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PRODUCTION OF POLYHYDRIC ALCOHOLS

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This invention relates to a process for the hydrolysis of halogenated organic compounds, and it provides a practical and economical process for the hydrolysis of halogenated organic compounds, particularly halogenated compounds of the polyhalide and halohydrin types to the corresponding polyhydric alcohols. The process of the invention is particularly adapted to the technical scale production of glycerols from the corresponding glycerol halohydrins, and to the production of glycols from the corresponding olefine dihalides and halohydrins.

Many methods and reagents have been proposed for hydrolyzing halohydrins and olefine halides to polyhydric alcohols, but these have not been sufficiently practical and free from defects to warrant their use in extensive commercial production of the valuable polyhydric alcohols. For example, various metal hydroxides, especially the alkali metal hydroxides, have been suggested as suitable agents for hydrolyzing a halohydrin or an olefine halide to a polyhydric alcohol, but these hydroxides give poor yields of the desired alcohol when used as recommended owing to conversion of the halohydrin into epoxide type of compounds and heavy condensation products and the olefine halide into unsaturated halides. Carbonates and bicarbonates have been employed separately and while these reagents give good yields of the desired polyhydric alcohols, the carbon dioxide gas liberated by the reaction leads to considerable difficulties in their use. Either some means must be provided for venting the carbon dioxide from the reaction zone without undue loss of volatile materials or else the reaction vessel must be built sufficiently strong to withstand the pressure accumulatively developed by the liberated carbon dioxide gas. The halohydrins have also been hydrolyzed by heating in the presence of water, but this reaction is so slow that it is quite unsuitable for use in a commercial process for manufacturing the polyhydric alcohols. A further unsuitable feature of the above known processes has been the use of an excess of the alkaline reagent over the stoichiometrically required amount resulting in a waste, in some cases, of a considerable quantity of this reagent.

An object of this inevntion is to provide a process which can be easily and economically operated batchwise or continuously to give high yields of the desired polyhydric alcohols from hydrolyzable halogen-containing compounds with the aid of comparatively inexpensive and readily available reagents. A still further object is to provide a process requiring substantially no excess of the alkaline reagent over the stoichiometric amount necessary. Other objects will be apparent from the description of the invention.

The present invention is based on the discovery that it is advantageous to execute the hydrolysis reaction under conditions in which the alkalinity of the reaction mixture is maintained within comparatively narrow limits. The most alkaline limit, beyond which it is not desirable to maintain the alkalinity, is substantially equivalent to that which would be produced, if the reaction mixture contained, disregarding the incidental halogenide ion, predominately carbonate ion as the anion. The least alkaline or most acidic limit, on the other hand, is substantially equivalent to that alkalinity which would be produced if the reaction mixture contained predominantly bicarbonate ion as the anion, again disregarding the incidental halogenide ion. By alkalinity, reference is made to the hydroxyl ion concentration and the most alkaline limit at which it is preferred to maintain the reaction mixture is that hydroxyl ion concentration which is inherent with an alkali metal carbonate solution at about the same temperature as the reaction mixture. The least alkaline limit is the hydroxyl ion concentration which is inherent with an alkali-metal bicarbonate solution at about the same temperature as the reaction mixture. This preferred range of alkalinity is conveniently termed the "carbonate-bicarbonate range." More particularly, the alkalinity of the reaction mixture is maintained between the alkalinity of a 0.075 normal aqueous solution of sodium bicarbonate and a 0.06 normal aqueous solution of sodium carbonate when these solutions are at the same temperature as the reaction mixture.

A high yield of the desired polyhydric alcohol may be obtained by reacting a suitable hydrolyzable halogenated organic compound with an aqueous metal hydroxide solution containing a salt of a strong base and a weak acid when the alkalinity of the reaction mixture is maintained within the preferred range. The alkalinity of the reaction mixture is maintained within the desired carbonate-bicarbonate range by regulating the rate of introduction of the metal hydroxide into the reaction mixture. The presence of the salt of a strong base and a weak acid is a highly desirable feature of the process since the presence of such a salt produces an accelerating action on the rate of hydrolysis of the halogen-containing compound which is of particular advantage in the commercial production of the

polyhydric alcohols. The presence of this salt is also useful in helping to maintain the reaction mixture within the desired range of alkalinity due to its buffering effect in the reaction mixture.

