

A NEW EXPLANATION OF AN OLD INCOMPATIBILITY.*

BY CHARLES W. BAUER.

We are all acquainted with the effervescence of carbon dioxide in preparing Compound Solution of Sodium Borate and again in making **Alkaline Aromatic Solution**. In searching for a chemical explanation of this phenomena we are unable to find any definite information other than a suggestion made by Scoville in his "Art of Compounding."¹

Scoville gives the equation advanced by Wm. Duncan but says it is hardly in accord with chemical principles. These equations suggest that glycerin reacts with borax to give boric acid and then boric acid reacts with glycerin to give a glyceryl boric acid which acts upon the carbonate. In the experimental work which follows it shows that a glyceryl boric acid is formed, but of a different formula than the one suggested by Duncan.

Before taking up the experimental work of this paper it may be advisable to consider the assay of boric acid given in the U. S. Pharmacopœia. In this assay glycerin is used. The purpose of the glycerin is expressed by Schimpf in his "Volumetric Analysis,"² as developing the acidity of the boric acid in regards to phenolphthalein to a great degree.

To say that glycerin brings out the acidity of boric acid is not a chemical explanation and glycerin is entirely ignored in the equation which represents this reaction. Attention is called to the large quantity of glycerin which is necessary in order for boric acid to show a hydrogen equivalent of one. Also that boric acid and sodium hydroxide in the absence of glycerin give an unsatisfactory end-point with phenolphthalein.

This information leads us to believe that boric acid evidently reacts with glycerin in some way to produce an acid which has a hydrogen equivalent of one. And that this acid in turn reacts with the sodium hydroxide.

A number of experiments were made and it was found that it required at least 3 parts by weight of glycerin to one part by weight of boric acid to give an acid which showed a hydrogen equivalent of one. Since glycerin has a molecular weight of about 92 and boric acid has a molecular weight of about 62, it shows that it takes two molecules of glycerin to react with one molecule of boric acid. This may be shown in the following way:

$$\begin{array}{ccccccc}
 1 & : & 3 & :: & 62 & : & X \\
 \text{Part by weight of} & & \text{Part by weight of} & & \text{M. W. of boric} & & \text{Wt. of glycerine} \\
 \text{boric acid} & & \text{glycerin} & & \text{acid} & & \\
 & & X = 186 & & & & \\
 & & 186:92 = 2 & & & & \\
 & & \therefore \text{Two M. W. of glycerin are required for one M. W. of boric} & & & & \\
 & & \text{acid.} & & & &
 \end{array}$$

Therefore for every molecular weight of boric acid it requires two molecular weights of glycerin or for every molecule of boric acid it takes two molecules of glycerin.

* Section on Practical Pharmacy and Dispensing, A. P. H. A., Rapid City meeting, 1929.

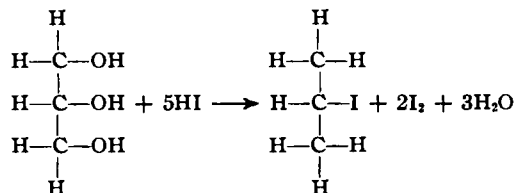
¹ Wilbur L. Scoville, "The Art of Compounding," page 327.

² Henry W. Schimpf, "Essentials of Volumetric Analysis," page 108.

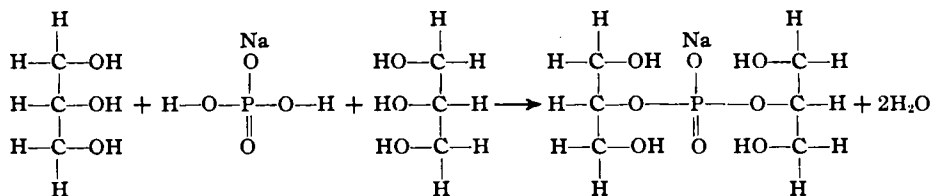
Before attempting to balance an equation between two molecules of glycerin and one molecule of boric acid which will give an acid that has only one replaceable hydrogen let us consider a few of the outstanding chemical properties of glycerin.

In studying the chemistry of glycerin we find that it is a trihydric alcohol which has one secondary and two primary alcoholic groups. The secondary alcoholic group will react with some acids and acid salts in an entirely different manner from the primary groups.

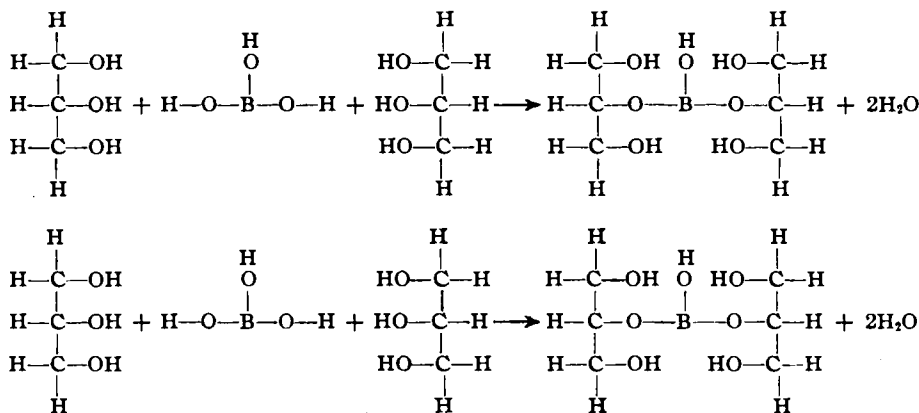
According to Gattermann in his "Practical Methods of Organic Chemistry," page 136, glycerin reacts with hydriodic acid to give Isopropyl Iodide.¹ This reaction can be explained by the following equation:



