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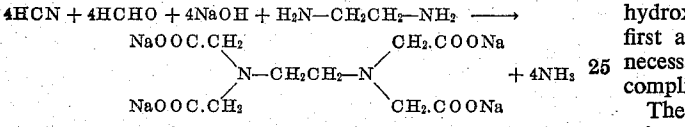
PROCESS FOR THE MANUFACTURE OF TETRA-SODIUM ETHYLENEDIAMINE TETRAACETATE

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The present invention relates to a process for the manufacture of tetra-sodium ethylenediamine tetra-acetate.

Briefly stated, this process is characterized by the addition, as a single stream, of an acid-stabilized aqueous solution of hydrogen cyanide and formaldehyde to ethylenediamine in an aqueous alkaline solution or suspension, at relatively high temperature—advantageously in the range from about 95° to about 110° C., and preferably at 100–105° C.—and at atmospheric pressure. The reaction involved is as follows:



The preparation of tetra-sodium ethylenediamine tetraacetate, as heretofore carried out, has been handicapped by the use of sodium cyanide and by the necessity, in order to avoid undesired hydrolysis, of adding the sodium cyanide and formaldehyde separately and alternately and in closely controlled amounts, continuing this stepwise procedure until complete carboxymethylation of the amine is achieved. The conversion of ethylenediamine, in this manner, to the tetra-sodium ethylenediamine tetraacetate requires at least four separate additions of sodium cyanide to the reactor at precisely timed intervals which, in turn, are dependent on the quantity of formaldehyde which has been added to the reactor.

To avoid the defects of this prior procedure, it has been proposed to carry out the reaction with pre-formed glycolonitrile instead of with the alternately added sodium cyanide and formaldehyde. Apart from the advantages involved in this solution of the problem, it is unavoidably burdened by the necessity of carrying out the separate preparation of the glycolonitrile as a first step of the overall process.

A primary object of the present invention is the embodiment of a process which is free of the deficiencies of the aforedescribed prior processes. This object is realized, as above indicated, by the expedient of employing an acid-stabilized equimolar mixture of hydrogen cyanide and formaldehyde, whereby these reagents can be added simultaneously, i. e. in the form of a single stream, to the reactor containing the heated solution of ethylenediamine and alkali metal hydroxide or other base. The preferred alkali hydroxide is, for practical reasons, sodium hydroxide, although the process can also be carried out with the use of other bases. The "single stream" expedient of the present invention results in a one-step process for the manufacture of the desired carboxymethylated ethylenediamine derivative using HCN as a starting material. This avoids the necessity of the alternate addition of the cyanide and formaldehyde and the entailed close supervision as required by the first above-described process, and also avoids the necessity of preparing glycolonitrile in a special first step as required by the second above-described process.

The single stream type of addition of the hydrogen cyanide and formaldehyde, according to the present invention, enables a much better control over the process

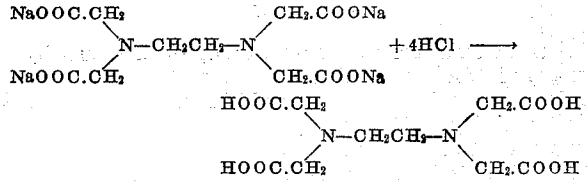
to be realized. It also makes possible the addition, if desired, of a calculated excess of either formaldehyde or of hydrogen cyanide to improve the product quality and yield.

Cyanide is, to a very large extent, prepared as the free acid. The use of hydrogen cyanide directly, according to the present invention, makes it unnecessary to neutralize the HCN by means of alkali to produce the previously-employed alkali metal cyanide. In this connection, shipment of hydrogen cyanide is cheaper than shipment of aqueous sodium cyanide since the maximum concentration that is practical with the sodium salt is about 40%, the remainder being water. This circumstance contributes to the superior economic feasibility of the process according to the present invention.

The present process which, as indicated, makes it possible to prepare the carboxymethylated product in a single reactor, also allows for greater flexibility of operation. Thus, it is possible by this process to prepare a wide variety of salts of the aminocarboxylic acid by the use of, for example, barium hydroxide, calcium hydroxide, potassium hydroxide, trimethyl-ammonium hydroxide, etc., as the base, instead of NaOH. In the first above-described process, for instance, it would be necessary to use different metal cyanides and thus to complicate storage problems.

