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QUATERNARY AMMONIUM BOROHYDRIDE COMPOSITIONS
AND METHOD OF PREPARATION
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Fig. 1.

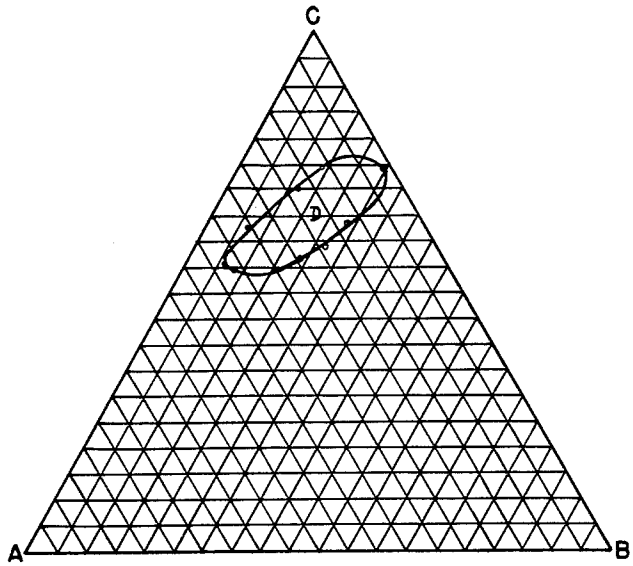
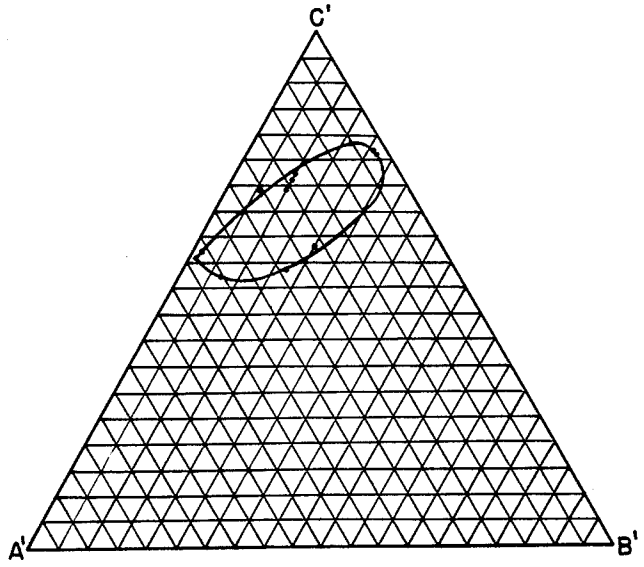


Fig. 2.



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QUATERNARY AMMONIUM BOROHYDRIDE COMPOSITIONS AND METHOD OF PREPARATION

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This invention relates to the preparation of substantially pure quaternary ammonium borohydrides of the group having a total number of carbon atoms from 5 to 15 inclusive in the organic substituent to the nitrogen atom, such as tetraethylammonium borohydride, tetrapropylammonium borohydride, benzyltrimethylammonium borohydride, triethylmethylammonium borohydride, ethylpyridinium borohydride, and methylisoquinolinium borohydride. More particularly, the invention relates to the preparation of such borohydrides by the reaction of a water soluble quaternary ammonium salt, such as the chloride or bromide, corresponding to the desired quaternary ammonium borohydride with an alkali metal borohydride, such as sodium borohydride or potassium borohydride in an aqueous medium.

In our copending application Serial No. 254,395, filed January 28, 1963, we have described the preparation of quaternary ammonium borohydrides of the above mentioned group by reacting a quaternary ammonium hydroxide with sodium or potassium borohydride in water to form an aqueous solution of the quaternary ammonium borohydride and the alkali metal hydroxide. The reaction is illustrated by the equation:

$$(C_2H_5)_4NOH+NaBH_4\rightarrow(C_2H_5)_4NBH_4+NaOH \quad (1)$$

It had been discovered that aqueous solutions of such quaternary ammonium borohydrides and an alkali metal hydroxide in certain concentrations, when permitted to settle, separate in two immiscible layers, the upper layer of which is essentially an aqueous solution of the quaternary ammonium borohydride and the lower layer is essentially an aqueous solution of the alkali metal hydroxide. Consequently, in order to recover substantially pure quaternary ammonium borohydride from the reaction mixture of the reaction illustrated by Equation 1 above, the amount of water in the reaction mixture was adjusted to produce a liquor having a concentration such that, when permitted to settle, it separated in two immiscible layers the upper layer of which was essentially an aqueous solution of the quaternary ammonium borohydride and the lower layer was essentially an aqueous solution of the alkali metal hydroxide.

