative coefficient.¹⁴

Summary

A simple method is described for measuring the specific resistance of non-aqueous solutions. This method has been used for specific resistances up to 5×10^{10} ohms.

The equivalent conductance for sodium triphenylboron and disodium tri- α -naphthylboron in ether solution has been determined at 0 and 25° and from 10^{-1} to 10^{-7} mole per liter.

The bearing of these results on the structure of disodium tri- α -naphthylboron is discussed.

(14) Kraus, "The Properties of Electrically Conducting Systems," Chemical Catalog Co., New York City, 1922, p. 144.

[CONTRIBUTION OF THE CHEMICAL LABORATORIES OF THE RICE INSTITUTE]

Synthesis of Certain Pyridine Derivatives of Barbituric Acid

BY CARL SELLNER KUHN AND G. HOLMES RICHTER

The discovery of the substituted barbituric acids as hypnotics was followed by their administration in conjunction with various other drugs which enhanced their effectiveness. The analgesics and antipyretics are the most commonly used for this purpose. Since many of these drugs are basic, such as the alkaloids and other heterocyclic nitrogen compounds, they will form very definite "molecular compounds" with the acidic barbituric acid derivatives.

The effectiveness of drugs of this type suggests that the heterocyclic substituted barbituric acids would be interesting compounds. In contrast to the easy preparation of the molecular compounds or salts mentioned above, the introduction of a heterocyclic residue in the 5-position of barbituric acids presents a much more difficult problem, since the active halides and the aldehydes of this class of compounds are limited in number or are difficult to synthesize. A review of the