COMBINATION OF BORATES WITH HYDROXY ACIDS

by

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In 1732 Le Fevre, a physician, mentioned a compound of borax and cream tartar. Soon after this Lemery made known his method of preparation and introduced it as a remedy. Formerly it was used as a styptic.but in modern times it has gone out of use.

The old German Pharmacopoeias used one part of borax with three parts of cream tartar to be dissolved in boiling water. This was then evaporated to one half and set aside for several days. The clear fluid was then separated from the precipitated cream tartar and calcium tartrate and the solution evaporated to dryness on a water bath.

The first research on this compound was undertaken by Prof. Dulk(1) of Konigsberg, who from the three parts cream tartar in the compound and one part borax derived the formulae:

$$NaO, 2BO_3.10HO. + 3\left(\begin{matrix}KO\\HO\end{matrix}\right\} C_8H_4O_{10} =$$

$$3(KO, C_8H_4O_{10}) + NaO, 2BO_3) + 13\,HO$$

or double

$$3\left(\begin{matrix}KO\\KO\end{matrix}\right\} C_8H_4O_{10} + 2(NaO, 2BO_3) + 3\,C_8H_6O_{12}.$$

Dulk believed that the cream tartar united directly with the borax to form a double soluble salt or that the cream tartar was decomposed and a neutral potassium tartrate formed.

(1) - Schweiggers Jahrbuch der Chemie und Physik, 1832.

This view was opposed by Duflos.(1). He concluded from experiments with boric acid tartrate, prepared by a different method, that the boric acid was able to act as a base in opposition to the tartaric acid and set up the following formulae:

$$NaO,2BO_3.10HO + 3\left(\begin{matrix}KO\\HO\end{matrix}\right\}C_8H_4O_{10} = \left.\begin{matrix}KO\\NaO\end{matrix}\right\}C_8H_4O_{10} + 2\left(\begin{matrix}KO\\BO_3\end{matrix}\right\}C_8H_4O_{10} + 3HO.$$

Duflos therefore considers the borax tartrate as a compound of rochelle salt with potassium boro tartrate in which latter salt the boric acid takes the place of a base. Finally, Duflos said what appears to contradict this view, that the solution of borax tartrate on standing sometimes deposits crystals of cream tartar and potassium tartrate.

According to Dulk one part boric acid can change four parts cream tartar into a soluble salt.

$$8\left(\begin{matrix}KO\\HO\end{matrix}\right\}C_8H_4O_{10} + 6(BO_3.3HO) = 4\left(\begin{matrix}KO\\KO\end{matrix}\right\}C_8H_4O_{10} + 6BO_3.4(C_8H_4O_{10}).$$

The cream tartar has according to Dulk, separated into a neutral potassium tartrate and free tartaric acid. The latter is united with the boric acid free from water. This method of observation was possible to him because he found that the tartrate had become free of water by its contact with boric acid.

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(1) - Schweigger's Jahrbuch der Chemie und Physik, 1832.

Therefore one part of cream tartar in the formation of potassium salts, has united with the boric acid.

Duflos held that these experiments of Dulk were inexact and experimented on the capacity of saturation of boric acid with cream tartar. He found one part boric acid is able to hold only three parts cream tartar in solution. He then tested the chemical composition of the compound and since he could ~~not~~ separate neither boric acid nor tartaric acid from the same by treating with mineral acids, he concluded that the boric acid is able to unite with the cream tartar and that the former acts as a base. He gives the formula for boric acid tartrate, dried over 100° degrees as:

$$\left.\begin{matrix}KO\\HO\end{matrix}\right\} C_8H_4O_{10} + BO_3.3HO = \left.\begin{matrix}KO\\BO_3\end{matrix}\right\} C_8H_4O_{10}.$$

and derives from this the composition of borax cream tartar which he looked at as a double salt of rochelle salt with potassium borate.

Soubeiran repeatedly worked with boro cream tartar.(1). He says the cream tartar is able to unite in larger proportions with the boric acid. That cream tartar saturated with boric acid contains BO_3 to $\left.\begin{matrix}KO\\HO\end{matrix}\right\} C_8H_4O_{10}$. All boric acid that is added in excess, he found could be taken away with alcohol.