It obviously would be advantageous if a water soluble quaternary ammonium salt, such as tetraethylammonium chloride, could be reacted in aqueous solution with an alkali metal borohydride to form the quaternary ammonium borohydride and recover the latter in good yield and high purity. The intended reaction is illustrated by the equation:

$$(C_2H_5)_4NCl+NaBH_4\rightarrow(C_2H_5)_4NBH+NaCl \quad (2)$$

The present invention is based in part upon our discovery that aqueous solutions of an alkali metal borohydride and quaternary ammonium salts of the group having a total number of carbon atoms from 5 to 15 inclusive in the organic substituent to the nitrogen and their reaction products in certain concentrations containing certain amounts of an alkali metal hydroxide, when permitted to settle, separate in two immiscible layers.

During our investigations we attempted to prepare a quaternary ammonium borohydride by reacting a quaternary ammonium halide with an alkali metal borohydride in an aqueous solution containing an alkali metal hydroxide, the quaternary ammonium halide, alkali metal borohydride, alkali metal hydroxide and water used being in amounts contemplated to provide a separation of the aqueous reaction liquor in two immiscible layers. The results were unsatisfactory since when the reaction liquor was permitted to settle to form two separate liquid layers, the upper layer contained substantial amounts of the quaternary ammonium halide and the alkali metal hydroxide. However, it was observed that the lower layer contained a substantial amount of the alkali metal halide formed as a by-product of the reaction.

As a result of the above observation, it was conceived that the reaction might be caused to proceed to completion by a plurality of reaction steps in each of which the quaternary ammonium halide is partially reacted with the alkali metal borohydride by intimately contacting an aqueous solution of the quaternary ammonium halide with an immiscible aqueous solution of an alkali metal hydroxide containing the alkali metal borohydride. Subsequent investigations proved that the reaction could be caused to proceed substantially to completion in this manner. The over-all reaction is illustrated by the equation:

$$NaBH_4+(C_2H_5)_4NCl+NaOH\rightarrow (C_2H_5)_4NBH_4+NaCl+NaOH \quad (3)$$

In accordance with one practice of the invention, an aqueous solution of a quaternary ammonium salt, such as the chloride, is placed in a separatory funnel together with an immiscible aqueous solution of an alkali metal hydroxide containing an amount of an alkali metal borohydride stoichiometrically equivalent to the quaternary ammonium halide. The mixture is agitated thoroughly and then allowed to set and separate in two separate layers. The bottom layer is withdrawn and another portion of the aqueous solution of alkali metal hydroxide and alkali metal borohydride added, followed by agitation and settling. This procedure is repeated until the aqueous solution of the quaternary ammonium halide has been contacted about five times with the aqueous solution of the alkali metal hydroxide containing an amount of alkali metal borohydride stoichiometrically equivalent to the quaternary ammonium halide. The final top layer is substantially free of hydroxide and halide ions and is essentially an aqueous solution of the quaternary ammonium borohydride.

The aqueous solution of the quaternary ammonium salt is more conveniently subjected to a plurality of reaction steps with the aqueous solution of the alkali metal borohydride and the alkali metal hydroxide as a continuous operation. This may be accomplished in any conventional continuous liquid-liquid extractor. Thus, the aqueous solution of the quaternary ammonium salt and the immiscible aqueous solution of alkali metal hydroxide and alkali metal borohydride are caused to flow countercurrent to one another continuously in a given path, an aqueous solution of the quaternary ammonium borohydride being removed continuously from one end of the path of countercurrent flow and an aqueous solution of alkali metal hydroxide and the alkali metal salt formed as a by-product of the reaction being removed continuously from the other end of the path. The York-Scheibel-type extractor is well suited for this operation. This extractor provides a mixer-settler system in which all the mixers and settlers are incorporated into a single vertical cylindrical column. Each stage consists of a mechanically agitated mixing section separated from the next stage by a packed settling section or porous wire cylinder.

