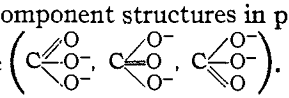
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Interaction of the Boron Sextet with Adjacent Groups

BY DAVID L. YABROFF, G. E. K. BRANCH AND H. J. ALMQUIST

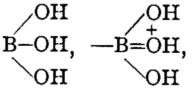
Many of the peculiarities in the chemistry of compounds having a nitrogen or oxygen atom adjacent to a double bond can be explained by Ingold's theory[1] of the tautomeric or T-effect. A T-effect is associated with the possibility of a tautomeric shift in which unshared electron pairs or those in double bonds are redistributed among the atoms of the molecule. The resulting structure cannot be depicted by a simple bond formula, for it is a combination of two or more possible structures. In a sense Ingold's theory is a revival of Laar's theory[2] of tautomerism. We shall depict the formulas of compounds having this type of tautomerism by enclosing the formulas for the component structures in parentheses. Thus for carbonate ion we shall write



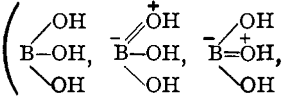
$\left(\mathrm{C}\begin{smallmatrix}/\!\!/\mathrm{O}\\-\mathrm{O}^-\\\diagdown\mathrm{O}^-\end{smallmatrix},\ \mathrm{C}\begin{smallmatrix}\diagup\mathrm{O}^-\\=\mathrm{O}\\\diagdown\mathrm{O}^-\end{smallmatrix},\ \mathrm{C}\begin{smallmatrix}\diagup\mathrm{O}^-\\-\mathrm{O}^-\\\diagdown\!\!\diagdown\mathrm{O}\end{smallmatrix}\right)$.

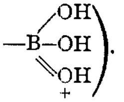
From quantum mechanical considerations Pauling[3] and Slater[4] have shown the possibility of these combination structures. They restrict the phenomenon to cases in which the component structures have the same multiplicity, approximately the same energy, and differ only in the arrangements of the electrons. It was the lack of this last restriction that made Laar's views untenable. The T-effects are to be regarded as chemical phenomena that result from the lowering of the potential energy of a molecule through resonance between its various possible structures.

In trivalent boron compounds a similar phenomenon might be expected. The tendency of a boron atom to complete its octet may draw two electrons from an adjacent structure. These electrons may be supplied by a double bond or by an unshared electron pair of an adjacent atom. This drawing of an electron pair (T-effect) is great when these unshared electrons belong to a nitrogen or oxygen atom, and small when they belong to a halogen atom or to a double bond. It is also possible that when a boron and an oxygen atom are attached to each other the unshared electrons of the oxygen combine completely with the boron atom. Boric acid may be

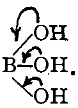


$\mathrm{B}\begin{smallmatrix}\diagup\mathrm{OH}\\-\mathrm{OH}\\\diagdown\mathrm{OH}\end{smallmatrix},\ -\mathrm{B}\begin{smallmatrix}\diagup\mathrm{OH}\\=\overset{+}{\mathrm{O}}\mathrm{H}\\\diagdown\mathrm{OH}\end{smallmatrix},$ or the combination formula





$\left(\mathrm{B}\begin{smallmatrix}\diagup\mathrm{OH}\\-\mathrm{OH}\\\diagdown\mathrm{OH}\end{smallmatrix},\ \overset{-}{\mathrm{B}}\begin{smallmatrix}/\!\!/\overset{+}{\mathrm{O}}\mathrm{H}\\-\mathrm{OH}\\\diagdown\mathrm{OH}\end{smallmatrix},\ \overset{-}{\mathrm{B}}\begin{smallmatrix}\diagup\mathrm{OH}\\=\overset{+}{\mathrm{O}}\mathrm{H}\\\diagdown\mathrm{OH}\end{smallmatrix},\ -\mathrm{B}\begin{smallmatrix}\diagup\mathrm{OH}\\-\mathrm{OH}\\\diagdown\!\!\diagdown\underset{+}{\mathrm{O}}\mathrm{H}\end{smallmatrix}\right)$. The latter formula might also be written as



$\mathrm{B}\begin{smallmatrix}\diagup\mathrm{OH}\\-\mathrm{OH}\\\diagdown\mathrm{OH}\end{smallmatrix}$.