According to Bernthsen and Sudborough in their textbook on "Organic Chemistry," page 815, glycerin will react with monosodium dihydrogen phosphate in the following manner:²



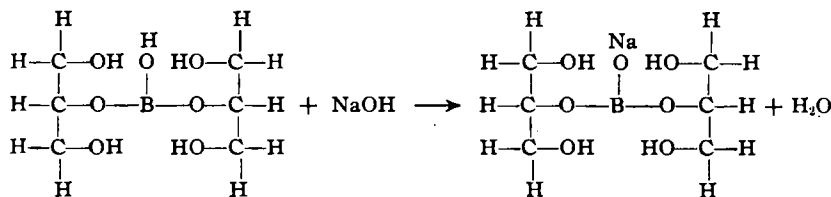
Using these equations as a starting point it is assumed that boric acid will react with glycerin in the following manner:



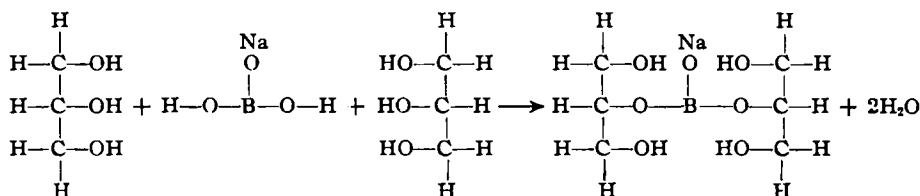
¹ Ludwig Gattermann, "Practical Methods of Organic Chemistry," page 136.

² August Bernthsen and John Joseph Sudborough, "Textbook of Organic Chemistry," page 815.

This explains why a large quantity of glycerin is necessary in the official assay of boric acid. This equation shows that for every molecular weight of boric acid 61.92 it requires two molecular weights of glycerin 2 (92.08) equals 184.16. It shows the reaction for the official assay.



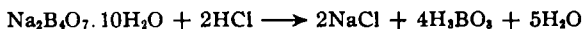
Since sodium dihydrogen phosphate reacts with glycerin to give monosodium glycerophosphate $(\text{C}_3\text{H}_5(\text{OH})_2)_2.\text{PO}_4\text{Na}$ it is reasonable to assume that sodium dihydrogen borate would react with glycerin to yield monosodium glyceroborate $(\text{C}_3\text{H}_5(\text{OH})_2)_2.\text{BO}_3\text{Na}$ and is illustrated by the following equation:



This brings us to the consideration of borax and how it reacts with glycerin.

Borax is a salt which is alkaline in behavior. In the official assay of borax the U. S. Pharmacopœia directs to titrate with normal hydrochloric acid and to use methyl orange as the indicator.

The equation for the reaction may be represented as follows:



This gives borax a hydrogen equivalent of two.

When borax is dissolved in water it is alkaline. If it is dissolved in glycerin, it is neutral, but when it is dissolved in glycerin with water, it is acid. The question now is, how can borax which is alkaline in behavior react with an alcohol to produce an acid? With the information we have on the reaction of glycerin with boric acid, we know that boric acid cannot be produced from borax in the presence of glycerin without forming glyceroboric acid.

If we study borax individually we find that in many of its reactions it acts like a metaborate. The best known of these are the bead tests in which we produce the metaborates. Again in treating calcium salts with a solution of borax, calcium metaborate is precipitated. This leads us to write the formula for borax as $(\text{NaBO}_2)_2.\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ which shows the metaborate radical.

The sodium glyceroborate $(\text{C}_3\text{H}_5(\text{OH})_2)_2.\text{BO}_3\text{Na}$ is neutral to phenolphthalein as was shown in the equation between glycerin, boric acid and sodium hydroxide.

We assume that when borax dissolves in water it undergoes hydrolysis to give $2\text{NaH}_2\text{BO}_3$ and $2\text{H}_3\text{BO}_3$. From the preceding experiments it suggests the following reactions with glycerin:

$$\frac{111.97}{112.22} \times 100 \text{ equals } 99.78\% \text{ of the theoretical amount.}$$

The experiment was repeated twenty-five times using *N*/10 NaOH. It required an average of 5.21 cc. of *N*/10 NaOH. Every cc. of *N*/10 NaOH corresponds to 0.004 Gm. of NaOH. Therefore it took 5.21×0.004 equals 0.02084 Gm. of NaOH.

$$0.1 : 381.76 : : 0.02084 : X$$

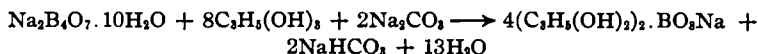
X equals 79.5588 Gm. of NaOH



According to the equation it would require two molecular weights of NaOH, or 80.02 Gm.

$$\frac{79.5588}{80.02} \times 100 \text{ equals } 99.42\% \text{ of the theoretical amount.}$$

The experiment was repeated using *N*/10 Na₂CO₃ to effect neutralization. Since sodium carbonate breaks down to sodium bicarbonate first, and sodium bicarbonate does not respond to phenolphthalein indicator, the equation may be represented as follows:



Every cc. of *N*/10 Na₂CO₃ corresponds to 0.0053 Gm. of Na₂CO₃.