The invention will be more fully understood from the following description in conjunction with the accompanying drawing in which:

FIG. 1 is a triangular graphical representation of the system water, sodium hydroxide, and an equimolar mixture of tetraethylammonium chloride and sodium borohydride; and

FIG. 2 is a triangular graphical representation of the system water, sodium hydroxide, and an equimolar mixture of tetraethylammonium bromide and sodium borohydride.

In the FIG. 1 of the drawing, the vertex A of the triangle represents 100 percent of an equimolar mixture of tetraethylammonium chloride and sodium borohydride. The vertex B represents 100 percent sodium hydroxide and the vertex C represents 100 percent water. The lines parallel to the line AB represent liquor compositions containing different amounts in percent by weight of water from 0 to 100. The lines parallel to the line AC represent liquor compositions containing different amounts of sodium hydroxide in percent by weight from 0 to 100. The lines parallel to the line BC represent liquor compositions containing different amounts in percent by weight from 0 to 100 of an equimolar mixture of sodium borohydride and tetraethylammonium chloride or the reaction products thereof. Consequently, any common intersection point within the triangle of lines parallel to the lines AB, AC, and BC represents the amounts in percent by weight of water, sodium hydroxide, and an equimolar mixture of tetraethylammonium chloride and sodium borohydride or the reaction products thereof in a given liquor composition.

The area bounded by the closed loop represents liquor compositions which, when permitted to settle, separate in two immiscible layers. Points within the triangle but outside the closed loop represent liquor compositions which do not form two immiscible liquid layers when permitted to settle. The closed loop was established empirically at room temperature as follows. Water was added to a given mixture of sodium hydroxide, tetraethylammonium chloride and sodium borohydride until just sufficient water was added to form a solution which would settle in two immiscible layers. This established a point on the lower part of the closed loop. Additional water then was added until a liquor was formed which did not settle in two immisible layers. This established a point on the upper part of the closed loop. This procedure was repeated with different mixtures of water, sodium hydroxide, tetraethyl ammonium chloride and sodium borohydride until all points on the loop had been determined.

In establishing the closed loop of FIG. 1 empirically, the most significant phase changes, viz. the first appearance of the two liquid phases and the reversion to a single liquid phase on further dilution, are readily detected visually by the opalescence exhibited by systems containing two liquid phases, when agitated vigorously. Titration with water of a single known mixture of quaternary ammonium chloride, sodium borohydride, and sodium hydroxide can, then, determine two points of the closed loop such as that shown in FIG. 1, namely, (1) the point of first appearance of two liquid phases, and (2) the point of disappearance of the two liquid phases. From the weights of the known mixture and the quantities of water required to reach these two points, the compositions represented by the two points can be calculated and plotted. Titration of several known mixtures of divergent composition permits rapid outlining of the closed loop.

The diagram in FIG. 1 of the drawing may be used to establish the compositions of the two immiscible solutions to be used in the practice of the invention. Thus, any point D within the closed loop may be selected. The point D represents a liquor composition which, when permitted to settle, will separate in two immiscible liquid layers. The solution of the tetraethylammonium chloride to be used in countercurrent operation is formed by dissolving an amount of tetraethylammonium chloride represented by the point D in a portion of the amount of water represented by the point D. The solution of sodium borohydride and sodium hydroxide is formed by dissolving in

the remaining portion of the amount of water represented by point D the amount of sodium hydroxide represented by the point D together with an amount of sodium borohydride which is the molar equivalent of the amount of tetraethylammonium chloride used.

The triangular graphical representation of FIG. 2 is similar to that of FIG. 1 except that the vertex A' represents 100 percent of an equimolar mixture of tetraethylammonium bromide and sodium borohydride, the vertexes B' and C' representing 100 percent sodium hydroxide and 100 percent water respectively. The closed loop in FIG. 2 was established empirically at room temperature in the same manner as the closed loop in FIG. 1 except that tetraethylammonium bromide was substituted for tetraethylammonium chloride.

For convenience we refer to the sodium hydroxide used in the practice of the invention as a "splitting agent." We have also discovered other compounds which serve the same purpose as the sodium hydroxide, such other compounds also being referred to as "splitting agents." Such other "splitting agents" are potassium hydroxide, potassium fluoride, potassium carbonate, potassium tartrate, sodium carbonate, sodium sulfate, potassium sulfate, and potassium citrate.

