4. The variation of reaction velocity with temperature was determined approximately in the case of chromium oxide.
5. A mechanism is provided by the activated adsorption of hydrogen which occurs on chromium oxide, zinc oxide and zinc chromite; on alumina, it is probably the water which is activated.
6. The existence of this exchange is important, since it may cause unintentional replacement of deuterium by the light isotope in a reaction mixture.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Electron Affinity of Free Radicals. VII. Triphenylboron and Tri-α-naphthylboron

BY HENRY E. BENT AND MAURICE DORFMAN

The title of this paper is open to the criticism that triphenylboron should not be classed as a free radical, analogous to triphenylmethyl. The electronic formula indicates that the three electrons of boron are all utilized in forming non-polar bonds with three phenyl groups and therefore the molecule would appear to be saturated and not capable of association. Molecular weight determinations indicate that no association occurs.[1] On the other hand, there are chemical reactions of boron compounds which would indicate that this compound is comparable to a free radical. The close parallel between C_2H_6 and $C(C_6H_5)_3$ on the one hand and B_2H_6 and $B(C_6H_5)_3$ on the other is perhaps not very significant. In the case of addition of sodium, however, there seems to be close similarity between triphenylboron and triphenylmethyl. Both compounds add sodium from dilute amalgam and in both cases the sodium is removed by mercury.[2] In the case of triphenylmethyl the free-energy change for the reaction has been determined, but in the case of triphenylboron only qualitative experiments have been reported. It seemed very desirable, therefore, to study triphenylboron quantitatively, especially so in view of the fact that in the case of triphenylmethyl the reaction may be considered to involve the addition of an electron to complete a group of eight electrons, while in the case of triphenylboron the addition of an electron results in only seven electrons around the boron atom. As might be expected the results reported below indicate that there is a much greater tendency to form the group of eight. The results give a measure of the difference between these two reactions.

Triphenylboron

In several respects the behavior of triphenylboron is quite different from that of triphenylmethyl. Shaking triphenylboron with 40% amalgam produced the sodium addition compound rapidly and quantitatively. However, shaking the addition compound with mercury or dilute amalgam gave quite erratic results. This was finally traced to a very slow reaction, requiring months for substantially equilibrium conditions to be established. The final data given in Table I were obtained from runs some of which were shaken for four months, the equilibrium being approached from both sides.

The second peculiarity of triphenylboron was the anomalous color observed when the sodium addition compound was shaken with mercury or dilute amalgam. The sodium addition compound has a very decided yellow color and could be recrystallized repeatedly in a closed system without alteration in the intensity of the color. However, when part of the sodium was removed by shaking with dilute amalgam or with mercury the color entirely disappeared. Analysis of the ether solution showed that not more than 70% of the sodium had been removed and therefore one would have expected a very decided color. Similar results were obtained when the equilibrium was approached from the other side. A dilute amalgam would introduce as much as 20% of an equivalent amount of sodium without the appearance of any color in the solution. That decomposition was not taking place was definitely proved by first preparing the sodium addition compound with 40% amalgam, then removing part of the sodium with mercury, and finally again shaking the solution with 40% amalgam. A very close check on the amount of triphenylboron taken originally

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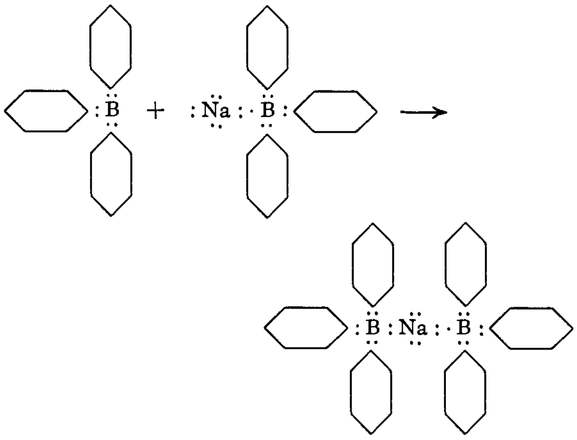
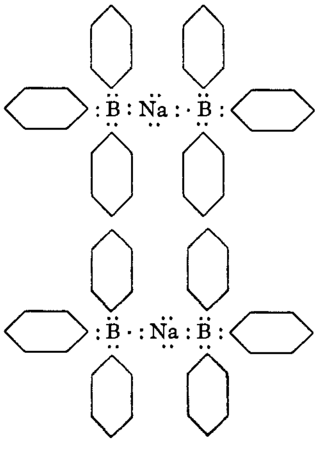
[1] Krause and Dittmar, *Ber.*, **63**, 2347 (1930).