An average of twenty-five experiments required 10.4 cc. of *N*/10 Na₂CO₃. Therefore 10.4×0.0053 equals 0.05512 Gm. of Na₂CO₃.

$$0.1 : 381.76 : : 0.05512 : X$$

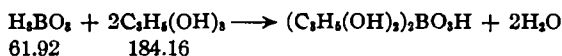
X equals 210.43 Gm.

$$\frac{210.43}{212.02} \times 100 \text{ equals } 99.25\% \text{ of the theoretical amount.}$$

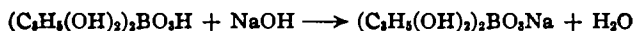
It was also found that if borax and sodium bicarbonate were mixed with about one-tenth the amount of water theoretically necessary to dissolve them and then the glycerin added that the effervescence was very rapid and would complete itself in fifteen minutes. When a large quantity of water was used to completely dissolve the borax and bicarbonate before adding the glycerin the effervescence was very slow and still showed reaction at the end of three hours. This is due to the carbon dioxide dissolving in the water and making the action reversible.

CONCLUSION.

Boric acid reacts with glycerin and water to form glyceroboric acid and water.

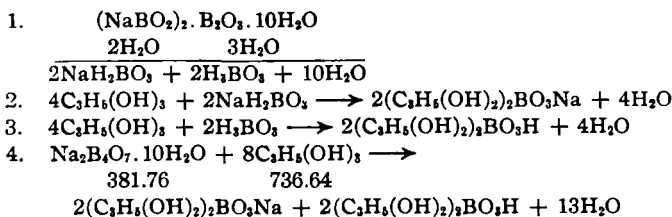


Glyceroboric acid reacts with sodium hydroxide to give sodium glyceroborate and water.

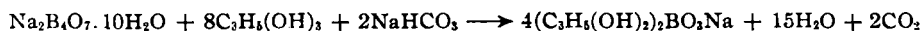


This accounts for the large quantity of glycerin required for the official assay of boric acid.

One molecule of borax reacts with water to give two molecules of monosodium dihydrogen borate NaH₂BO₃ and two molecules of boric acid H₃BO₃. Monosodium dihydrogen borate and boric acid react with glycerin to give monosodium glyceroborate and glyceroboric acid, respectively.



The monosodium glyceroborate is neutral to phenolphthalein while glyceroboric acid is acid to the same indicator and causes the effervescence with the bicarbonate. Glycerin and borax mixed with water and sodium bicarbonate react to produce monosodium glyceroborate, carbon dioxide and water.



John C. Krantz, Jr., asked the author if this explanation is incompatible with one he has given—that in the presence of glycerin, one molecule of borax decomposes into two molecules of sodium meta-borate plus one molecule of boric acid; and that, in turn, this boric acid reacts with the glycerin?

The author stated if that explanation is used, not so much glycerin would be required. In using a small quantity of glycerin, and then adding more, there is greater acidity.

HISTORICAL FRAGMENTS.*

BY EDWARD KREMERS.

No. 23. *Le Mort's "Pharmacia."*

Possibly the earliest textbook on pharmacy that bears the simple title "Pharmacy" is that of Jacobus le Mort published in 1684. Yet pharmaceutical historians all but ignore him and his treatise. Phillippe-Ludwig¹ dismiss him with mere mention and the record of five treatises, among them the

"Pharmacia et Chymia medico-physica rationibus et experimentis superstructa. Lugd. Batav. 1676, 1684, 1688, 1696."

Schelenz² copied only part of Ludwig's statement. Wootton does not mention him at all. LaWall³ merely refers to him as the originator of paregoric, a statement apparently based on a semi-editorial comment in the *Chemist & Druggist*.⁴ Medical historians appear to ignore him completely. Kopp, the chemical historian, twice refers to him: the first time⁵ in connection with the general development of pharmaceutical chemistry and the rôle played therein by pharmacists; the second time⁶ in connection with the special history of calomel. Poggendorff's account⁷ is of necessity brief, but his treatment of the man and his writings is more

* Section on Historical Pharmacy, A. Ph. A., Rapid City meeting, 1929.

¹ "Geschichte der Apotheke" (1855), page 580.

² "Geschichte der Pharmacie," page 550.

³ "Four Thousand Years of Pharmacy," page 420.

⁴ *C. & D.*, 62 (1903), 831.

⁵ "Geschichte der Chemie," Bd. II, page 116.

⁶ *Ibid.*, Bd. IV, page 193.

⁷ "Biographisch-literarisches Handwörterbuch."