The invention provides a process particularly adapted to the technical scale conversion of olefine polyhalides, olefine halohydrins, glycerine halohydrins and their homologues, analogues and suitable substitution products to the corresponding polyhydric alcohols. For example, the ethylene dihalides may be hydrolyzed to ethylene glycol, the propylene dihalides may be hydrolyzed to propylene glycol, the butylene dihalides may be hydrolzed to the corresponding butylene glycols, the amylene dihalides may be hydrolyzed to the corresponding amylene glycols, etc. The related organic dihalides wherein the halogen atoms are not linked to vicinal carbon atoms may also be hydrolyzed to the corresponding glycols. For example, the 1,3-dihalopropanes may be hydrolyzed to trimethylene glycol, 1,3-dihalobutane may be hydrolyzed to the corresponding glycol, 1,3-dihalo-2-methyl propane may be hydrolyzed to 1,3-dihydroxy-2-methyl propane, 1,4-dihalobutane may be hydrolyzed to 1,4-dihydroxy butane, etc. The olefine halohydrins and related compounds may be hydrolyzed to the corresponding glycols. For example, the ethylene halohydrins may be hydrolyzed to ethylene glycol, the propylene halohydrins to propylene glycol, the butylene halohydrins to butylene glycol, etc. Furthermore, related compounds which do not have a halogen atom and a hydroxy group linked to vicinal carbon atoms may be hydrolyzed to the corresponding glycols. For instance, 3-halopropanol-1 may be hydrolyzed to trimethylene glycol, 4-halobutanol-1 may be converted to 1,4-dihydroxybutane, 3-halo-2-methylpropanol-1 may be hydrolyzed to 1,3-dihydroxy-2-methyl propane, 1-halo-3-hydroxy-2-methyl butane may be hydrolyzed to the glycol, 1,3-dihydroxy-2-methyl butane, etc.

The glycerine halohydrins form a preferred group of compounds which may be treated in accordance with the process of the invention and practically and economically converted to the corresponding glycerols. The compounds such as glycerine monobromhydrin, glycerine dibromhydrin, glycerine monochlorhydrin, glycerine dichlorhydrin, alpha-methyl glycerine monochlorhydrin, alpha-methyl glycerine dichlorhydrin, alpha, alpha'-dimethyl glycerine monochlorhydrin, beta-methyl glycerine monochlorhydrin, beta-methyl glycerine dichlorhydrin, and the like and their homologues may be hydrolyzed to the corresponding glycerols. In like manner, the polyhalogenated organic compounds containing single halogen atoms linked to vicinal carbon atoms may be hydrolyzed to the corresponding polyhydric alcohols. For example, 1,2,3-trichloropropane (glycerine trichlorhydrin) may be hydrolyzed to glycerine, 1,2,3-trichlorobutane may be hydrolyzed to alpha-methyl glycerine, 2-methyl-1,2,3-trichloropropane may be hydrolyzed to beta-methyl glycerine, etc.

It will be apparent from the foregoing description that the halogenated organic compounds which may be treated in accordance with the process of the invention may be of aliphatic, cycloaliphatic or aralkyl character. Furthermore, said compounds may be saturated or unsaturated. When the treated compound contains a plurality of halogen atoms, said halogen atoms may be the same or dissimilar.

The alkali metal hydroxides are the most suitable hydroxides to use in hydrolyzing the suitable halogen-containing compounds although other basic metal hydroxides, including the alkaline earth metal hydroxides, may be used if desired. The alkali metal hydroxides such as lithium hydroxide, sodium hydroxide, potassium hydroxide, rubidium hydroxide and cesium hydroxide are particularly suitable because they possess high solubility in the aqueous reaction medium and because they do not form insoluble compounds with any of the salts of a strong base and a weak acid which may be used in conjunction with them. Ordinarily sodium hydroxide is preferred because of its low cost and availabiliy.