---

(1) Ingold, *Rec. trav. chim.*, **48**, 797 (1929).

(2) Laar, *Ber.*, **18**, 648 (1885).

(3) Pauling, THIS JOURNAL, **53**, 3225 (1931); *Phys. Rev.*, **37**, 1185 (1931).

(4) Slater, *ibid.*, **37**, 489 (1931).

The necessity for the theory of the T-effect or some other similar theory arises from the impossibility of explaining the vagaries of chemical properties on I- and D-effects[1] alone. These latter effects arise from the electrical dipoles which result from the unequal sharing of an electron pair between two unlike atoms. The direction of the two effects is the same, but the I-effect is considered as being induced from atom to atom along a chain, whereas the D-effect is considered as acting directly through space by virtue of the charge created by the small dipoles. It is reasonable to assume that the pull exerted on a shared electron pair by an atom will increase with increasing nuclear charge.[5] We shall assume, therefore, that the elements boron, carbon, nitrogen, oxygen, and fluorine are in the order of increasing negativity or electron attractions. We shall also assume that in the absence of T-effects an hydroxyl group exerts a greater pull on electrons than a phenyl group.

The evidence for T-effects in boron compounds consists of showing apparent reversals of the assumed order of negativities. Similar reversals are found in compounds with oxygen or nitrogen atoms adjacent to double bonds and have been explained as T-effects. The theory of the T-effect is merely a mechanism that connects these apparently unrelated phenomena.

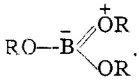
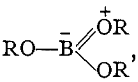
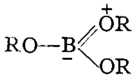
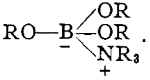
Evidence from the Formation of Addition Compounds

Boron compounds of the type BX_3 (with only a sextet of electrons about the boron atom) are characterized by their tendency to combine with molecules having atoms with unshared electron pairs. This reaction is similar in certain respects to the addition of a hydrogen ion to an unshared pair of electrons and is obviously dependent on the nature of the groups attached to the central boron atom. Groups that pull electrons from the boron atom increase its effective positive charge and enhance its combining power, whereas groups that supply electrons to the boron atom decrease its combining power. The I-effects of both chlorine atoms and alkoxyl groups pull electrons from the boron atom, while in both cases the T-effects arising from the presence of the unshared electron pairs tend to supply the boron atom with electrons. In halogen atoms the I-effects predominate over the T-effects, but in alkoxyl groups the reverse is true. Hence the boron atom in a boron trihalide has a greater combining power than one in a boric acid derivative, but as this order is predictable from the I-effects alone, it does not necessarily show the existence of T-effects.

Both the I-effects and T-effects of alkyl and aryl groups are less than those of alkoxyl groups. Consequently if only I-effects exist, a boron atom in a derivative of boric acid should have a greater combining power than one in a boron alkyl or aryl compound. The reverse phenomenon is

---

[5] Latimer and Rodebush, THIS JOURNAL, **42**, 1419 (1920); Latimer and Porter, *ibid.*, **52**, 206 (1930).