(1) - Journal de Pharm. XI., p.560; XXV., p.24.

In addition to the theory of Duflos, Soubeiran formulated the hypothesis that the boric acid appears in the compound as a base, like ~~the~~ potassium, although ~~the~~ boric acid contains three fold amount of oxygen more than potassium.

Soubeiran and Capitain found that heating boric acid cream tartar to 280° it lost 8.2% water, which is equivalent to two atoms(1). One can trace out from this an analogy of the composition of the two salts, and the belief of the view expressed by Duflos over the chemical constitution of the two preparations, would be still be more strengthened.

In the year 1857 H. Rose made public a series of experiments of the action of boric acid with tartaric acid. (2). He displaced the solution of a known amount of borax with differamounts of tartaric acid. He found that the addition of one equivalent of tartaric acid to one equivalent of borax separated the greatest amount of boric acid. By farther addition of tartaric acid, the same decreases, and with a proportion of three equivalents of tartaric acid to one equivalent of borax the separation was completely hindered. These results led him to the conclusion that the boric acid must react with the

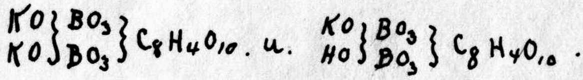
(1) - Journal de Pharm. XXV., p.744.
(2) - Journal f.p. Chemie, 73, p.170.

tartaric acid like a weak base;but on investigating the properties of boric acid he found facts which contradicted the adoption of its basic nature. Boric acid ought to behave in like manner and combine to a greater degree with the stronger acids,but in all these acids the boric acid dissolves by heating,but again separates by cooling. In order to distinguish which of the two acids acts in the compound as a base H.Rose subjected a solution of boric acid in tartaric acid to electrolysis.In order to prevent the decomposition of tartaric acid,he used a weak Grove's chain. After a few hours free boric acid had appeared on the positive pole while on the negative pole he found tartaric acid and boric acid. Finally he showed the difference between the browning of tumeric paper with an alkali and with boric acid. By immersion of tumeric paper in a weak alkali,the paper is colored brownish red,but boric acid does not change the color of the paper while wet but on drying becomes a redish brown color.

In 1848 Dr.Krug gave his results of a series of experiments on the action of boric acid on tartaric acid and the chemical composition of "boraxtartrate" and boric acid tartrate(1) He also investigated the precipitate formed by mixing one part

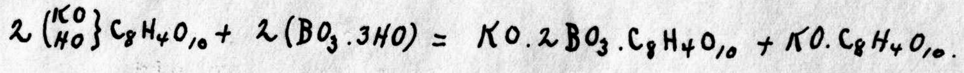
(1) - Archive der Pharmacie, Jahrg. 1848.

of borax and three parts tartaric acid, in solution which up to this time, had been considered to be calcium tartrate. He proved that the precipitate was mostly cream tartar and that the borax can not change more than two parts cream tartar into a soluble salt and unite with it chemically. He considered boric acid tartrate like Duflos, that is equal proportions of boric acid and cream tartar. Upon the addition of neutral potassium tartrate, cream tartar separates out. From this he concluded that the "boric acid tartrate" could not possibly be a neutral salt. And since the experiment to unite boric acid with tartaric acid gave a negative result, he threw aside the Duflos theory concerning the constitution of the two preparations and assumed the existence of a characteristic double acid, borotartaric. Krug represented a neutral and acid salt for this acid and gave them the formulae:



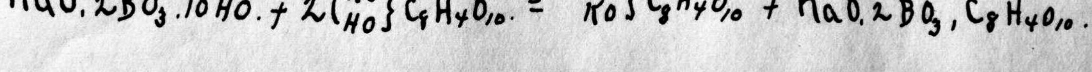
$$\left.\begin{matrix}KO\\KO\end{matrix}\right\}\left.\begin{matrix}BO_3\\BO_3\end{matrix}\right\}C_8H_4O_{10}.\ \text{u.}\ \left.\begin{matrix}KO\\HO\end{matrix}\right\}\left.\begin{matrix}BO_3\\BO_3\end{matrix}\right\}C_8H_4O_{10}.$$