The tetraethylammonium chloride may be replaced by other water soluble quaternary ammonium salts which are inert with respect to the splitting agent used. As illustrative of quaternary ammonium salts which are inert toward each of the above mentioned splitting agents we may mention benzyltrimethylammonium hydroxide, tetraethylammonium bromide, tetrapropylammonium chloride, tetraethylammonium carbonate, benzyltrimethyl sulfate, tetrapropylammonium nitrate, tetraethylammonium acetate, tetraethylammonium tartrate, and tetraethylammonium citrate.

In a manner similar to that previously described in connection with the drawing, a triangular graphical representation may be established empirically at any desired temperature for any system of water, alkali metal borohydride, any quaternary amomnium salt contemplated by the invention, and any splitting agent. These diagrams may be used to determine the concentration of the aqueous solution of quaternary ammonium salt which may be used with an aqueous solution of an alkali metal borohydride, such as sodium borohydride or potassium borohydride, and a selected splitting agent.

The invention is illustrated further by the following examples.

Example 1

Sixty-seven grams of an aqueous solution containing 38.7 percent by weight of tetraethylammonium chloride (0.156 mole) were placed in a separatory funnel with 49.5 grams of a stabilized aqueous solution of sodium borohyrdide containing 11.9 percent by weight of sodium borohydride (0.156 mole) and about 40 percent by weight of sodium hydroxide. The mixture was agitated thoroughly and allowed to separate in two separate layers. The bottom layer was withdrawn and an additional 49.5 grams of the aqueous solution of sodium borohydride and sodium hydroxide was added to the top layer, followed by agitation and settling. The procedure was repeated three more times so that the tetraethylammonium chloride solution had been contacted with the stoichiometric quantity of sodium borohydride a total of five times. The water was removed from the final top layer and the solid dried. Analysis showed the product contained 98 percent pure tetraethylammonium borohydride, containing 1.67 percent by weight of sodium hydroxide and a trace of sodium borohydride.

Example 2

185 grams of an aqueous solution containing 35 percent by weight of tetraethylammonium bromide (0.31 mole) were treated with 99 grams of the same solution of sodium

borohydride and sodium hydroxide a total of five times as described in Example 1. The final upper product layer was essentially free of hydroxide and bromide and contained 2.09 percent of active hydrogen.

Example 3

A batch, countercurrent reaction of tetraethylammonium bromide and sodium borohydride was carried out in the following manner: A feed solution containing 37.5% tetraethylammonium bromide in water was contacted in a five-stage batch, countercurrent manner with a stabilized water solution of sodium borohydride which contained 11.8% sodium borohydride and 38.5% sodium hydroxide. 212.2 grams of the quaternary ammonium bromide solution and 128.4 grams of the sodium borohydride solution were used in each stage. The apparatus consisted of five glass separatory funnels used as mixers and settlers. After sufficient cycles had been carried out to ensure equilibrium, the upper layer which had contacted five successive lower layers in a countercurrent manner was isolated and found to contain tetraethylammonium borohydride in good yield and purity. The lower layer which had contacted five successive upper layers in a countercurrent manner was also isolated and found to consist essentially of an aqueous caustic solution in which the by-product sodium bromide was dissolved.

Example 4

The operations of Example 3 were repeated using a liquid-liquid laboratory York-Scheibel extraction column to carry out the countercurrent reaction. The aqueous tetraethylammonium bromide solution was fed into the bottom of the column and the stabilized water solution of sodium borohydride was fed near the top of the column. Mixing and settling of the counterflowing liquid phases was effected by alternate stirring and settling as carried out in a York-Scheibel-type extractor. A light phase was taken off the top of the column and found to consist of a concentrated aqueous solution of tetraethylammonium borohydride in good yield and purity. A heavy phase was taken off the bottom of the column and found to consist of an aqueous solution of sodium hydroxide and sodium bromide with a very small amount of unreacted sodium borohydride.

Example 5

An aqueous solution of tetrapropylammonnium borate was mixed with an aqueous solution of potassium borohydride and potassium fluoride. The solutions contained 1 mole of tetrapropylammonium borate, 1 mole of potassium borohydride, and 3 moles of potassium fluoride. When the reaction mixture was allowed to stand, it separated into two liquid layers. The upper layer was separated and dried at 60° C. in a vacuum oven. The dry, crystalline product was tetrapropylammonium borohydride of a high state of purity.