The process of the invention is applicable generally to primary and secondary amines, i. e. to amines having at least one replaceable hydrogen atom attached directly to an amino nitrogen atom. Illustrative of such amines are for example, in addition to the already-mentioned ethylene-diamine, ethylamine, chloroethylamine, n-butylamine, dodecylamine, 1-2-propylenediamine, diethylenediamine, diethylenetriamine, triethylenetetramine, N-monoethoxyetheylenediamine, cyclohexylamine, and many others.

The products of the process are useful as detergents, wetting agents, metal-ion sequestering agents, or as intermediates for the preparation of the same. Thus, for example, the tetra-sodium ethylenediamine tetraacetate can be converted according to the following equation into the ethylenediamine tetraacetic acid:



Ethylenediamine tetraacetic acid is a well-known sequestering agent. The use of iron chelates of ethylenediamine tetraacetic acid for the treatment of iron deficiencies (chlorosis) in orange and grapefruit groves is, for example, known. It is also known to use the calcium disodium salt in pharmaceuticals to prevent calcium-depletion in the body.

The following is a representative presently-preferred embodiment of the present invention, as applied to the carboxymethylation of ethylenediamine:

Example 1

An acid-stabilized solution of formaldehyde-hydrogen cyanide is prepared by the dropwise addition, at about 5° C., of 6 N H_2SO_4, to 340 parts by weight of aqueous formaldehyde (37% HCHO by weight) until the pH is less than 1. While maintaining the indicated low temperature, 119 parts by weight of hydrogen cyanide are added, with stirring. It is desirable to maintain the solution at 0–5° C. until used.

A solution consisting of 300 parts of water, 384 parts of 50% aqueous sodium hydroxide solution and 60 parts

of ethylenediamine is heated to 100° C. with stirring. The previously-prepared acid-stabilized HCN—HCHO solution is then added to the alkali-ethylenediamine solution slowly, with stirring, addition preferably being effected beneath the surface of the latter and being completed in the course of about 3 hours. Upon completion of the addition, an additional 16.2 parts by weight of 37% aqueous formaldehyde are added. The resulting solution contains 380 parts of tetrasodium ethylenediamine tetraacetate.

The tetra-sodium ethylenediamine tetraacetate may, if desired be recovered from the said solution in any appropriate and per se known manner, as for example by evaporation and recrystallization.

In lieu of sulfuric acid, the acid stabilization may be also effected with another mineral acid, as for example hydrochloric acid, phosphoric acid, phosphorous acid and the like.

The following example illustrates the conversion of the tetra-sodium ethylenediamine tetraacetate to the free ethylenediamine tetraacetic acid:

Example 2

500 parts by weight of water are added to 1460 parts by weight of the tetra-sodium ethylenediamine tetraacetate-containing solution, obtained according to the second paragraph of Example 1. While stirring, hydrochloric acid (33%) is added until the pH is about 2. Ethylenediamine tetraacetic acid precipitates, and is filtered off, washed chloride-free, and dried. A yield of 96–98% is obtained.

The following examples illustrate the application of the invention to other amines:

Example 3

An acid-stabilized solution consisting of 85.1 parts by weight of 37% formaldehyde and 29.7 parts by weight of hydrogen cyanide is added beneath the surface to a solution consisting of 500 parts by weight of water, 104 parts by weight of 50% aqueous sodium hydroxide solution and 105 parts by weight of diethanolamine at 100° C. in the course of 3 hours. Upon completion of the addition, 4.0 parts of 37% formaldehyde are added. The resulting solution contains 108 parts by weight of sodium dihydroxyethylglycinate.

Example 4

An acid-stabilized solution consisting of 256 parts by weight of 37% formaldehyde and 89 parts by weight of hydrogen cyanide is added beneath the surface to a solution consisting of 400 parts by weight of water, 312 parts by weight of 50% aqueous sodium hydroxide solution and 104 parts by weight of aminoethylethanolamine at 100° C. in the course of 3 hours. Upon completion of the addition, and then after the further addition of 12.15 parts by weight of 37% formaldehyde, the resulting solution contains 341 parts by weight of trisodium hydroxyethylethylene-diamine triacetate.