From this he derived the constitution of both preparations and considered boric acid tartrate as:



$$2\left(\begin{matrix}KO\\HO\end{matrix}\right\}C_8H_4O_{10}+2(BO_3.3HO)=KO.2BO_3.C_8H_4O_{10}+KO.C_8H_4O_{10}.$$

For the boraxtartrate Krug gives the following formula:



$$NaO.2BO_3.10HO.+2\left(\begin{matrix}KO\\HO\end{matrix}\right\}C_8H_4O_{10}.=\left.\begin{matrix}KO\\KO\end{matrix}\right\}C_8H_4O_{10}+NaO.2BO_3,C_8H_4O_{10}.$$

And it is therefore a double salt of sodium acid borotartrate with neutral potassium tartrate. Krug did not carry out any other representation concerning the constitution of his borax-tartrate. But it appears as though he assumes that the boric acid simply adds itself to the tartaric acid.

H. Wackenroder with the assistance of H.Ludwig,H Custer and E.Steffel soon afterwards wrote a disquisition on the composition of borax tartrate and gave one part borax to two and one half parts tartaric acid.(1). They derived the formula from the amount of water given off.

$$NaO.2BO_3.10HO. + 5\left(\begin{matrix}KO\\HO\end{matrix}\right\} C_8H_4O_{10} - 25\,HO =$$

$$4(KO, C_8H_4O_{10}) + (KO, BO_3) + 2\,NaO, BO_3) + BO_3 . C_8H_4O_{10}.$$

This consists of three parts, the first, $4(KO.C_8H_4O_{10})$, he looked upon as the neutral salt of tartaric acid. The second, consisted of potassium and sodium borate. The last part, $BO_3.C_8H_4O_{10}$, he calls boric acid tartrate. The last shows a basic character like Duflos' theory.He did not succeed to separate either boric acid or tartaric acid from the salt with alcohol.So Wackenroder does not take the last part as separate but combined with the other two.The difference of the results of Krug and Wackenroder persuaded Wittstein to investigate the

(1) - Archive der Pharmacie,1849.Bd.58,p.4.

matter.(1). Later he wrote an article on the work of Krug. He agreed with Krug and claimed that the cream tartar soluble, and that consisting of equal atoms of boric acid and tartaric acid is a double salt of potassium acid borotartrate with potassium tartrate. $KO.2BO_3.C_8H_4O_{10} + KO.C_8H_4O_{10}$. and derived for borax tartrate the formula: $NaO.C_8H_4O_{10}.2BO_3 + \left.\begin{matrix}KO\\KO\end{matrix}\right\} C_8H_4O_{10}$. He gives no consideration of the constitution of these hypothetical borax tartrates.

Fehling says .that Wittstein did not disprove the investigations of Duflos, nor did he establish the correctness of his own, on which account the investigations of Duflos are still accepted as being correct.(2).

In 1869 Duve took up the problem. He took different portions of cream tartar and borax or boric acid, dissolved them in boiling water and allowed the excess cream tartar to separate by crystalization. From the amount cream of tartar then obtained he deduces the composition of the soluble "borocreamtartar". In like manner he reversed the conditions, using an excess of boric acid. His general conclusions are as follows:

1. Direct combination of boric acid with tartaric acid

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(1) - Buchners Repertorium 1850, Bd.106, p.1.
(2) - Hand worterbuch der Chemie, II.p.2.

does not take place, but the latter will through the effect of boric acid be changed into the monobasic isomer, isotartaric acid.

2. The theory of Duflos that the boric acid in its combination with tartaric acid salts acts as a base is not correct. The boric acid in the salts does not act as a base but combines with the tartaric acid to form a double acid. These borotartrates are only known in their salts and can not be isolated.

3. The alkalies have the property in a high degree of forming easily soluble bortartrates, while the alkaline earth constitutes more difficult soluble or insoluble salts and it is impossible for the heavy metals to unite with the bortartrate.