evidence of a T-effect or of the formation of compounds of the type  $\mathrm{RO{-}}\overset{-}{\mathrm{B}}\begin{smallmatrix}/\!\!/\,\overset{+}{\mathrm{O}}\mathrm{R}\\ \diagdown\,\mathrm{OR}\end{smallmatrix}$. If the lack of combining power of the boron atom in a boric acid derivative is due to a T-effect, all the oxygen atoms tend to supply the boron atom with electrons, and the more oxygen atoms there are the less is the combining power of the boron atom. If the borate is  $\mathrm{RO{-}}\overset{-}{\mathrm{B}}\begin{smallmatrix}/\!\!/\,\overset{+}{\mathrm{O}}\mathrm{R}\\ \diagdown\,\mathrm{OR}\end{smallmatrix}$, a single oxygen is sufficient to saturate the boron atom, and the presence of additional oxygen atoms will tend to decrease this saturation owing to their I-effects. This follows because in  $\mathrm{RO{-}}\underset{-}{\mathrm{B}}\begin{smallmatrix}/\!\!/\,\overset{+}{\mathrm{O}}\mathrm{R}\\ \diagdown\,\mathrm{OR}\end{smallmatrix}$ the positive charge is effectively nearer the alkoxyl groups, because of the polarizability of the double bond, than it is in an addition compound such as  $\mathrm{RO{-}}\underset{-}{\mathrm{B}}\begin{smallmatrix}/\,\mathrm{OR}\\ -\,\mathrm{OR}\\ \diagdown\,\underset{+}{\mathrm{N}}\mathrm{R_3}\end{smallmatrix}$.

The combining power of a boron atom in a given compound is correlated with the weakness of the bases (substances with unshared electron pairs) with which stable addition compounds are formed at room temperature. These must be true addition compounds containing four-bonded boron. Boron trihalides form stable addition compounds not only with amines,[6] but also with alcohols,[6a,7] ethers,[6a,8] esters,[6a,8,9] organic acids,[6a,10] acid anhydrides,[6a] amides[6a] and nitriles.[6a,6e,11] Some of these substances lack basic properties in the ordinary sense, but have unshared electron pairs. Boron triphenyl forms addition compounds with aliphatic amines and with aniline, but not with diphenylamine.[12] Phenylboric acid forms addition compounds with aliphatic amines and with pyridine but not with weaker bases.[13] The formation of these compounds is assisted by the addition of two more molecules of phenylboric acid. Isobutyl borate does not form addition compounds even with as strong a base as ammonia.[14] The evidence from the formation of addition compounds is therefore in favor of the existence of a T-effect, when a boron atom is singly bonded to an oxygen. As chemical properties are always dependent on many factors,[15] a structure should not be assigned to a substance on a single line of

---

(6) (a) Bowlus and Nieuwland, THIS JOURNAL, **53**, 3825 (1931); (b) Davy, *Phil. Trans.*, **102**, 368 (1812); (c) Kraus and Brown, THIS JOURNAL, **51**, 2690 (1929); (d) Berzelius, *Pogg. Ann.*, **2**, 148 (1824); (e) Johnson, *J. Phys. Chem.*, **16**, 1 (1912).

(7) Gasselin, *Ann. chim. phys.*, [7] **3**, 5 (1894).

(8) Sugden and Waloff, *J. Chem. Soc.*, 1492 (1932).

(9) Morgan and Taylor, *ibid.*, 1497 (1932).

(10) Meerwein, *Ann.*, **455**, 250 (1927).

(11) Patein, *Compt. rend.*, **113**, 85 (1891); Gautier, *ibid.*, **63**, 920 (1866); Martius, *Ann.*, **109**, 80 (1859); *Jahresb.*, 71 (1858).

(12) Krause, *Ber.*, **57**, 813 (1924).

(13) Branch and Yabroff, THIS JOURNAL, **54**, 2569 (1932); Yabroff and Branch, *ibid.*, **55**, 1663 (1933).

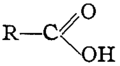
(14) Councler, *J. prakt. Chem.*, [2] **18**, 383 (1879).

(15) The most obvious other factors in the formation of the addition compounds of trivalent boron compounds are the crystal lattice energy and the solubility relationships.

evidence, but on an accumulation of lines. We shall proceed to other types of evidence for the T-effects that arise from the unsaturated character of a trivalent boron atom.