[2] (a) Krause and Polack, *ibid.*, **59**, 777 (1926); (b) Bent, THIS JOURNAL, **52**, 1498 (1930).

was obtained by titrating the final amount of sodium with dilute acid.

Since all reactions appeared to be clean cut and reversible and the materials were evidently of high purity, the most natural explanation of the above phenomena would be to assume that triphenylboron reacts with the sodium addition compound to form a colorless addition product. The equation given below indicates a possible mechanism by which this reaction might take place. The small ionization constant of sodium triphenylboron (which will be reported later) indicates that we are to consider practically all of this material in the form of ion pairs. The unshared electrons of the sodium then offer the possibility of combining with the boron atom of another molecule of triphenylboron to form a coördinate covalent bond. The resulting compound may be much more stable than most compounds of this type due to the possibility of resonance in the final compound as a result of structures of the following type. As these two structures are identical we might expect the resonance energy to have a rather large stabilizing effect on the compound.





It is interesting to note that the same type of resonance is possible for triphenylboron and for sodium triphenylboron as has been assumed by Pauling and Wheland[3] and Hückel[4] for triphenylmethyl.

Boron trifluoride was prepared according to the method of Schiff.[5] Triphenylboron was then prepared essentially according to the method of Krause and Polack.[2a] After the reaction of the Grignard reagent prepared from bromobenzene with the boron trifluoride is completed the ether solution is transferred to another flask by nitrogen pressure. The ether is then removed by distillation and finally the complex decomposed as the triphenylboron is distilled *in vacuo* at a temperature of between 300 and 350°. Anhydrous ether is then distilled into the flask containing the triphenylboron. Fractional crystallization from ether in a closed system is carried out three times, the ether being finally removed by heating to 130° while exhausting the apparatus. The product melted sharply at 137° (Krause gives 136° uncorr.). As a further check on the purity, repeated titrations of the sodium addition compound gave the calculated amount of sodium.

The equilibrium data are given in Table I. The first run was shaken for five weeks and the fourth run for one week. These runs are probably not quite as reliable as the other four runs which were shaken for four and a half months. The values of log K_2 in the sixth column are for the reaction

$$R + Na = Na^+ + R^-$$

assuming the ionization constant to be 10^{-4}. As has been pointed out in the last two papers of this series, this value of 10^{-4} is undoubtedly too large but will be used in com-

TABLE I

EQUILIBRIUM DATA FOR THE ADDITION OF SODIUM TO TRIPHENYLBORON AT 25°

In Runs 1–3 a dilute amalgam was shaken with triphenylboron. In Runs 4–6, a dilute amalgam was shaken with sodium triphenylboron.

The meaning of the symbols is the same as in earlier papers of this series. K refers to an equilibrium constant and R represents triphenylboron.

K_2 is for the reaction $Na + R \longrightarrow NaR$

K_3 is for the reaction $NaR \longrightarrow Na^+ + R^-$

Further details of the computation are given in the first paper of this series.[2b]

ΔF is calculated neglecting the reaction $NaR + R \longrightarrow NaR_2$. The energy change for this reaction is probably not large.

Run	G. atoms of triphenyl boron × 10^4	G. atoms of sodium triphenyl boron × 10^4	Moles of ether	Mole fraction of amalgam	log K_2 $K_3 = 10^{-4}$	ΔF
1	2.48	0.256	0.11	0.0516	7.89	
2	1.235	.336	.281	.0503	8.23	
3	1.593	.329	.306	.0530	8.42	
4	2.12	.908	.51	.0520	8.46	
5	0.980	1.035	.298	.0514	8.94	
6	.726	1.065	.308	.0513	9.08	
				Average	8.44	−11.50 kcal.