Having thus disclosed the invention, what is claimed is:

1. A method for carboxymethylation of amines which comprises gradually adding an aqueous mineral acid-inhibited substantially equimolar mixture of hydrogen cyanide and formaldehyde to an aqueous solution of an alkaline hydroxide and an amine having at least one replaceable hydrogen atom attached directly to each amino nitrogen, said solution being maintained during said addition at a reaction temperature in the range of about 95–110° C. whereby carboxymethylation of the amine to the corresponding acetate salt takes place with the simultaneous liberation of ammonia.

2. A process according to claim 1, wherein the acid inhibition is effected by the incorporation of a mineral acid in the hydrogen cyanide-formaldehyde mixture and by maintaining the temperature of said liquid mixture below about 5° C. until used.

3. A process according to claim 1, wherein the acid inhibition is effected by the incorporation of hydrochloric acid in the hydrogen cyanide-formaldehyde mixture and by maintaining the temperature of said liquid mixture below about 5° C. until used.

4. A process according to claim 1, wherein the acid inhibition is effected by the incorporation of sulfuric acid in the hydrogen cyanide-formaldehyde mixture and by maintaining the temperature of said liquid mixture below about 5° C. until used.

5. A method for the preparation of a tetra salt of ethylenediamine tetraacetate by the gradual addition of a mineral acid-inhibited equimolar mixture of hydrogen cyanide and formaldehyde to an aqueous solution of ethylenediamine and an alkaline hydroxide at a temperature of about 95° to about 110° C., whereby carboxymethylation of the amine to the corresponding tetra-salt of ethylenediamine tetraacetate takes place with simultaneous liberation of ammonia.

6. A method for the preparation of a tetra salt of ethylenediamine tetraacetate by the gradual addition of a mineral acid-inhibited equimolar mixture of hydrogen cyanide and formaldehyde to an aqueous solution of ethylenediamine and an alkaline hydroxide at a temperature of 100–105° C., whereby carboxymethylation of the amine to the corresponding tetra-salt of ethylenediamine tetraacetate takes place with simultaneous liberation of ammonia.

7. A method for the preparation of tetra-sodium ethylenediamine tetraacetate by the gradual addition of a mineral acid-inhibited equimolar mixture of hydrogen cyanide and formaldehyde to an aqueous solution of ethylenediamine and sodium hydroxide at a temperature of 100–105° C., whereby carboxymethylation of the amine to the tetra-sodium ethylenediamine tetraacetate takes place with simultaneous liberation of ammonia.

8. A method for the carboxymethylation of amines which comprises gradually adding an aqueous mineral acid-inhibited substantially equimolar mixture of hydrogen cyanide and formaldehyde at a temperature of about 0–5° C., to a hot, cyanide-free, aqueous solution of an alkaline hydroxide and an amine having at least one replaceable hydrogen atom attached directly to each amine nitrogen atom, whereby the number of mols of cyanide and formaldehyde added to the hot alkaline solution are at all times substantially equal, said alkaline solution being maintained during said addition at a reaction temperature in the range of about 95–110° C. whereby carboxymethylation of the amine to the corresponding acetate salt takes place with the simultaneous liberation of ammonia.

9. A method for the preparation of tetra-sodium ethylenediamine tetraacetate by the gradual addition of a mineral acid-inhibited mixture of hydrogen cyanide and formaldehyde at a temperature of about 0–5° C. and at a pH of less than 1, to a hot, cyanide-free, aqueous solution of sodium hydroxide and ethylenediamine at a temperature of about 95° to about 110° C., whereby carboxymethylation of the amine to the tetra-sodium ethylenediamine tetraacetate takes place with simultaneous liberation of ammonia.

References Cited in the file of this patent

UNITED STATES PATENTS

2,175,805	Jacobsen	Oct. 10, 1939
2,205,995	Ulrich et al.	June 25, 1940
2,387,735	Bersworth	Oct. 30, 1945
2,407,645	Bersworth	Sept. 17, 1946
2,419,157	Parry	Apr. 15, 1947
2,461,519	Bersworth	Feb. 15, 1949
2,511,487	Thompson	June 13, 1950

OTHER REFERENCES

Smith et al.: Jour. Org. Chem., vol. 14 (1949), pp. 355–61.