4. The boric acid tartrate is a saturated combination of one part boric acid with onepart tartaric acid. It is potassium acid monobortartrate. $\left.\begin{matrix}KO\\HO\end{matrix}\right\}\begin{matrix}C_8H_3O_9\\BO_3\end{matrix}$.

5. The bortartrate is a saturated combination of one part borax with two parts tartaric acid. It is a composed of potassium and sodium monobortartrate with potassium acid monobortartrate which is represented by this formula.

$$\left.\begin{matrix}KO\\NaO\end{matrix}\right\}\begin{matrix}C_8H_3O_9\\BO_3\end{matrix} + \left.\begin{matrix}KO\\HO\end{matrix}\right\}\begin{matrix}C_8H_3O_9\\BO_3\end{matrix}.$$

In 1858 Dubrunfant worked with tartaric acid and boric acid and found they united in the proportion of one part boric acid with two parts tartaric acid.(1).

In 1888 H.Landholt took up the investigation of borates and tartrates.(2). He estimated boric acid by adding to the solution twenty gr. of tartaric acid, to every one hundred ccs. and found if $C =$ grams of boric acid and α angle of rotation after addition of tartaric acid that $C = 1.4$, $\alpha -14.4$.

Gaetano Magnanini worked for several years on the action of borates and tartrates, also of boric acid and organic acids. In 1890 he published his results on the conductivity of boric acid plus tartaric acid.(3).He found the greater the quantity of boric acid the greater the conductivity; also that hydrolytic dissociation took place with dilution.

A little later, in 1891, he published a second series of results.(4).He found that boric acid increased the conductivity of acids which contain one or more (OH) groups. It changed the conductivity of salicylic, lactic, glyceric, gallic, mandelic and glyceric acids, but did not change conductivity of acetic, benzoic, butyric, succinic and crotonic acids.

(1) Archiv~~e~~ der Pharmacie, 144, p.56.
(2) Berichte 1888, 191.
(3) Z.Ph.Ch. 6.67-90.
(4) Gazz.Chim. ital. 2.9. & Z.Ph.Ch. 9-230.

In 1892 he published his results of the investigation of 24 acids. He found:

1. That acids with no OH groups produce no increase in conductivity.

2. Acids containing at least one OH in α position to COOH or Arom. oxyacids with OH in O -position have their conductivity increased.

3. OH groups not in α or O-position produce only a slight increase in conductivity.

No increase with:

oxypropionic, oxybutteric, m-oxybenzoic, p- oxybenzoic, o-cumaric, vanillic and tropic~~säure~~ acids.

In view of the many conflicting statements in regard to this reaction it was thought that an investigation of these solutions by means of physical chemical methods might throw some light on the subject. Insofar as Biot and Landolt had worked upon the optical properties of these mixtures and Magnanini had already studied the electrical conductivity, these physical methods were omitted in the present investigation although a thorough study of them would perhaps not be without additional interest.

In this work the freezing point method was used with the object of ascertaining in what stochiometric relation these substances combine and to find if possible the size of the complex molecule which results.

The apparatus used was the ordinary apparatus designed by Beckmann, with a thermometer graduated to one hundredths of a degree and allowing of judging to one thousandths of a degree. The chemicals used in the work were bought as chemically pure, but were recrystallized to insure the proper amount of water of crystallization.

The sodium hydroxide solution was made by the action of metallic sodium on water and its strength determined. During the work it was carefully protected from the carbon dioxide of the air. The method of making the dilutions were as follows:

First the freezing point of distilled water was determined by putting water in the inner tube of the apparatus and freezing it in the usual manner. Here as in all subsequent determinations of the freezing point three readings were always taken. The water was then removed from the apparatus and ten ccs. of the solution to be determined was put into the tube and the freezing point determined. Five ccs. of pure distilled water was then accurately measured into the solution and the freezing point again determined. Then five more ccs.

of water were added and the freezing point again determined. Now ten ccs. of the solution were taken out of the tube and five ccs. of water added. Proceeding in this way the different dilutions in tables 1,2,3,and 4,were obtained,after having made up the original solutions of the strength as stated at the head of the tables. In tables 5 and 6 the volume was kept constant and boric acid or borax added in molecular proportions to the original solution,always adding one molecular equivalent at a time. The results of the investigation will be found in the following tables.