Any salt of a strong base and a weak acid may be used in the process such as may be obtained by reacting a strong base including the alkali metal hydroxides, the strong amino bases and the like with a weak acid including carbonic acid, phosphoric acid, phosphorous acid, pyrophosphoric acid, boric acid, arsenious acid, arsenic acid, telluric acid, formic acid, acetic acid, propionic acid, butyric acid, maleic acid, succinic acid, glutaric acid, phthalic acid, phenol, alkyl phenols and the like. A preferred group of salts which are particularly effective for use in the process of the invention are the alkali metal arsenites, arsenates, borates, carbonates, phosphates, pyrophosphates, tellurates, phenolate, and cresolates. The alkali metal carbonates, in particular sodium carbonate and bicarbonate, are especially suited because of their cheapness, availability, and inherent favorable characteristics and action in the process. These preferred salts are very desirable for use with alkali metal hydroxides, since with such a combination no insoluble precipitate will be formed and the beneficial effect of the salts will be fully realized.

The process of the invention may be executed in a wide variety of manners. For instance, a suitable batchwise method is to introduce a solution of the reactant to be hydrolyzed into a reaction vessel equipped with heating means and agitating means such as a stirring device. The halogen-containing compound to be hydrolyzed to a polyhydric alcohol may be placed in the reaction vessel with a desired quantity of a salt of a strong base and a weak acid together with such an amount of water as may be desirable. The metal hydroxide may then be introduced into the reaction mixture, preferably as an aqueous solution, at a rate whereby the alkalinity of the reaction mixture is maintained within the desired carbonate-bicarbonate range. If desired, the metal hydroxide and the salt of a strong base and a weak acid may be introduced simultaneously to the reaction vessel containing the hydrolyzable halogen-containing compound; or, the metal hydroxide, the salt and the halogen-containing compound may all three be introduced into the reaction vessel. In every case the alkalinity of the reaction mixture is maintained within the preferred range by regulating the relative rate of introduction of the metal hydroxide. This control of the alkalinity may be aided by use of suitable electrodes and auxiliary apparatus so that a measure of the alkalinity may be obtained at all times during the course of the reaction. At the end of the hydrolysis, the polyhydric alcohol may be recovered by any of the usual methods known to the art.

A continuous method of operation such as the following may be more desirable especially for large scale production. A solution of a hydrolyzable compound such as, for example, a halohydrin

may be continuously introduced into a reaction vessel, such as either a long tubular vessel or a vessel wherein the length is not great as compared to the width, equipped with heating means. Agitation is effected by withdrawing the reaction mixture with a pumping system which recycles a part of the mixture to the reaction vessel. The metal hydroxide solution is introduced continuously into the reaction mixture simultaneously with the solution of a salt of a strong base and a weak acid. It is usually convenient to introduce the hydroxide and the salt as a single solution. If desired the reaction vessel may be equipped with suitable electrodes and other apparatus for regulating the rate of introduction of the hydroxide so that the alkalinity of the reaction mixture is maintained substantially constant within the desired range. The rate of circulation is preferably kept substantially greater than the rate of introduction of the reactants. The reaction mixture is continuously withdrawn from the reaction vessel and since in such a system as described the reaction is substantially but not entirely complete, the exit solution containing some unhydrolyzed halohydrin may be passed to a waiting vessel where the alkalinity remaining in the solution from the reaction vessel can complete the reaction.

By conducting the hydrolysis reaction with halohydrins under conditions of controlled alkalinity within the carbonate-bicarbonate range, the large proportion of heavy condensation products obtained by prior workers, who did not control the alkalinity when using metal hydroxides, is eliminated. When the reaction mixture is maintained substantially more alkaline than carbonate, the heavy condensation products increase rapidly with increasing alkalinity. On the other hand, by maintaining the alkalinity less alkaline than bicarbonate the rate of the reaction decreases to a point which is undesirable for commercial production of the polyhydric alcohols. Another undesirable result which may be obtained by not maintaining the reaction mixture at least as alkaline as bicarbonate is that the amount of unhydrolyzed halohydrin remaining in the solution leaving the reaction zone will be unreasonably large when a continuous method of operation is used. By regulating the introduction of the metal hydroxide so that the reaction mixture is maintained at least as alkaline as bicarbonate when sodium carbonate is used as the salt of a strong base and a weak acid, there is no liberation of gaseous carbon dioxide which would be very troublesome to dispose of especially in a continuous application of the process.