We claim:

1. In a method for preparing a quaternary ammonium borohydride selected from the group consisting of tetraethylammonium borohydride, tetrapropylammonium borohydride, benzyltrimethylammonium borohydride, triethylmethylammonium borohydride, ethylpyridinium borohydride, and methylisoquinolinium borohydride wherein the quaternary ammonium borohydride is formed by the reaction in an aqueous medium of a water-soluble quaternary ammonium salt corresponding to the quaternary ammonium borohydride with a substantially equimolar amount of an alkali metal borohydride selected from the group consisting of sodium borohydride and potassium borohydride, the improvement which comprises conducting said reaction in the presence of a compound which is substantially inert under the conditions of said reaction and which is selected from the group consisting of sodium hydroxide, potassium hydroxide, potassium fluoride, potassium carbonate, potassium tartrate, potassium sulfate, sodium carbonate, sodium sulfate, and potassium citrate, and adjusting the amount of water in the reaction mixture such that two immiscible layers are formed, one of which is essentially an aqueous solution of the quaternary ammonium borohydride and the other is essentially an aqueous solution of said compound and a salt corresponding to said quaternary ammonium salt.

2. The method as claimed by claim 1 wherein said selected quaternary ammonium salt is a tetraethylammonium salt.

3. The method as claimed by claim 1 wherein said selected quaternary ammonium salt is a benzyltrimethylammonium salt.

4. The method as claimed by claim 1 wherein said selected quaternary ammonium salt is a tetrapropylammonium salt.

5. As a composition of matter an aqueous liquor consisting of a quaternary ammonium borohydride selected from the group consisting of tetraethylammonium borohydride, tetrapropylammonium borohydride, benzyltrimethylammonium borohydride, triethylmethylammonium borohydride, ethylpyridinium borohydride, and methylisoquinolinium borohydride, a compound selected from the group consisting of sodium hydroxide, potassium hydroxide, potassium fluoride, potassium carbonate, potassium tartrate, potassium sulfate, sodium carbonate, sodium sulfate, and potassium citrate, and a salt selected from the group consisting of sodium and potassium salts and having two immiscible layers, one of which is essentially an aqueous solution of the quaternary ammonium borohydride and the other is essentially an aqueous solution of said compound and said salt.

6. A composition as claimed by claim 5 wherein the quaternary ammonium salt is a tetraethylammonium salt.

7. A composition as claimed by claim 5 wherein the quaternary ammonium salt is a tetrapropylammonium salt.

8. A composition as claimed by claim 5 wherein the quaternary ammonium salt is a benzyltrimethylammonium salt.

9. In a method for causing sodium borohydride to react with tetraethylammonium chloride to form tetraethylammonium borohydride in the presence of sodium hydroxide, the steps which comprise selecting a point within the enclosed area of FIGURE 1, forming a first solution by dissolving the amounts of sodium hydroxide and sodium borohydride represented by said point in a portion of the amount of water represented by said point, forming a second solution by dissolving an amount of tetraethylammonium chloride represented by said point in the remaining portion of the amount of water represented by said point, causing said first solution and said second solution to flow countercurrent to one another in a given path at room temperature thereby causing the tetraethylammonium chloride and sodium borohydride to react progressively whereby said first solution substantially free of sodium borohydride and containing sodium chloride and substantially all of said sodium hydroxide in solution therein is removed from one end of said path and said second solution substantially free of tetraethylammonium chloride and containing tetraethylammonium borohydride in solution therein is removed from the opposite end of said path.

10. In a method for causing sodium borohydride to react with tetraethylammonium bromide to form tetraethylammonium borohydride in the presence of sodium hydroxide, the steps which comprise selecting a point within the enclosed area of FIGURE 2, forming a first solution by dissolving the amounts of sodium hydroxide and sodium borohydride represented by said point in a portion of the amount of water represented by said point, forming a second solution by dissolving an amount of tetraethylammonium bromide represented by said point in the remaining portion of the amount of water represented by said point, causing said first solution and said

second solution to flow countercurrent to one another in a given path at room temperature thereby causing the tetraethylammonium bromide and sodium borohydride to react progressively whereby said first solution substantially free of sodium borohydride and containing sodium bromide and substantially all of said sodium hydroxide in solution therein is removed from one end of said path and said second solution substantially free of tetraethylammonium bromide and containing tetraethylammonium borohydride in solution therein is removed from the opposite end of said path.

References Cited by the Examiner

Banus et al.: J.A.C.S., vol. 74, pp. 2346–2348 (1952).

CHARLES B. PARKER, *Primary Examiner.*