In the first column under Vol.in tables 1,2,3,and 4, will be found the number of litres in which one gram molecule of borax or its equivalent in boric acid,(4 molecules),is dissolved,the dilutions being made as before described. The results are given in the second column of the tables. In the third column are given the results obtained by freezing the solution of rochelle salt or of tartaric acid of the strength given under Vol. In the following columns are given the results obtained with mixtures of rochelle salt and tartaric acid respectively with boric acid,borax,or borax plus sodium hydroxides,or (sodium monoborate)(1) in the molecular propor-

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(1) - Kahlenberg und Schreiner,Uber Borsaure und ihre Salze. Ztsch f.Phys. Chem. XX.p.555.

tions given at the head of each column. As already stated tables 5 and 6 are made upon a different plan,here the volume was kept constant. In the other tables the borax or boric acid was kept constant while tartaric acid was varied,but in these latter experiments the tartaric acid was constant and the boric acid and borax varied in molecular proportion as stated in the tables.

In table I. are the results obtained by freezing a solution of one molecule of borax and two molecules sodium hydroxide alone and with 1,2 and 3 molecules of Rochelle salt respectively. Kahlenberg and Schreiner have already shown that a solution of one molecule of borax plus two molecules of sodium hydroxide are equivalent to four molecules of sodium monoborate,and that this latter salt is perfectly neutral considered from a chemical standpoint,although it does give an alkaline reaction,in other words there are no free hydroxyl ions in the solution. The above solution is therefore a perfectly neutral solution,with no hydroxyl ions and no hydrogen ions. The object of the investigation was to start with this neutral solution and to work down through the partially acid solutions to that in which only the acids reacted(table 6). It is

It is evident that when we have in a solution four molecules of sodium monoborate and one molecule of rochelle salt we ought to get the sum of the lowerings of the freezing points of the respective solutions, leaving out of consideration the mutual effect of the depression of the dissociation, which is of course only slight and can therefore be neglected without serious effects resulting therefrom.

Table I.

Borax + Sodium Hydroxide + Rochelle Salt or Sodium Monoborate + Rochelle Salt.

Vol.	1 mol. borax + 2 NaOH.	1. mol. Rochelle Salt.	1. mol. borax + 2 NaOH + 1 mol. R. Salt.	1 mol. borax + 2 NaOH + 2 mol. R. Salt.	1. mol. borax + 2 NaOH + 3 mol. R. salt.
10	1.260	.495	1.442	1.664	1.868
15	.880	.334	1.011	1.236	1.378
20	.685	.254	.802	.941	1.089
30	.470	.184	.572	..667	.773
40	.370	.134	.432	.515	.614
60	.256	.084	.296	.365	.423
80	.220	.061	.236	.280	.323

Now an examination of the results in table 1 shows that for Vol.10 we ought to get in the fourth column of the table 1.260 plus 0.495 or 1.755 but we get only 1.442 showing that the total number of molecules and ions in the solution is smaller than the sum of the molecules and ions in the separate solutions of the same strength, and hence it follows that combination has taken place. The same considerations hold true for the results given in the fifth and sixth columns and also for the other dilutions in each column. The results obtained by diluting each solution show that a hydrolytic splitting up of the complex molecule takes place as the dilution increases.

Table II.

Borax plus Rochelle Salt.

Vol.	1. mol. borax.	1. mol. R. Salt.	1 mol. borax + 1 .. R. Salt.	1 mol. borax + 2 .. R. Salt.	1 mol. borax + 3 .. R. Salt.
10	.629	.495	-	1.230	1.593
15	.539	.334	-	.895	1.165
20	.444	.254	.517	.610	.933
30	.334	.184	.438	.505	.650
40	.271	.134	.335	.425	.516
60	.189	.084	.230	.290	.360
80	.149	.061	.188	.232	.290

In the table II. are the results given by solutions of borax and rochelle salt. Here the solution is more of an acid character than in table I., for borax, although alkaline in reaction, is nevertheless an acid salt. The first two dilutions in column 4 could not be determined as a precipitate always formed, but which redissolved when more rochelle salt was added or when the solution was diluted. For want of time this precipitate was not examined. The results in this table are in general about the same as in table I.