The effect of varying the alkalinity within even the preferred range where the undesirable effects are small is evident from the following results which were obtained by hydrolyzing an aqueous solution of glycerine monochlorhydrin with 10% sodium hydroxide containing 1% sodium carbonate. All factors were substantially the same except that the alkalinity of the reaction mixture was different in each experiment.

Temperature ° C.	Alkalinity normality		Weight ratio of glycerol to heavy products	Per cent weight chlorine in glycerol
	$CO_3^=$	HCO_3^-		
157	0.00	0.075	17.9:1	1.02
164	0.02	0.02	12.5:1	0.63
167	0.06	0.00	9.1:1	0.13

The desirable effect produced by simultaneously introducing a salt of a strong base and a weak acid along with the metal hydroxide may be illustrated by the results obtained in experiments wherein glycerin dichlorhydrin was hydrolyzed with 20% sodium hydroxide. In the first two experiments, the hydroxide solution contained sodium carbonate equivalent to about 5% of the total alkalinity and in the second two experiments about double this quantity was used. The temperature was kept at 169° C. in each experiment and the other conditions were constant with the exceptions noted.

Alkalinity normality		Per cent dichlorhydrin unreacted	Ratio of glycerol to heavy products
$CO_3^=$	HCO_3^-		
0.010	0.019	1.5	25.3:1
0.006	0.021	2.5	------
0.010	0.041	0.8	------
0.000	0.046	1.4	39.0:1

It is seen from the above results that by doubling the amount of sodium carbonate in the third experiment as compared to the second, the rate of the reaction is increased resulting in a decrease in the amount of unreacted dichlorhydrin even though the alkalinity maintained is practically identical in the two experiments. The results of the first and fourth experiments show that doubling the amount of carbonate permits a lower alkalinity to be maintained during the hydrolysis to give the same amount of unreacted dichlorhydrin with a resulting increase in the ratio of glycerol to heavy condensation products. In general, it is preferred to have present in the reaction mixture sufficient salt of a strong base and a weak acid to permit substantially complete hydrolysis being effected at an alkalinity whereat a high ratio of polyhydric alcohol to by-products may be obtained. When hydrolyzing glycerine halohydrins in a continuous manner, it is preferred to introduce into the reaction mixture a sufficient amount of a salt of a strong base and a weak acid to at least be equivalent to about 5% of the alkalinity of the metal hydroxide introduced.

The temperature at which the hydrolysis reaction is conducted is another governing factor on the rate of reaction. With other things equal, the higher the reaction temperature, the more rapid the rate. In general, it is desirable to effect the hydrolysis reaction at a temperature of from about 50° C. to 250° C. and preferably at from 75° to 200° C. for glycerine halohydrins. Since the reaction is effected preferably in the liquid phase and to avoid loss of reactants and products, the pressure on the reaction mixture should be at least equal to and preferably greater than the total vapor pressure of the reaction mixture at the temperature used for the hydrolysis reaction. At lower temperatures, ordinary atmospheric pressure is often satisfactory, but at higher temperatures, it is usually necessary to use pressures substantially greater than atmospheric. Pressures above 100 lbs. per sq. in. and preferably between 150 and 300 lbs. per sq. in. are suitable for glycerine halohydrins when operating at above 150° C. while atmospheric pressure is satisfactory for temperatures below 100° C.

Even though the rate of reaction is slower at lower temperatures with the necessity of using a larger apparatus for a given rate of production of polyhydric alcohol, it may be desirable at times to use lower temperatures rather than higher be-

cause the by-product impurities, to be removed in refining the polyhydric alcohol, produced is less.

Another factor influencing the rate of hydrolysis is the dilution of the reactants. With other factors the same, the reaction would be most rapid with the reactants at infinite dilution. This is, of course, a state impossible to realize and furthermore since in the practical application of our process the cost of recovering the polyhydric alcohol from a dilute solution will be higher than from a more concentrated one, the dilution to be used is largely governed by economic considerations. In general, however, it may be said that the dilution with water should be such that a reasonably rapid rate of reaction will be realized.