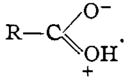
Evidence from the Dissociation Constants

The Derick factor[16] for a chlorine atom is greater than that for a carbonyl group, yet the carboxylic acids are much stronger than hypochlorous acid. Pauling[17] explains this apparent anomaly by use of combination structures for carboxylic acids, *e. g.*,



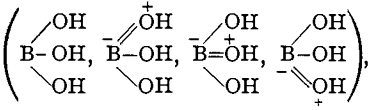
$\mathrm{R{-}C({=}O){-}OH}$

and



$\mathrm{R{-}C({-}O^-){=}\underset{+}{O}H}$.

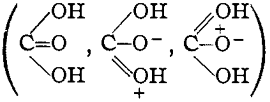
The contribution of the latter form tends to put a positive charge on the hydroxyl group and assists the dissociation of hydrogen ion. A similar anomaly exists in the strengths of boric acid ($K = 6 \times 10^{-10}$)[18] and chloral ($K = 10^{-11}$).[19] Boric acid is the stronger but chloral contains the more negative group (CCl_3 has about the same negativity as a chlorine atom). If boric acid is a combination structure of



$\left(\mathrm{B(OH)_3},\ \mathrm{(HO)_2\overset{-}{B}{=}\overset{+}{O}H},\ \mathrm{(HO)_2\overset{-}{B}{=}\overset{+}{O}H},\ \mathrm{(HO)_2\overset{-}{B}{=}\underset{+}{O}H}\right)$,

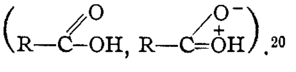
a positive charge is induced on the hydroxyl group, and the dissociation of hydrogen ion is increased.

Pauling[17] explained the greater weakness of carbonic than of other carboxylic acids on the basis of the smaller charge on any one hydroxyl group resulting from the additional state in the combination structure, or



$\left(\mathrm{(HO)_2C{=}O},\ \mathrm{HO{-}C({-}O^-){=}\underset{+}{O}H},\ \mathrm{HO{-}C({-}O^-){=}\overset{+}{O}H}\right)$

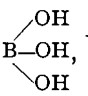
instead of



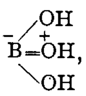
$\left(\mathrm{R{-}C({=}O){-}OH},\ \mathrm{R{-}C({-}O^-){=}\overset{+}{O}H}\right)$.[20]

In a similar way boric acid may be weaker than phenylboric acid, though the differences must of necessity be smaller. For this reason the dissociation constant of phenylboric acid was measured. It was found to be approximately three times as large as that of boric acid.

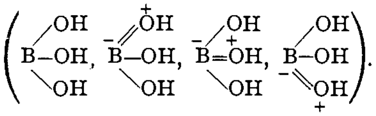
The strength of boric acid does not differentiate between the formulas



$\mathrm{B(OH)_3}$,



$\mathrm{(HO)_2\overset{-}{B}{=}\overset{+}{O}H}$, and



$\left(\mathrm{B(OH)_3},\ \mathrm{(HO)_2\overset{-}{B}{=}\overset{+}{O}H},\ \mathrm{(HO)_2\overset{-}{B}{=}\overset{+}{O}H},\ \mathrm{(HO)_2\overset{-}{B}{=}\underset{+}{O}H}\right)$.

The second formula shows a positive charge on the hydroxyl group as well as the last, and the first formula might also be that of an appreciably acidic substance because of the possible reaction, $B(OH)_3 + OH^- = B(OH)_4^-$. But the fact that

---

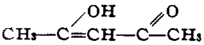
(16) Derick, THIS JOURNAL, **33**, 1153 (1911); **34**, 74 (1912); **40**, 537 (1918).

(17) Pauling, Lectures at the University of California, 1932.

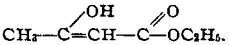
(18) Landolt and Börnstein, Vol. 2, Ed. 5, 1923, p. 1120.

(19) Reference 18, p. 1125.