In table III. the results of the still more acid mixture of borax and tartaric acid and while the results are similar to those in the other experiments, yet they are so much more pronounced that it will be well to consider the a little more in detail.

Table III.

Borax and Tartaric Acid.

Vol.	1 mol. borax.	1 mol. T. acid	1 mol. borax + " " T. acid.	1 mol. borax + 2 " T. acid.	1 mol borax +3 " T. acid.	1 mol. borax +4 " T. acid.	1 mol borax + 5 " T. acid.
10	.629	.840	.868	.865	.935	1.070	1.190
15	.539	.535	.656	.655	.665	.765	.812
20	.444	.387	.515	.535	.526	.595	.635
30	.334	-	.355	.352	.365	.430	.451
40	.271	-	.270	.275	.295	.337	.358
60	.189	-	.195	.192	.192	.235	.273
80	.149	-	.145	.185	.165	.185	.208

Thus in the stronger solution Vol. 10 we ought to get in the fourth column the sum of .629 and .840 or 1.469 but we get only .868 which is just about the same figure that is given by the tartaric acid alone .840. Hence we must conclude that the number of molecules and ions in this solution is the same as the number of molecules and ions in the tartaric solution or that one molecule of borax and its dissociation products have united with one molecule of tartaric acid and its dissociation products. On adding a second molecule of tartaric acid we get no further lowering in thefreezing point. Where if no combination took place we should expect a further lowering to the extent of about .840. Hence this second molecule of tartaric acid combines with the complex borotartaric molecule already existing in the solution. The results in the other two columns, while not so striking as the first two, yet they clearly show that further combination takes place, for in each case we ought to get about .840 as increase in the lowering if no combination took place while we find only .070 and .145 respectively. As in the other tables the effect of dilution of the solution is a hydrolytic splitting of the complex molecules or ions into the original components and their dissociation products.

Table IV.

Boric Acid plus Rochelle Salt.

Vol.	(4 mol. H_3BO_3)	1. mol. R. Salt.	4 mol. H_3BO_3 + 1 " R. Salt.	4 mol. H_3BO_3 + 2 " R. Salt.	4 mol. H_3BO_3 + 3 " R. Salt.
10	.800	.495	.870	1.069	1.365
15	.567	.334	.642	.804	1.011
20	.417	.254	.502	.625	.788
30	.290	.184	.381	.460	.565
40	.228	.134	.280	.358	.449
60	.176	1084	.182	.244	.230
80	.123	.061	.140	.187	.255

In table IV. are given the results obtained with boric acid and rochelle salt. Here we find nothing strikingly different from the results obtained in tables I and II., although we might expect to get about the same results in the case of borax and tartaric acid, the only difference being that in one solution we have a salt of boric acid and free tartaric acid and in theother, free boric acid and a salt of tartaric acid.

The results in tables V. and VI. confirm the conclusions drawn from the other experiments, although no definite stochiometric relation can be recognized.

Table V.

Tartaric Acid Solution plus Borax.

One molecule of Tartaric acid in 10 litres.

	Lowering
Tartaric acid solution	.840
" " " 1 mol.borax	1.075
" " " 2 " "	1.522
" " " 3 " "	1.928
" " " 4 " "	2.460
" " " 5 " "	2.472
" " " 6 " "	2.558

Table VI.

Tartaric Acid plus Boric Acid.

One molecule tartaric acid in 10 litres.

	Lowering
Tartaric acid solution.	.840
" " " 1 mol.boric acid	.824
" " " 2 " " "	.932
" " " 3 " " "	1.105
" " " 4 " " "	1.240
" " " 5 " " "	1.441

From ~~In~~ the foregoing experimental results it is evident that combination between tartaric acid or tartrates and boric acid or borates does ~~not~~ take place and not simply molecule for molecule, but in a different ratio. In order to get this ratio the experimental results must be carried beyond the limits reached in this work if indeed it can be found at all, on account of the great number of ions, both simple and complex, which exist in the solution and the latter no doubt vary as the composition of the solution is changed.

Approved

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