It is not necessary that the halohydrins or the polyhalides be in a substantially pure state for use in the process. Crude solutions containing various salts and other impurities which might, for example, be obtained from the manufacture of the halohydrins may be used. Furthermore, mixtures of halohydrins or polyhalides of various chemical structure may be hydrolyzed to polyhydric alcohols without first separating the mixture into individual constituents.

Although the invention has been disclosed hereinbefore with certain specific embodiments and variants thereof, it is to be understood that our invention is to be limited only by the scope of the appended claims.

We claim as our invention:

1. A process for the production of glycerine which comprises effecting the hydrolysis of glycerine chlorhydrin at a temperature of from about 50° C. to about 250° C. in a liquid aqueous alkaline reaction mixture containing a sodium carbonate, sodium hydroxide being continuously added to the reaction mixture during the reaction, with respect to the rate of hydrolysis of said chlorhydrin in an amount sufficient to maintain its alkalinity between the alkalinity of a 0.075 normal aqueous solution of sodium bicarbonate and a 0.06 normal aqueous solution of sodium carbonate when these solutions are at the operating temperature of the reaction mixture.

2. A process for the production of glycerine which comprises effecting the hydrolysis of glycerine halohydrin at a temperature of from about 50° C. to about 250° C. in a liquid aqueous alkaline reaction mixture containing an alkali metal carbonate an alkali metal hydroxide being continuously added to the reaction mixture during the reaction, with respect to the rate of hydrolysis of said halohydrin, in an amount sufficient to maintain its alkalinity between the alkalinity of a 0.075 normal aqueous solution of sodium bicarbonate and a 0.06 normal aqueous solution of sodium carbonate when these solutions are at the operating temperature of the reaction mixture.

3. A process for the production of a polyhydric alcohol which comprises effecting the hydrolysis of an olefine halohydrin at a temperature of from about 50° C. to about 250° C. in a liquid aqueous alkaline reaction mixture containing an alkali metal carbonate, an alkali metal hydroxide being continuously added to the reaction mixture during the reaction, with respect to the rate of hydrolysis of said halohydrin, in an amount sufficient to maintain its alkalinity between the alkalinity of a 0.075 normal aqueous solution of sodium bicarbonate and a 0.06 normal aqueous solution of sodium carbonate when these solutions are at the operating temperature of the reaction mixture.

4. A process for the production of a polyhydric alcohol which comprises effecting the hydrolysis of an olefine halohydrin at a hydrolyzing temperature in a liquid aqueous alkaline reaction mixture containing a salt from the group consisting of alkali metal arsenites, arsenates, borates, carbonates, phosphates, pyrophosphates, tellurates, phenolates and cresolates, an alkali metal hydroxide being continuously added to the reaction mixture during the reaction with respect to the rate of hydrolysis of said halohydrin, in an amount sufficient to maintain its alkalinity between the alkalinity of a 0.075 normal aqueous solution of sodium bicarbonate and a 0.06 normal aqueous solution of sodium carbonate when these solutions are at the operating temperature of the reaction mixture.

5. A process for the production of a polyhydric alcohol which comprises effecting the hydrolysis of a compound from the group consisting of olefine halohydrins and olefine polyhalides at a temperature of from about 50° C. to about 250° C. in a liquid aqueous alkaline reaction mixture containing a salt from the group consisting of alkali metal arsenites, arsenates, borates, carbonates, phosphates, pyrophosphates, tellurates, phenolates and cresolates, an alkali metal hydroxide being continuously added to the reaction mixture during the reaction with respect to the rate of hydrolysis of said compounds, in an amount sufficient to maintain its alkalinity between the alkalinity of a 0.075 normal aqueous solution of sodium bicarbonate and a 0.06 normal aqueous solution of sodium carbonate when these solutions are at the operating temperature of the reaction mixture.