(20) In order to avoid the possibility of decrease in the acidic strength through decomposition, the explanation would perhaps have been better applied to the anomaly of the greater acidic strength of



$\mathrm{CH_3{-}C(OH){=}CH{-}C({=}O){-}CH_3}$ than of



$\mathrm{CH_3{-}C(OH){=}CH{-}C({=}O){-}OC_2H_5}$.

phenylboric acid is stronger and not weaker than boric acid is not readily explained by any but the combination structure, and is equally well explained by this structure whether the reaction is an addition of hydroxide ion or a dissociation of hydrogen ion. In both the other structures, additional hydroxyl groups would increase the acidic strength.

Evidence from Benzene Substitution

If we accept the theory of the T-effect arising from the juxtaposition of a boron sextet and an hydroxyl group, it also implies that there is a T-effect between a boron atom and an attached phenyl group in which electrons are pulled from the benzene ring. In substitution reactions of aromatic compounds the benzene ring is activated and its ability to supply electrons to the boron sextet is greatly enhanced. Evidence for tautomeric interaction between the benzene ring and the boron atom should therefore be sought in the substitution reactions of the phenyl nucleus.

The above hypothesized T-effect between a boron atom and a phenyl group not only supplies electrons to the boron atom but pulls electrons from the phenyl group, a process which, according to Ingold,[1] leads to meta substitution reactions of the benzene ring. Meta orientation by a trivalent boron atom is analogous to ortho-para orientation by a trivalent nitrogen atom, for these orientations are due to T-effects that arise from the tendencies of trivalent nitrogen and trivalent boron to form additional bonds. When a trivalent nitrogen atom forms an additional bond it becomes positively charged and its orienting power is inverted. Since substitution reactions are much faster with aromatic amino compounds than with aromatic derivatives of the $—NH_3^+$ group, the presence of a very small quantity of trivalent nitrogen results in ortho-para substitution. Inversion of the orienting power (from *o-p* to *m*) is obtained only in the presence of very concentrated acids. When trivalent boron compounds form addition products, the boron atom acquires a negative charge and ortho-para orienting power. As ortho-para substitutions are in general faster than meta substitutions, the inversion of the orienting power of the boron atom (from *m* to *o-p*) does not require practically complete formation of an addition compound, but may be expected when only a very small fraction of the boron has a higher valence than three. In this last point the analogy between the meta orienting power of the trivalent boron atom and the ortho-para orienting power of trivalent nitrogen breaks down.

The orientations of substituents into phenylboric acid and into acetanilide are analogous. In both, the atom attached to the benzene ring has a T-effect (primary T-effect), in one leading to meta, and in the other to ortho-para substitution. In both substances this atom (B or N) is attached to a group (OH or $COCH_3$) that also has a T-effect (secondary T-effect) tending to invert the orientation by changing the valency of the atom. In both, this second group has a greater interaction with the trivalent atom than has the benzene ring. This is shown by the smaller tendency of isobutyl borate than of boron triphenyl to form addition compounds with bases, and by the smaller tendency of acetamide than of aniline to form addition compounds with acids. In both substances the primary T-effect should predominate over the secondary since the substitutions occur when the benzene rings are activated, and consequently can supply or absorb electrons with great ease. The reactions of the substances differ in that trivalent boron produces the fundamentally slow meta substitution, and hence its meta directing influence is less complete than the ortho–para directing influence of the trivalent nitrogen atom.

Ainley and Challenger[21] nitrated phenylboric acid in the presence of sulfuric acid and found that approximately 70% of the meta isomer was formed in accordance with expectations. Seaman and Johnson[22] also studied the nitration of phenylboric acid and found that nitration with fuming nitric acid alone at low temperature led to an 80% yield which consisted of approximately 85% of the meta derivative and about 15% of the ortho derivative. In the presence of a large excess of acetic anhydride a 65% yield was obtained, the product being a mixture of 95% of the ortho derivative and 5% of the para derivative. From the above considerations, this ortho–para orientation should be attributed to the formation of a small concentration of an addition compound of phenylboric acid and acetic anhydride.