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

(4) Hückel, *Z. Physik*, **83**, 632 (1933).

(5) Schiff, *Ann., Supplement*, **5**, 172 (1865–1867).

paring these results with the data on triphenylmethyl until we are able to give a more precise value to this ionization constant. This point will be discussed in more detail in a later communication.

Work with potassium and lithium amalgams was not carried to completion. In the case of potassium a precipitate was formed and in the case of lithium only a small amount of the addition compound was formed.

Tri-α-naphthylboron

The directions of Krause and Nobbe[6] were followed. Bromonaphthalene obtained from Eastman Kodak Co. was fractionated under reduced pressure. The crude product obtained by decomposition of the magnesium complex with ice water, was crystallized three times, m. p. 200° uncorr. (Krause gives 203° corr.). An added check on the purity of the material was obtained in the analyses of the disodium addition compound. These have already been reported in a communication.[7] These analyses established the fact that tri-α-naphthylboron combines with two atoms of sodium. Shaking a solution of this compound, which is very intensely colored, causes the solution to pass from a black through a brown to a light yellow. In every case more than half of the sodium was removed. This indicates that the second sodium is removed quite readily. This is confirmed by an experiment in which tri-α-naphthylboron was added to a solution of the disodium derivative. The color immediately changed to a brown indicating that the reaction $R + RNa_2 \longrightarrow 2RNa$ takes place, in which "R" represents tri-α-naphthylboron. This experiment also indicates that the monosodium derivative is brown. The "black" solution of the disodium derivative is found, on high dilution, to have a purplish tint. Inasmuch as the second sodium is held much less firmly than the first and the total amount of sodium in solution in an equilibrium determination was always less than one equivalent, it is not necessary to consider the second sodium in the calculations.

The monosodium derivative behaved in every way like sodium triphenylboron. The removal of sodium was slow and was not complete even with large volumes of mercury which one would calculate should remove essentially all of the sodium. In order to avoid any uncertainty, however, as in the case of triphenylboron the equilibrium was approached from both sides. As in the case of triphenylboron, the introduction of a small amount of sodium did not produce the intensity of color which one would have expected. The explanation is probably the same as that given for triphenylboron. The experimental results are given in Table II.

TABLE II

EQUILIBRIUM DATA FOR THE ADDITION OF SODIUM TO TRI-α-NAPHTHYLBORON

In Runs 1 and 2 a dilute amalgam was shaken with sodium tri-α-naphthylboron. In Runs 3 and 4 a dilute amalgam was shaken with tri-α-naphthylboron.

Run	Moles of R × 10^4	Moles of NaR × 10^4	Moles of ether	Mole fraction of amalgam	Log K_2 K_3 = 10^{-4}	ΔF
1	0.834	0.385	0.281	0.0508	8.46	
2	1.160	.575	.296	.0494	7.60	
3	0.961	.133	.250	.0522	7.72	
4	1.206	.210	.302	.0515	7.89	
				Average	8.17	−11.2 kcal.

Tri-α-naphthylboron reacted with metallic potassium to give a very dark solution, similar in color to the disodium derivative. However, the solubility was apparently much less than in the case of sodium and consequently no analysis was made of the product of the reaction.

Conclusions

1. Triphenylboron and tri-α-naphthylboron behave like free radicals in that they add sodium. The free-energy change for the reaction, however, is considerably smaller, as one might expect from the fact that a group of seven electrons is formed around the boron atom. The reaction is also very slow.
2. The color of the equilibrium mixtures is much lighter than one would expect from their sodium content. This is interpreted in terms of a definite complex.
3. Tri-α-naphthylboron is found to add two atoms of sodium, giving the boron an effective valence of five.
4. The second atom to add to tri-α-naphthylboron is found to be held very much less firmly than the first.

CAMBRIDGE, MASS.

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[6] Krause and Nobbe, *Ber.*, **64**, 2112 (1931).

[7] Bent and Dorfman, THIS JOURNAL, **54**, 2132 (1932).