6. A process for the production of a polyhydric alcohol which comprises effecting the hydrolysis of a compound from the group consisting of olefine halohydrins and olefine polyhalides in a liquid aqueous alkaline reaction mixture containing a salt of a strong base and a weak acid, a basic metal hydroxide being continuously added to the reaction mixture during the reaction, with respect to the rate of hydrolysis of said compounds, in an amount sufficient to maintain its alkalinity between the alkalinity of a 0.075 normal aqueous solution of sodium bicarbonate and a 0.06 normal aqueous solution of sodium carbonate when these solutions are at the operating temperature of the reaction mixture.

7. A process for the production of a polyhydric alcohol which comprises effecting the hydrolysis of a halogen-containing compound hydrolyzable to a polyhydric alcohol in a liquid aqueous alkaline reaction mixture containing a salt of a strong base and a weak acid, a basic metal hydroxide being continuously added to the reaction mixture during the reaction, with respect to the rate of hydrolysis of said compounds, in an amount sufficient to maintain its alkalinity between the alkalinity of a 0.075 normal aqueous solution of sodium bicarbonate and a 0.06 normal aqueous solution of sodium carbonate when these solutions are at the operating temperature of the reaction mixture.

8. A continuous process for the production of glycerine which comprises continuously introducing glycerine chlorhydrin, an aqueous solution of an alkali metal hydroxide and an aqueous solution of an alkali metal carbonate into a liquid aqueous alkaline reaction mixture heated to a temperature of from about 50° C. to about 250° C., said introduction of the alkali metal hydroxide solution being regulated, with respect to the rate

of hydrolysis of said chlorhydrin, so that the alkalinity of the reaction mixture is maintained between the alkalinity of a 0.075 normal aqueous solution of sodium bicarbonate and a 0.06 normal aqueous solution of sodium carbonate when these solutions are at the operating temperature of the reaction mixture, and continuously withdrawing a part of the reaction mixture.

9. A continuous process for the production of a polyhydric alcohol which comprises continuously introducing an olefine chlorhydrin, an aqueous solution of an alkali metal hydroxide and an aqueous solution of an alkali metal carbonate into a liquid aqueous alkaline reaction mixture heated to a temperature of from about 50° C. to about 250° C., said introduction of the alkali metal hydroxide solution being regulated, with respect to the rate of hydrolysis of said chlorhydrin, so that the alkalinity of the reaction mixture is maintained between the alkalinity of a 0.075 normal aqueous solution of sodium bicarbonate and a 0.06 normal aqueous solution of sodium carbonate when these solutions are at the operating temperature of the reaction mixture, and continuously withdrawing a part of the reaction mixture.

10. A continuous process for the production of a polyhydric alcohol which comprises continuously introducing a compound from the group consisting of olefine halohydrins and olefine polyhalides, an alkali metal hydroxide and a salt from the group consisting of alkali metal arsenites, arsenates, borates, carbonates, phosphates, pyrophosphates, tellurates, phenolates and cresolates into a liquid aqueous alkaline reaction mixture heated to a temperature of from about 50° C. to about 250° C., regulating the rate of addition of the alkali metal hydroxide with respect to the compound undergoing hydrolysis and its rate of hydrolysis so that the alkalinity of the reaction mixture is maintained between the alkalinity of a 0.075 normal aqueous solution of sodium bicarbonate and a 0.06 normal aqueous solution of sodium carbonate when these solutions are at the operating temperature of the reaction mixture, and continuously withdrawing a part of the polyhydric alcohol-containing reaction mixture.

11. A continuous process for the production of a polyhydric alcohol which comprises continuously feeding a halogen-containing compound hydrolyzable to a polyhydric alcohol, a basic metal hydroxide and a salt of a strong base and a weak acid into a heated liquid aqueous alkaline reaction mixture while regulating the rate of addition of the metal hydroxide with respect to the halogen-containing compound and its rate of hydrolysis so that the alkalinity of the reaction mixture is maintained between the alkalinity of a 0.075 normal aqueous solution of sodium bicarbonate and a 0.06 normal aqueous solution of sodium carbonate when these solutions are at the operating temperature of the reaction mixture, and continuously withdrawing a part of the polyhydric alcohol-containing reaction mixture.

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