Experimental Section

Materials.—The method of preparation of phenylboric acid has already been described.[13] It was recrystallized four times from water and air dried.

$K\alpha$ **of Phenylboric Acid.**—The dissociation constant of phenylboric acid was obtained by measurement of the *P*H of partially neutralized solutions. This method is particularly applicable to acids of the order of strength of 10^{-9}, and avoids the errors that arise from traces of impurities. A series of solutions was prepared containing a constant amount of phenylboric acid. To these were added varying amounts of carbon dioxide-free sodium hydroxide solution and the whole was diluted to a definite volume. The *P*H of each solution at 20° was determined by the usual hydrogen electrode apparatus. The results are given in the two tables below. Since any activity or fugacity correction must be extremely small at the low concentrations used, the dissociation constants were calculated by means of the simple buffer equation, $K\alpha = \mathrm{H}^+$ (salt/acid), which is sufficiently accurate in the case of an acid of the strength of phenylboric acid. Since an accumulation of errors is obtained at the ends, only the three middle constants were used in each series. The average value for these gives $K\alpha = 1.9 \times 10^{-9}$ at 20°.

---

[21] Ainly and Challenger, *J. Chem. Soc.*, 2171 (1930).

[22] Seaman and Johnson, THIS JOURNAL, **53**, 711 (1931).

TABLE I

PHENYLBORIC ACID + SALT = 0.005 MOLAL

Salt present, %	P_H	$K_\alpha \times 10^9$	Average $K_\alpha \times 10^9$
25	8.16	2.31	
40	8.51	2.06	2.00
50	8.70	2.00	
60	8.89	1.94	
75	9.21	1.85	

TABLE II

PHENYLBORIC ACID + SALT = 0.01 MOLAL

Salt present, %	P_H	$K_\alpha \times 10^9$	Average $K_\alpha \times 10^9$
25	8.38	1.39	
40	8.58	1.75	1.78
50	8.76	1.74	
60	8.91	1.84	
75	9.21	1.85	

Summary

It has been shown that the interaction of trivalent boron with adjacent groups may lead to certain anomalies which are not explainable on the basis of negativities alone. These discrepancies are all readily explained by the use of combination formulas which have been justified by Pauling from quantum mechanical considerations. The apparent anomalies in the addition compounds of boron, in the dissociation constants of boric acid and phenylboric acid, and in the orientation of phenylboric acid have been discussed. The dissociation constant of phenylboric acid was measured and found to be three times as great as that of boric acid.

BERKELEY, CALIFORNIA

RECEIVED FEBRUARY 15, 1933
PUBLISHED JULY 6, 1933

[INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

A Comparison of the Toxicity of Nicotine and Anabasine[1]

BY W. A. GERSDORFF

In a study of the lethal action of toxic substances a proper comparison of the relationship between concentration and time of death may be obtained only by determining the complete curves which are the graphic expression of this action. These curves are obtained by a series of toxicological tests at a number of concentrations of the substances. Such series of tests were made with nicotine and anabasine, the goldfish being used as the test animal.

Freshly distilled samples of nicotine and anabasine were obtained from C. R. Smith of this Laboratory. The anabasine had been separated by him from an imported sample of anabasine sulfate obtained in the extraction of the alkaloids from *Anabasis aphylla* L.[2] and found to be chemically identical with neonicotine (β-pyridyl-α′-piperidine),[3] differing only in being levorotatory, whereas synthetic neonicotine is inactive. Neo-

---

(1) Presented before the Division of Biological Chemistry at the spring meeting, March 26–29, 1933, of the American Chemical Society at Washington, D. C.

(2) Orechoff and Menschikoff, *Ber.*, **64**, 266–274 (1931).

(3) Smith, THIS JOURNAL, **54**, 397–399 (1932).